NMR EXAMINATION OF CYCLIC DIALKOXY CARBONIUM IONS (1, 3-DIOXOLENIUM CATIONS)

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DONALD ANDREW TOMALIA

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This is to certify that the

thesis entitled

NMR EXAMINATION OF CYCLIC DIALKOXY CARBONIUM IONS (1,3-DIOXOLENIUM IONS)

presented by

Donald Andrew Tomalia

has been accepted towards fulfillment
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Harold Hart
Major professor

Date May 8, 1968

ABSTRACT

NMR EXAMINATION OF CYCLIC DIALKOXY CARBONIUM IONS (1,3-DIOXOLENIUM IONS)

by Donald Andrew Tomalia

Members of the following four families of cyclic dialkoxy carbonium ions (1,3-dioxolenium cations) were prepared by allowing appropriate 2-bromoethyl esters to react with silver tetrafluoroborate according to the method of Meerwein:[1]

I. 2-Alkyl-1,3-dioxolenium Cations

II. 2,2'-Alkylene-1,3-dioxolenium Dications

III. 2-Aryl-1,3-dioxolenium Cations

IV. 2,2' and 2,2',2''-Aryl-1,3-dioxolenium Dications and Trications

Families II and IV represent new examples in this series.

An alternate method for the preparation of 2-alkyl-1,3-dioxolenium cations was discovered which involved the combination of 2-hydroxy, methoxy or acetoxyethyl esters with an excess of fluorosulfonic acid (FSO_3H). When FSO_3H was added to the ester, 1,3-dioxolenium cations were generated immediately as the major product. Addition of the esters to FSO_3H gave rise to only small amounts of 1,3-dioxolenium cations accompanied by a predominance of diprotonated ester species. The diprotonated species converted slowly but completely to 1,3-dioxolenium cations with time. Evidence is presented for the first example of protonation of the etheral oxygen in an ester.

A systematic nmr examination of these four families of cations in liquid sulfur dioxide (-20°) or FSO_3H revealed that the equivalent protons of the dioxolenium moiety could be used as a probe for assessing the

electron density in the dioxolenium ring as a function of the 2-substituent. A good qualitative correlation was obtained by comparing the chemical shifts of eleven 2-alkyl-1,3-dioxolenium cations.[2]

In a similar manner, a good quantitative correlation of proton-nmr chemical shifts with Hammett σ values was obtained for fifteen meta and para-substituted 2-aryl-1,3-dioxolenium cations. This represents the first quantitative correlation, by proton magnetic resonance, of charge densities in a carbonium ion system.[3] From this relationship and the chemical shifts of the 2,2'-m-phenylene and 2,2'-p-phenylene-1,3-dioxolenium dications, Hammett σ values for the meta and para substituted dioxolenium moieties were found to be +0.84 and +0.97, respectively. The latter value is the largest positive σ value reported to date. Application of this Hammett σ relationship and the dioxolenium moiety probe for determining Hammett σ values for higher energy carbonium ions is described.

Nmr examination of 2,2'-alkylene-1,3-dioxolenium dications showed that charge repulsion could be assessed as the number (n) of methylene insulating groups was varied.[4] Dications containing five or six methylene insulating groups reflected practically total loss of charge repulsion and exhibited nmr chemical shifts which were reminiscent of mono-2-alkyl-1,3-dioxolenium cations. By decreasing the number of methylene groups one found a smooth, monotonic increase in charge repulsion (as demonstrated by larger dioxolenium proton deshielding values). Deshielding was at a maximum for n = 1. Definitive evidence for the dication containing no insulating groups (i.e., n = 0) was not obtained.

An empirical relationship was conceived which correlated the nmr chemical shifts of the dioxolenium ring protons in these dications with the number of methylene insulating groups (n) between the cationic centers (Equation 1). Alternatively, the chemical shifts of the alpha protons

$$\delta = 5.30 + \frac{1.60}{(n+1)^2} \qquad (1)$$

were related to the number of methylene groups (n) between the positive centers by the following equation:

$$\delta = 2.94\ (1 + \frac{1}{n^2}) \qquad (2)$$

The latter equation could be applied to other dicarbonium ion systems (e.g. acyl dications),[5] possessing alpha protons, by choosing suitable parameters.

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2. H. Hart and D. A. Tomalia, Tetrahedron Letters, 29, 3383 (1966).

3. D. A. Tomalia and H. Hart, ibid, 29, 3389 (1966).

4. H. Hart and D. A. Tomalia, ibid, 15, 1347 (1967).

5. G. A. Olah and M. B. Comisarow, J. Am. Chem. Soc., 88, 3313 (1966).

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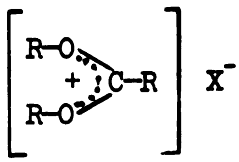
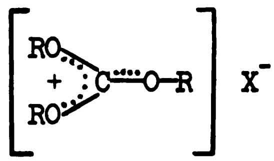
INTRODUCTION

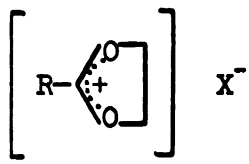
Carbonium ions have been proposed as fleeting intermediates in many organic reactions since the early work of Meerwein[1] and Whitmore.[2] Although the first example of a stable isolable carbonium ion was reported by Seel in 1943,[3] kinetic and stereochemical evidence for their intervention in reactions was common. The first use of nmr spectroscopy as a means for characterizing carbonium ions was reported in 1958 by Doering and coworkers,[4] at which time nmr spectral evidence was presented for the heptamethylbenzenonium ion. Since that time, techniques developed primarily by Olah and Deno have made possible the direct observation of many of these transient intermediates by nmr spectroscopy. Early progress in this area of carbonium ion chemistry was reviewed in 1963 by Deno[5a,b] and more recently by Olah.[6] Since that time such a considerable volume of pertinent work has appeared in the literature that several texts have recently been published on the subject.[7a,b] At the present, alkyl,[8a-e] cycloalkyl,[9a-e] benzyl,[10a-e] alkynyl,[11a,b] alkenyl,[12a-f] oxo,[13a-g] fluoro,[14a-c] hydroxy,[15a,b] alkoxy,[16a-d] arylalkyl,[17a,b] cations as well as bridged phenonium[18a-c] and benzenonium[19a,b] ions have been examined in some detail by nmr spectroscopy. These investigations have generally included attempts to qualitatively correlate proton chemical shifts with expected charge densities on the attached carbons. Although one successful quantitative correlation of fluorine nmr chemical shifts with stabilization energies has been reported for para-fluorine substituted triphenylmethyl cations,[20] in no instance has a quantitative correlation of charge densities with proton chemical shifts been demonstrated. In most cases the carbonium ion structures were simply not amenable to correlation with linear free energy parameters, such as Hammett σ values, but Olah has suggested that such a correlation might be possible with the benzyl cation system.[10e]

Conspicuously absent from the literature at the onset of our investigation was an nmr spectral examination of alkoxy carbonium ions. Very recently Taft and Ramsey[21] reported spectral data for a number of acyclic dialkoxy and trialkoxy carbonium ions of the type shown below;





however, the cyclic dialkoxy carbonium ions (2-substituted-1,3-dioxolen-

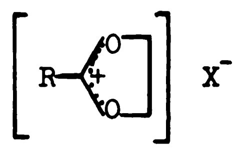


ium cations) were considered of more interest for several reasons. _A priori_ it was thought that the cyclic cation system might provide an interesting carbonium ion model, whereby the equivalent dioxolenium ring protons could be used as a probe for assessing charge delocalization or interaction with 2-substituents. It was also predicted that probe chemical shift deviations due to 2-substituent anisotropy effects would be at a minimum since the cyclic structure removes the probe protons from the immediate vicinity of the 2-substituent. Finally, using Meerwein's method[22] one can introduce a wide variety of 2-substituents thus making possible a systematic and extensive investigation of charge density on the probe as a function of the 2-substituent.

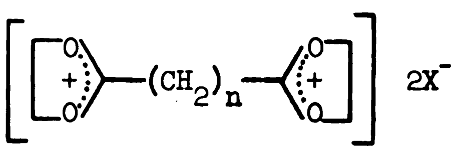
The investigation reported, herein, describes a systematic nmr spectral examination of these 2-substituted-1,3-dioxolenium cations and presents three new synthetic routes to these systems. Nmr data for 2-(_meta_ and _para_-substituted aryl)-1,3-dioxolenium cations provide the first example of a quantitative correlation of carbonium ion charge density with proton nmr chemical shift as well as a unique and novel method for the determination of Hammett σ values for hydrolytically unstable moieties. Similarly a quantitative relationship between proton chemical shift and charge separation was demonstrated for 2,2'-alkylene-bis-1,3-dioxolenium dications by using derived equations.

The dioxolenium cations will be treated and presented as members of four distinct families of this series as described below:

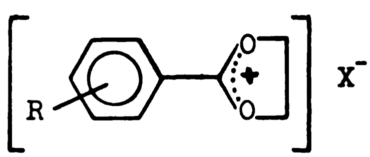
I. 2-Alkyl-1,3-dioxolenium Cations:



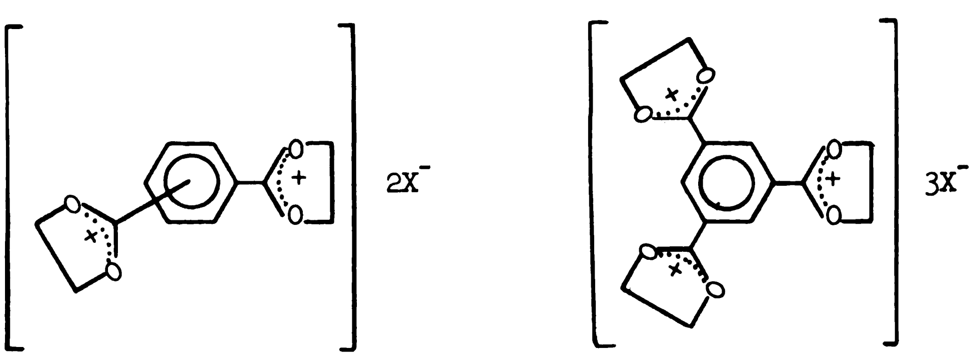
II. 2,2'-Alkylene-bis-1,3-dioxolenium Dications:



III. 2-Aryl-1,3-dioxolenium Cations:

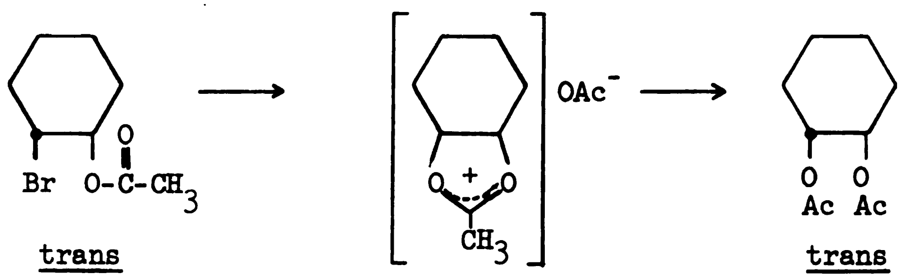


IV. 2,2' and 2,2',2"-Aryl-1,3-dioxolenium Dications and Trications:

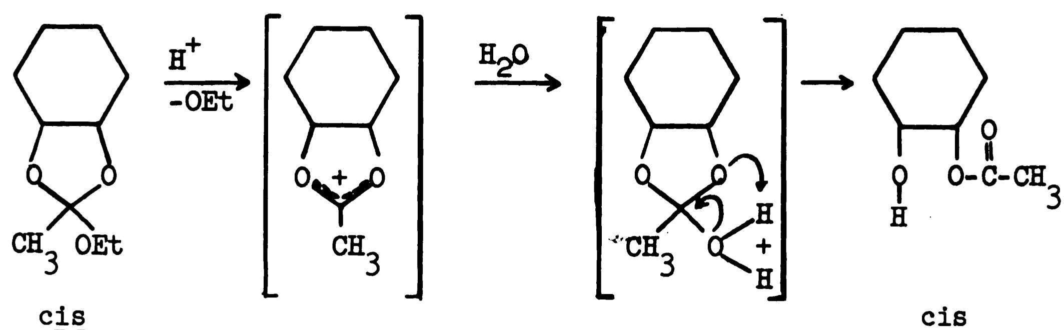


II. HISTORICAL

2-Substituted-1,3-dioxolenium cations were first postulated by Winstein[23] in 1942 as transient intermediates to account for the exclusive formation of a trans-diacetate product from the reaction of trans-2-acetoxycyclohexyl bromide with silver acetate. Similarly the acid catalyzed

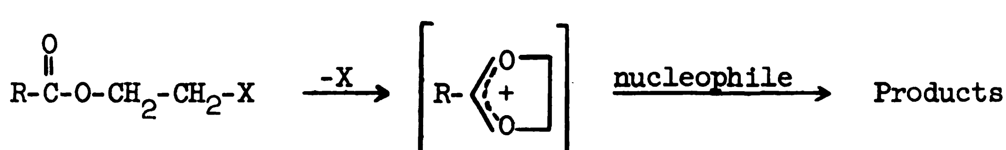


hydrolysis of cyclic ortho esters[24] was proposed to involve such a cationic intermediate yielding in this case a cis product.



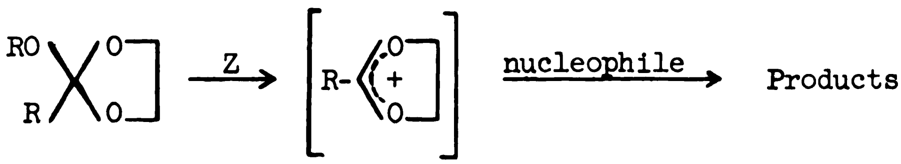
A survey of the literature makes it apparent that these cationic intermediates are involved in a wide variety of organic reactions. The numerous examples can be grouped in three general categories.

A. Displacement of a β-Substituent by Participation of a Carboxy Group



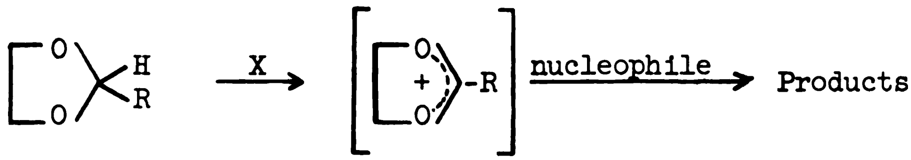
When X is halogen the reactions are usually metal-assisted and involve silver salts, organometallic reagents, or in some cases Lewis acids. When X is an ether, hydroxy, or ester function, however, the reactions are generally acid-catalyzed, requiring protonation of the function or reaction with a Lewis acid before displacement. In special cases where the β-substituent is a labile group such as a tosylate or oxythallate, simple solvolysis presumably yields the transient 1,3-dioxolenium cations.

B. Acid-Catalyzed Hydrolysis of Cyclic Ortho Esters



Where Z is a protic or Lewis acid.

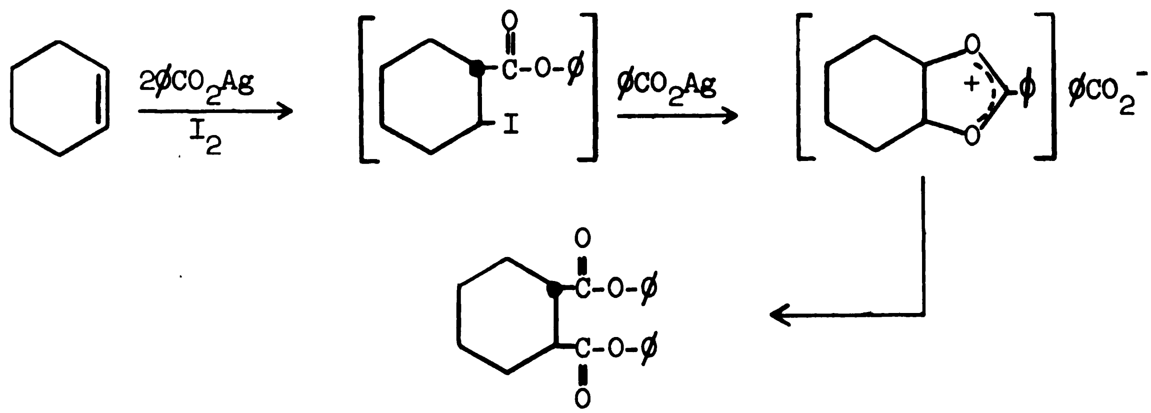
C. Oxidation of a Cyclic Acetal



Where X = Cl_2, Br_2 or $BrCCl_3$.

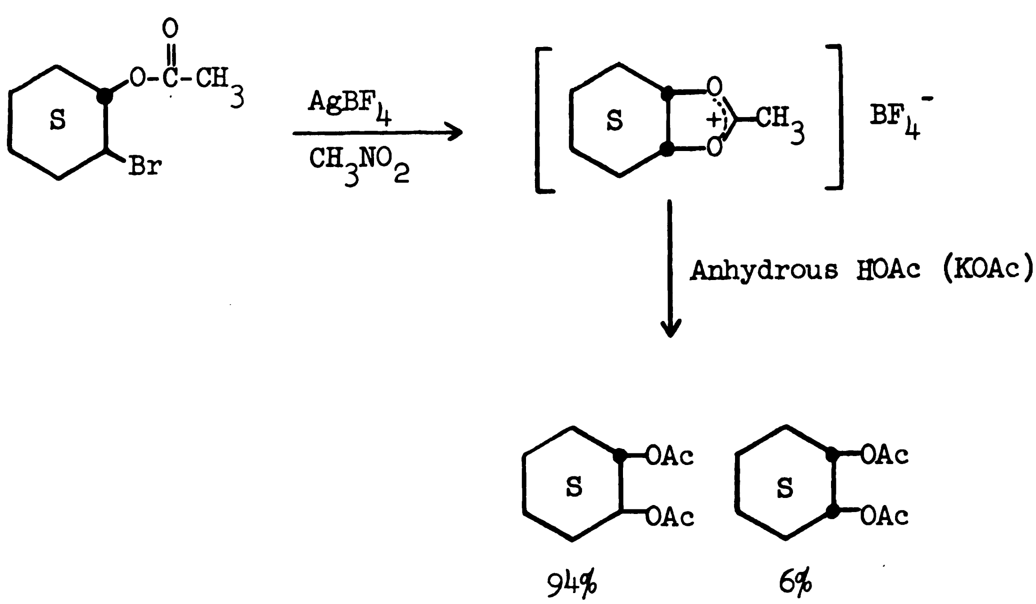
Group A embraces the largest number and variety of reactions which are believed to proceed through 1,3-dioxolenium intermediates. In 1939, several years before Winstein's classical work on acetoxy neighboring group effects, Tipson[25] noted that treatment of an acetohalogenosugar with silver acetate in acetic acid, toluene or similar solvent resulted in the formation of a sugar acetate having the C-1 and C-2-acetoxy groups in a trans relationship. Isbell[26] later pointed out that this result could be rationalized by the ability of the C-2 acetoxy group to participate only if it was trans to the halogen but not if it was cis. Winstein's subsequent work[23] clarified these early observations in the carbohydrate field and thus provided an explanation for many other acetoxy participation reactions; these have been reviewed by Pascu[27] and Lemieux.[28]

Similarly, Prevost type reactions[29-33] are assumed to proceed through cyclic cationic intermediates since trans products are obtained



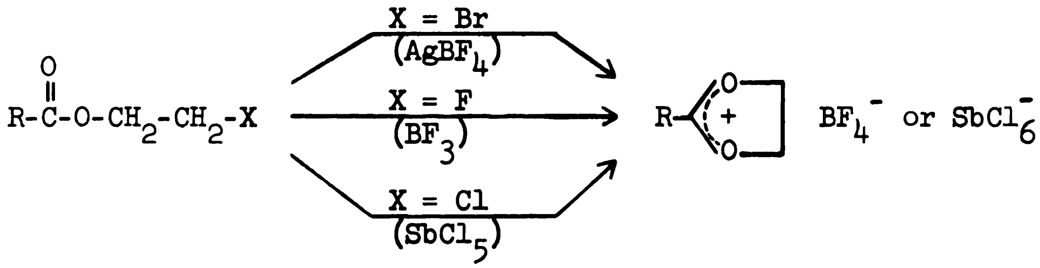
exclusively. In these cases, initial addition of the halogen followed by reaction with one equivalent of the silver salt provides the 2-haloalkyl benzoate precursor to a 1,3-dioxolenium cation. Subsequent reaction of the second equivalent of silver salt generally yields a trans product.

More recently Winstein and coworkers[34] have provided compelling evidence for the above speculation by isolating the analogous 2-methyl-cis-4,5-tetramethylene-1,3-dioxolenium cation intermediate from the reaction of trans-2-acetoxycyclohexyl bromide with silver tetrafluoroborate.

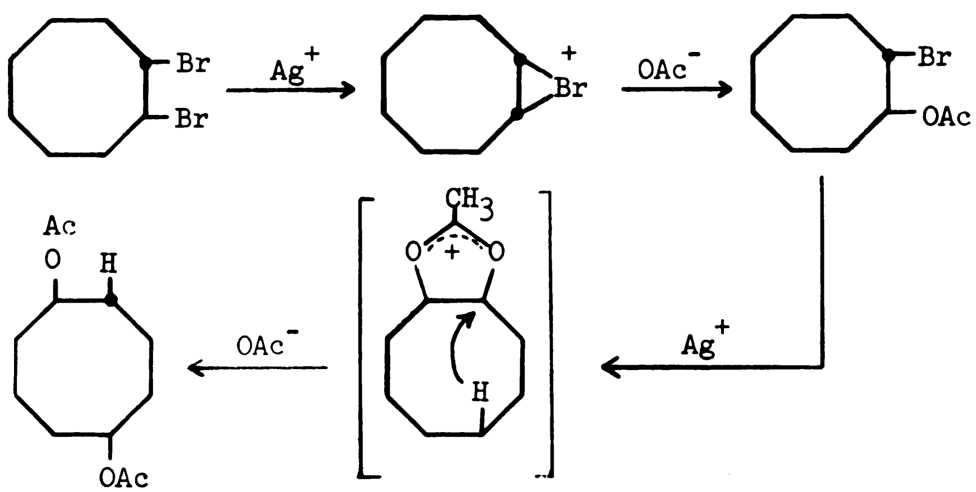


Reactions of the salt with acetate ion under anhydrous conditions paralleled the Prevost reaction in that the trans-diacetate was produced almost exclusively.

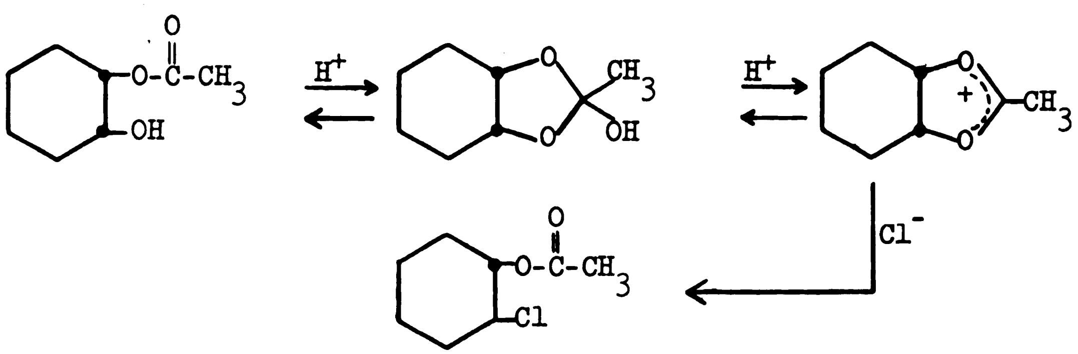
The above method for the preparation and isolation of 1,3-dioxolenium cations from silver tetrafluoroborate and 2-haloethyl esters was discovered by Meerwein and coworkers in 1958.[22] Subsequent work by Meerwein[35] showed that Lewis acids such as BF_3 and $SbCl_5$ were also effective for the preparation of these cations.



Finally, another interesting example, which involves the reaction of a vicinal dihalide with a silver salt, was reported by Cope and coworkers.[36] A 1,3-dioxolenium cation is believed to intercede and undergo a transannular reaction by a 1,5 hydride shift according to the mechanism shown below:

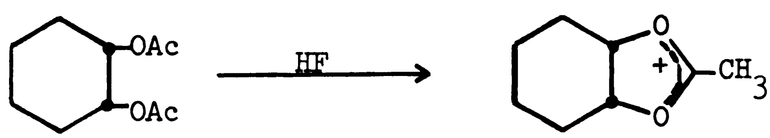


Whereas all evidence indicates that metal assisted reactions involve "hindside" participation of a carboxy group, evidence gathered thus far for the acid-catalyzed cyclization of alcohols and esters to 1,3-dioxolenium cations indicates that "front-side" participation of the carboxy group occurs in these cases. This type of mechanism was first suggested by Winstein and Boschan in 1956[37] to explain the facile conversion of cis-2-acetoxycyclohexanol to trans-2-acetoxycyclohexyl chloride with concentrated HCl, a reaction for which the following path has been proposed:



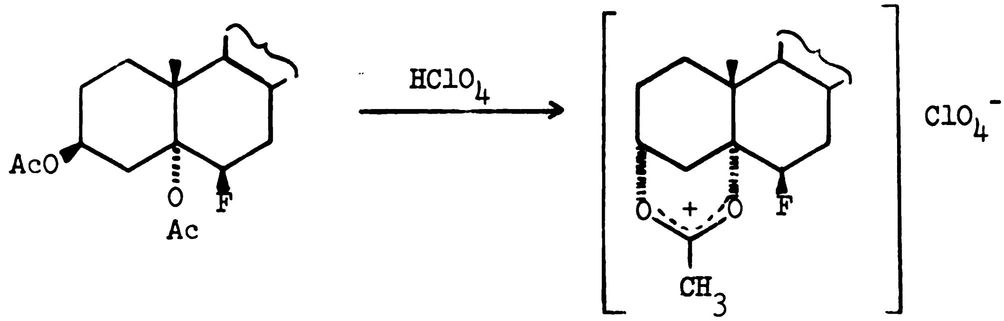
In contrast, the conversion of the trans-2-acetoxycyclohexanol, under the same conditions, proceeds with considerable difficulty.

Similarly, Pedersen has very recently shown[38] by nmr studies that cis-1,2-diacetoxycyclohexane undergoes complete conversion in 6-8 hours to the 2-methyl-1,3-dioxolenium cation in anhydrous hydrogen fluoride at room temperature. The trans-1,2-diacetoxycyclohexane, however, did not

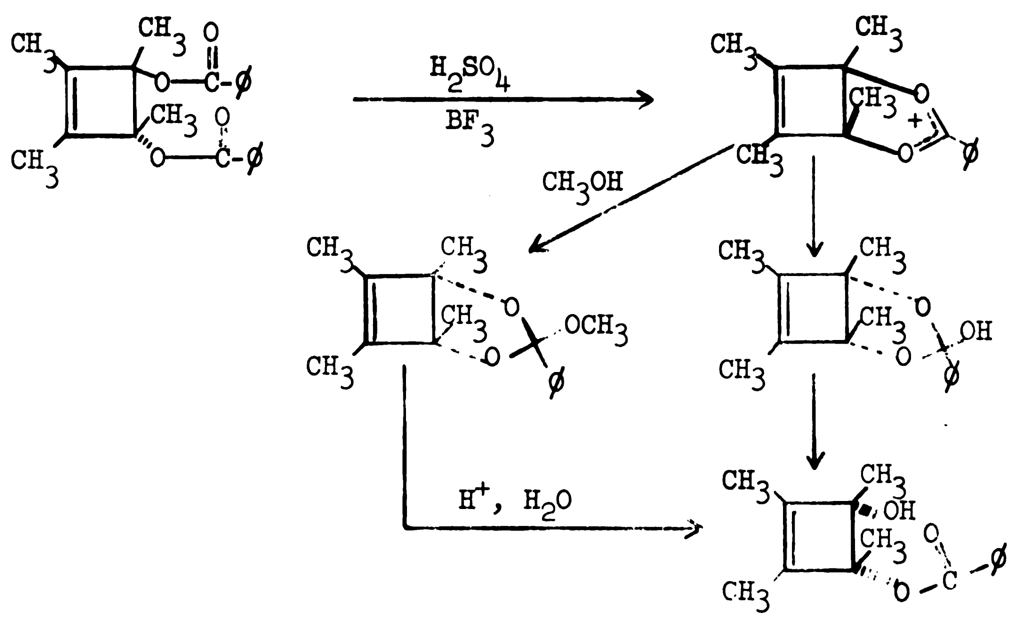


undergo any reaction under these conditions even after several days.

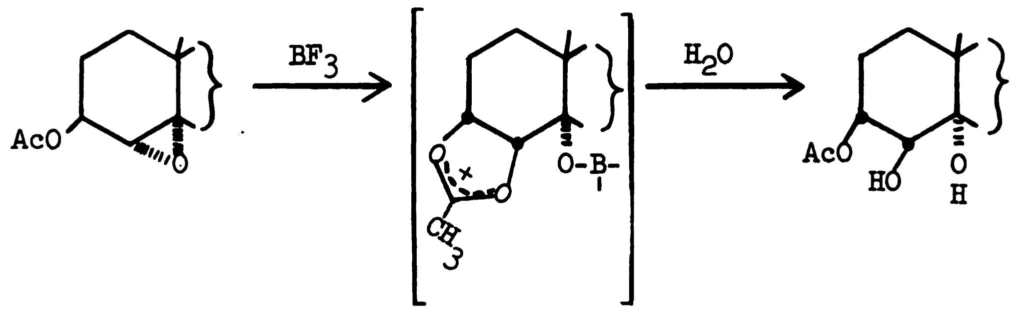
It is interesting that 3β, 5α-diacetoxy-6β-fluorocholestane converts readily to the analogous six membered 1,3-dioxenium cation in perchloric acid even though the acetoxy groups have a trans relationship to each other.[39]



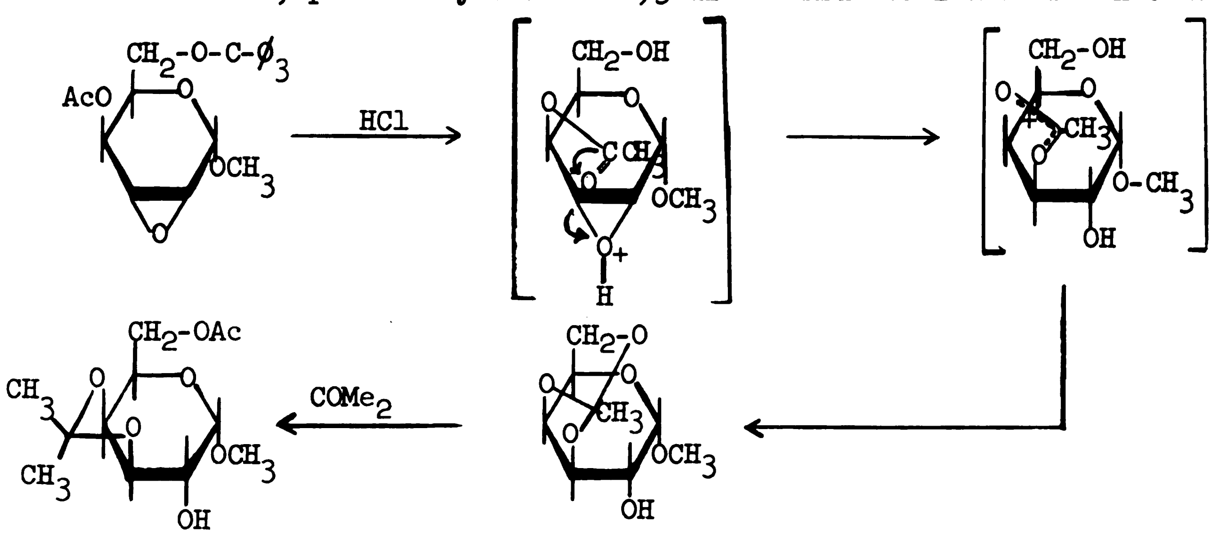
The first spectral characterization of a 1,3-dioxolenium cation as an intermediate in a reaction was reported by Wilcox and Nealy in 1963.[40] They found that when benzoate esters of either cis or trans-1,2,3,4-tetramethylcyclobutene-3,4-diol were treated with 97% sulfuric acid or boron trifluoride these cationic species were generated and could be identified by nmr spectroscopy. Chemical proof of structure consisted of decomposing these cations in methanol and water to give an ortho ester and a cis-hydroxy benzoate, respectively. This criterion was employed earlier by Winstein and coworkers as a proof of structure.[23,24]



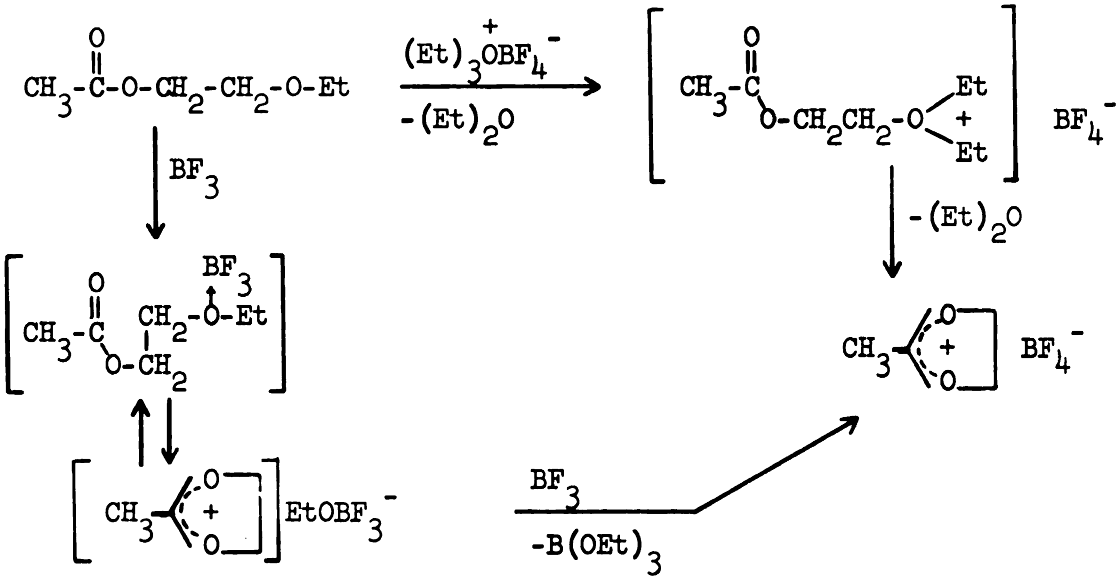
1,3-Dioxolenium ion intermediates have been proposed in the Brønsted and Lewis acid-catalyzed ring opening of vicinal epoxides (cyclic ethers) bearing a neighboring trans-acetoxy group.[41,42] Coxon and coworkers[43] found that 3β-acetoxy-4α, 5α-epoxycholestane gives a stable 3β, 4β-bridged ionic complex with BF_3, which upon hydrolysis gave the corresponding diol.



Buchanan[41,44] has shown that a Brønsted acid can cause a similar transformation, presumably via the 1,3-dioxolenium cation as shown below:

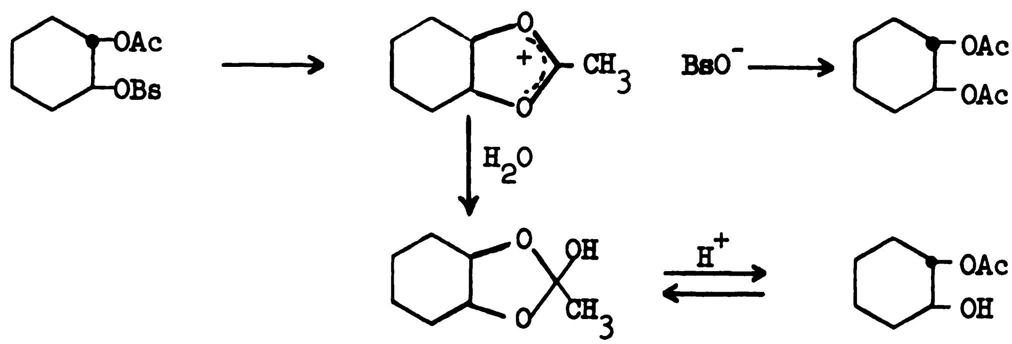


In the case of acyclic ethers, Meerwein and coworkers[35] were able to prepare 2-methyl-1,3-dioxolenium tetrafluoroborate in good yield by the reaction of 2-ethoxyethyl acetate with either triethyloxonium tetrafluoroborate or BF_3 according to the following equations:



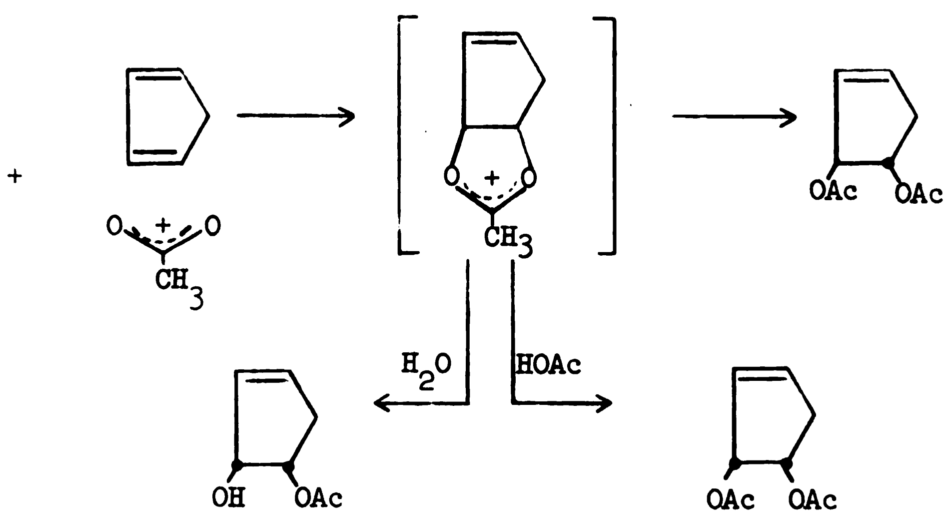
The latter reaction is extremely slow and generally requires 1/2-1 year for completion. Antimony pentachloride reacts in a similar but more rapid manner to give a 56% yield of the above cation as a hexachloroantimonate salt.

In special cases where labile groups are located β to a carboxy group, participation occurs readily under solvolytic conditions to give products derived from 1,3-dioxolenium cation intermediates. This aspect has been investigated in considerable detail by Winstein and coworkers.[23,45] They found that <u>trans</u>-2-acetoxycyclohexyl brosylate solvolyzes in acetic acid to <u>trans</u>-1,2-diacetoxycyclohexane, presumably <u>via</u> the 1,3-dioxolenium cation, several hundred times faster than does <u>cis</u>-2-acetoxycyclohexyl brosylate. The enhanced rate is undoubtedly due to anchimeric assistance by the acetoxy group in the <u>trans</u> isomer, whereas solvolysis of the <u>cis</u> isomer is governed by the rate at which the substrate loses brosylate ion, since anchimeric assistance is geometrically not possible.

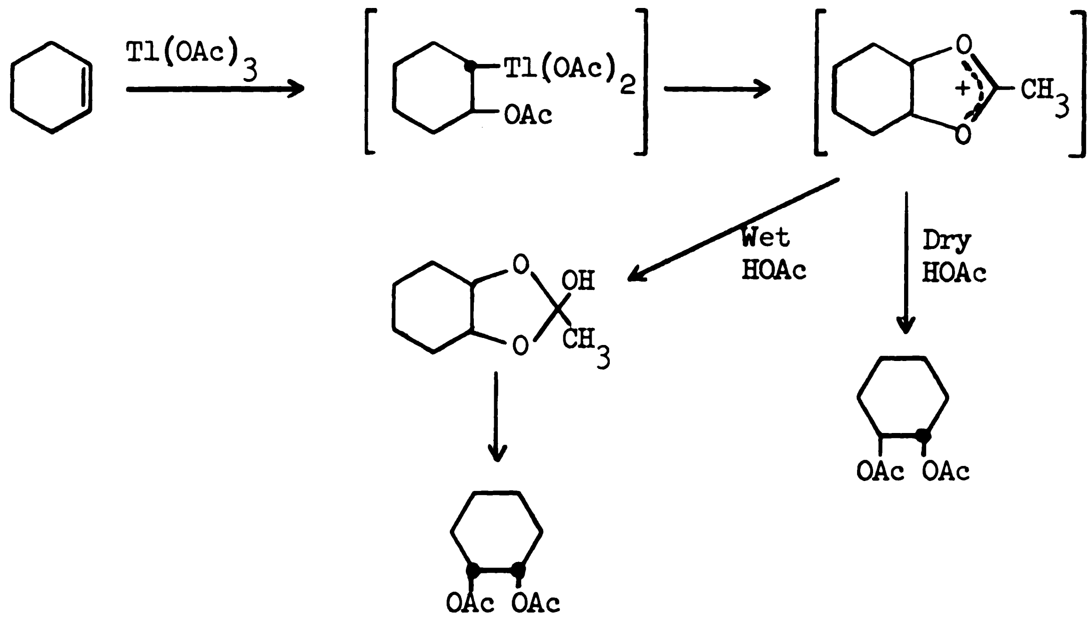


More recently Schneider and Lang[46] examined the anchimeric effects of the benzoyloxy group in cis and trans-2-benzoyloxycyclohexyl tosylates in anhydrous acetic acid. The relative rates for the cis and trans isomer were foun to be 4.6×10^{-4} and 0.26 respectively, compared to cyclohexyl tosylate as 1.00.

Several olefin oxidations have been reported in the past decade which are best explained in terms of 1,3-dioxolenium ion intermediates. Brutcher and Vara[47] found that cyclopentadiene undergoes a facile oxidation with lead tetraacetate to give the trans diacetate in the presence of acetate anion, the cis hydroxyacetate in wet acetic acid and cis diacetate in anhydrous acetic acid. These authors interpret the above transformations according to the following reaction scheme:



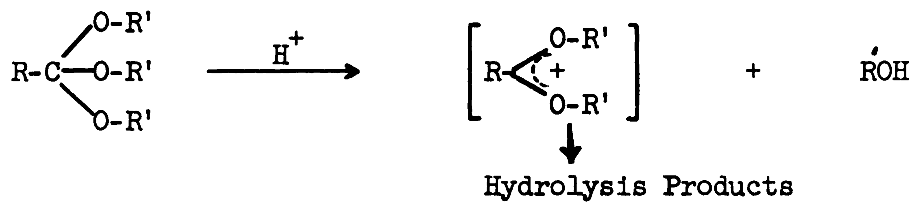
Grinstead[48] postulated the intermediacy of 1,3-dioxolenium salts in the oxidation of olefins with thallium salts to hydroxyesters and diols. Later work by Winstein and Anderson[49] on the stereochemistry of this reaction in acetic acid supported this conjecture. These workers envisioned the reaction mechanism in the following manner:



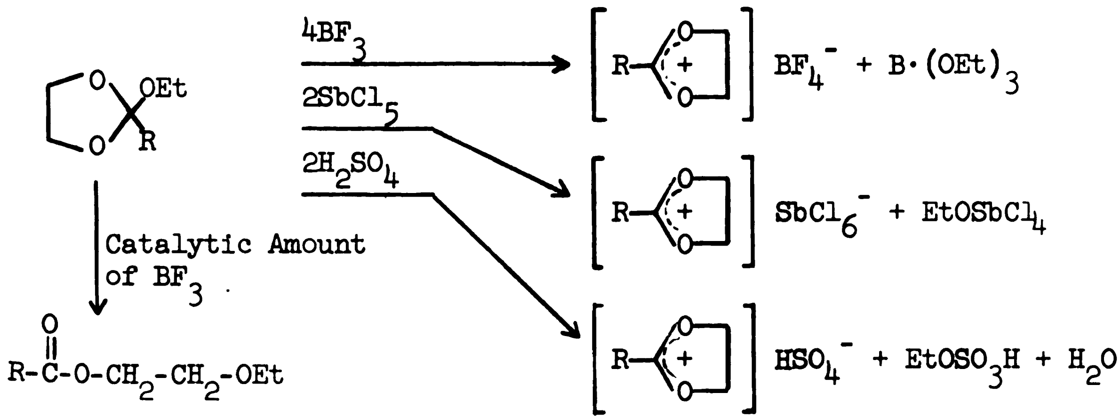
In anhydrous acetic acid the diacetate was mainly <u>trans</u> (up to 88%), whereas in wet acetic acid the diacetate was primarily <u>cis</u> (up to 81%). The significant reversal of diacetate stereochemistry by water is considered to be a criterion for the intermediacy of a 1,3-dioxolenium cation.

Recent work reported by Olson[50] on the selenium dioxide oxidation of ethylene in acetic acid has implicated 1,3-dioxolenium cations as intermediates in these reactions.

Alkoxycarbonium ions have been suspected as intermediates in the acid-catalyzed hydrolysis of acetals, ketals and orthoesters for some time.[51] In the case of an orthoester a dialkoxycarbonium ion would be the expected intermediate. Under normal reaction conditions their isolation was

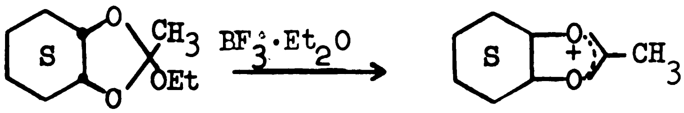


precluded in that nucleophilic species were usually present thus leading to their destruction. It was not until the pioneering work of Meerwein and coworkers that this speculation was soundly corroborated. In an extensive investigation which began in 1955[52] Meerwein found that both acyclic[22] and cyclic[35] dialkoxycarbonium ions could be prepared and isolated by treating appropriate orthoesters with an excess of a Lewis acid (BF_3, $SbCl_5$) or a Brønsted acid possessing weakly nucleophilic anions (i.e., H_2SO_4). An excess of these reagents was essential in order to complex any nucleophilic species which were generated in the reaction. By using only a catalytic amount of the acid reagents one merely observed ring opening to the corresponding 2-alkoxyethyl ester. These reactions led to the 1,3-dioxolenium cations in high yield (60-97%), unless electron

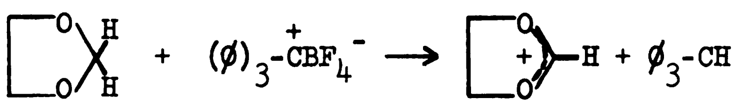


withdrawing groups are present in the 2 or 4 position. For example, BF_3 will not convert the following dioxolanes to the cations, but prefers to remain as a complex, and $SbCl_5$ transforms the 4-substituted dioxolane to the corresponding dialkoxycarbonium ion in only 21% yield.

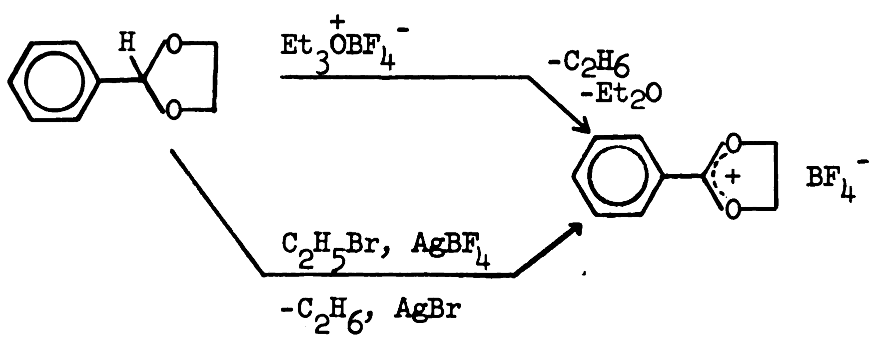
According to recent work by Winstein, this was the method of choice for the preparation and isolation of 2-methyl-cis-4,5-tetramethylene-1,3-dioxolenium tetrafluoroborate.[34]



1,3-Dioxolenium cations have been prepared and isolated in several instances by the oxidation of 2-substituted-1,3-dioxolanes. Meerwein[52] first reported this general method in 1955 when he isolated the parent 1,3-dioxolenium tetrafluoroborate in 62% yield by the reaction of 1,3-dioxolane with trityl tetrafluoroborate. Meerwein provided subsequent variations[53]

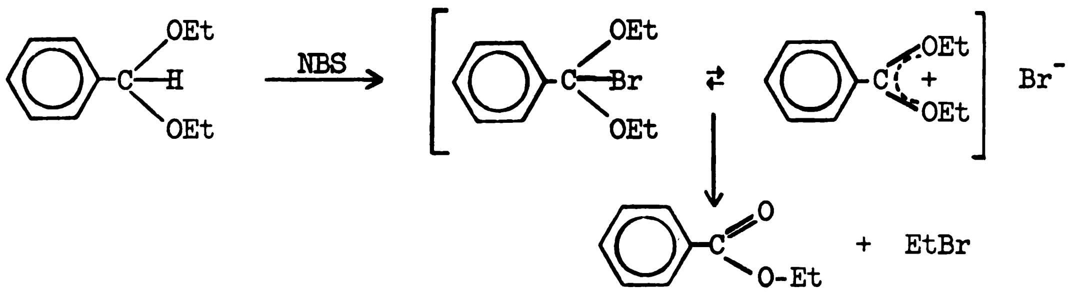


of this reaction by oxidizing 2-phenyl-1,3-dioxolane to the corresponding cation with triethyloxonium tetrafluoroborate and also with a mixture of ethyl bromide and silver tetrafluoroborate. In the latter case, a very

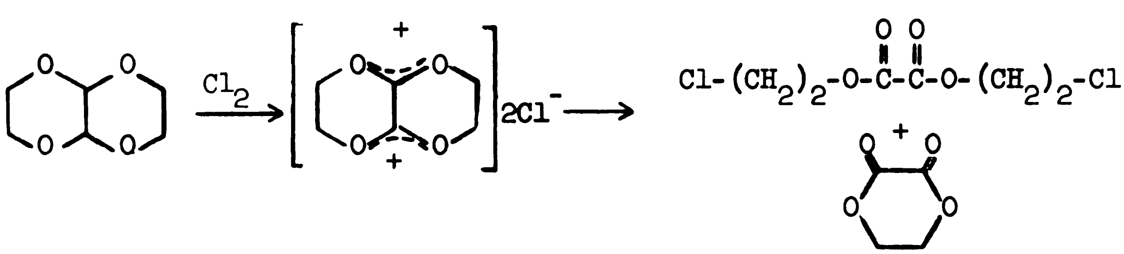


transient primary carbonium presumably affects the oxidation.

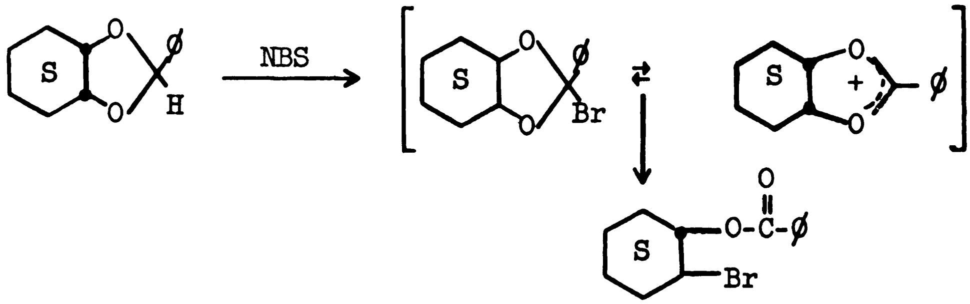
Dialkoxycarbonium ions have been implicated as intermediates in the halogenation of acetals. Marvell and Joncich[54] found that the bromination of benzaldehyde diethylacetal with N-bromosuccinimide proceeded smoothly to give a bromine-free product which was identified as ethyl benzoate. It was conjectured that this product arose in the following manner:



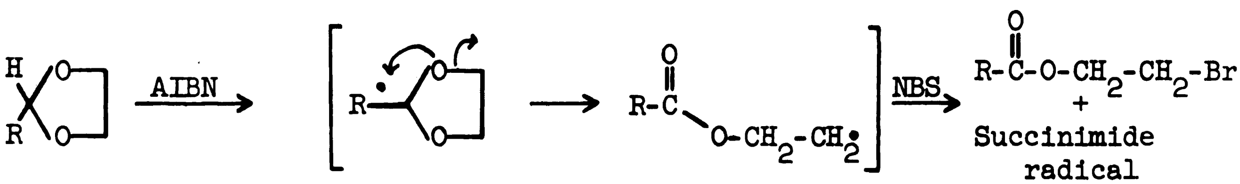
Cyclic dialkoxycarbonium ions were suggested as transient intermediates in the chlorination and bromination of cyclic acetals. Cort and Pearson[55] found that the halogenation of 1,3-dioxolane with bromine or chlorine gave the corresponding 2-bromo- or 2-chloroethyl formate directly. Chlorination of trans-1,4,5,8-tetraoxadecalin yielded a mixture of bis-2-chloroethyl oxalate and 2,3-dioxo-1,4-dioxane. These products were believed to have resulted from a dication as shown below:



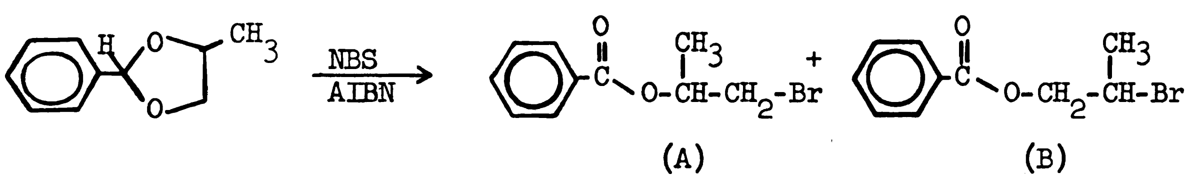
Schmitz and coworkers[56a] proposed a 1,3-dioxolenium cation as an intermediate in the oxidation of 2-phenyl-cis-4,5-tetramethyl-1,3-dioxolane with N-bromosuccinimide. This conjecture was based on the fact that trans-2-bromoalkylbenzoate was obtained exclusively and would be the expected product from such a cationic intermediate, whereas a radical rearrangement might be expected to give a cis-trans mixture.



More recently Prugh and McCarthy[56b] postulated a radical rearrangement mechanism to account for the formation of 2-bromoethyl esters from the reaction of NBS and catalytic amounts of 2,2'-azobisisobutyronitrile (AIBN) with 2-substituted-1,3-dioxolanes. These authors could not provide a



plausible explanation, however, for the unusual ring opening aptitude of 2,4-disubstituted-1,3-dioxolanes under these conditions. 2-Phenyl-4-methyl-1,3-dioxolane gave a 92% yield of an isomer mixture of (A) and (B) with NBS and AIBN. The isomer ratio of A : B, however, was found to be 5 : 1 and seemingly inconsistent with the proposed radical rearrangement

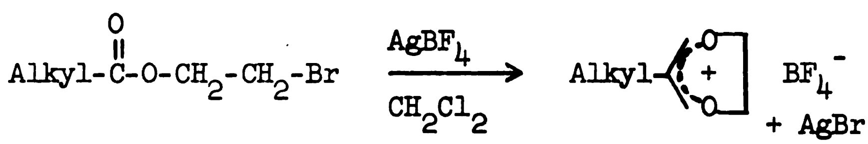


mechanism, which would require preferred rearrangement of a dialkoxybenzyl radical to a primary methylene radical rather than a secondary radical. In view of the evidence[56,57] supporting S_N2-like ring opening reactions of 1,3-dioxolenium cations the above product distribution may be best rationalized _via_ such a cationic intermediate.

III RESULTS

A. <u>2-Alkyl-1,3-Dioxolenium Cations</u>:

The 2-alkyl-1,3-dioxolenium cations used in this investigation were prepared according to a modified version of the Meerwein method.[22] By allowing equimolar amounts of 2-bromoethyl esters and anhydrous silver tetrafluoroborate to react in methylene chloride at 25-30° for 1-5 hours, 1,3-dioxolenium tetrafluoroborates were generally obtained as nice white isolable salts in yields of 43-93% (see Table I). Interestingly, 2-(p-methoxystyryl)-1,3-dioxolenium tetrafluoroborate, which was brilliant canary yellow, was the only colored salt observed in this entire series and will be commented on later. It was necessary to use distilled or purified ester precursors for the cations or low yields and inferior products invariably resulted. Conversion of the esters to 1,3-dioxolenium cations was



unambiguously ascertained by observing the disappearance of the A_2X_2 nmr pattern characteristic for the esters and the formation of a sharp singlet for the equivalent ring methylene protons of the cations.

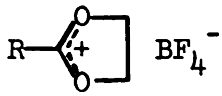
The 2-alkyl-1,3-dioxolenium tetrafluoroborates were generally soluble in methylene chloride with the exception of several which contained a double bond as part of the 2-substituent, [i.e., 2-vinyl, 2-isopropenyl, <u>trans</u>-2-propenyl, 2-styryl and 2-(p-methoxystyryl)].

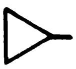
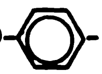
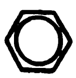
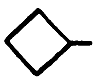
All of the 2-alkyl cation salts were soluble in acetonitrile, liquid sulfur dioxide or fluorosulfonic acid. The last two solvents served as excellent media for nmr analysis of these cations.

These salts were extremely moisture sensitive; several examples have been reported[57] to undergo facile ring opening with water to produce

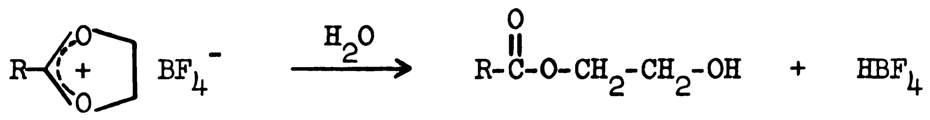
TABLE I

2-Alkyl-1,3-dioxolenium Tetrafluoroborates



	R	Mp, °C.	% Yield	Reaction Time, Hr.	Nmr Spectrum
1.	Et_2N-	53-54.5	69	1	37
2.		124.5-126	66	2	38
3.	$(CH_3)_2C=CH-$	61-62	65	2	39
4.	CH_3-O-  $-CH=CH-$	220-223	71	1	40
5.	$CH_3-CH=CH-$	150-152	79	1	41
6.	 $-CH=CH-$	178-179.5	67	1.75	42
7.		31-32	56	1	43
8.	$(CH_3)_3C-$	151.5-152.5	72	2	44
9.	CH_3-	170-172	83	1	45
10.	$CH_2=\overset{CH_3}{\overset{\vert}{C}}-$	155-156.5	81	2	46
11.	$CH_2=CH-$	151-152.5	43	4.5	47

2-hydroxyethyl esters. For this reason all operations were carried out in a glove box under scrupulously dry conditions. Under anhydrous storage con-



ditions the purified salts appear to have long shelf lives (i.e., 2 years) whereas impure samples tend to deteriorate within several weeks to a dark, amorphous mass.

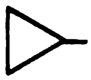
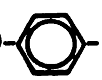
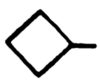
The ester precursors were readily prepared in yields of 25-87% by refluxing equivalent amounts of 2-bromoethanol with the appropriate acid chloride in carbon tetrachloride for 3-24 hours (see Table II). These 2-bromoethyl esters were generally obtained as distillable, colorless liquids or as crystallizable solids. The esters exhibited expected carbonyl absorptions in the 1700-1800cm^{-1} region as well as giving appropriate elemental analyses and nmr spectra (see Spectra 1-11).

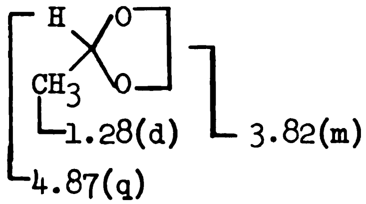
Nmr spectra of the cations were obtained both in liquid sulfur dioxide (-20°) and in fluorosulfonic acid (FSO_3H) (see Spectra 37-47). A downfield solvent shift of approximately 0.16 ppm was observed in going from FSO_3H to SO_2. Tetramethylsilane (TMS) was used as the internal standard in sulfur dioxide; in FSO_3H, the reference was tetramethylammonium tetrafluoroborate ($TMA \cdot BF_4$). The latter compound was assumed to have an absorption peak at -3.10 ppm downfield from tetramethylsilane, the value reported for this material in 100% H_2SO_4.[58] Compared to several 2-alkyl-1,3-dioxolanes, the ring protons in the corresponding cations were generally shifted downfield 1.4 to 1.7 ppm in FSO_3H. For example 2-methyl-1,3-dioxolane had the following chemical shifts (δ) in CCl_4 compared to 2-methyl-1,3-dioxolenium tetrafluoroborate in FSO_3H:

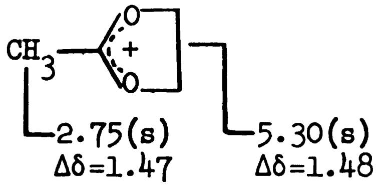
TABLE II

2-Bromoethyl Alkyl Esters

$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}CH_2{-}Br}$$

R	Mp or Bp	% Yield	Reaction time, hr.	Nmr Spectrum
$(Et)_2N-$	77-79°/1.5mm	56	20	1
	81-82°/10mm	87	5	2
$(CH_3)_2C{=}CH-$	78-79°/4mm	73	10	3
CH_3O-$-CH{=}CH-$	50.5-51.5	84	3	4
$CH_3-CH{=}CH-$	114-115°/40mm	50	4	5
$-CH{=}CH-$	44.5-46	62	24	6
	79-80°/5mm	77	15	7
$(CH_3)_3C-$	94-95°/34mm	25	10	8
CH_3-	160-161°/740mm	(Eastman Kodak)		9
$CH_2{=}\overset{CH_3}{\overset{\vert}{C}}-$	46-49°/5mm	(Borden Company)		10
$CH_2{=}CH-$	52-53°/5mm	(Borden Company)		11



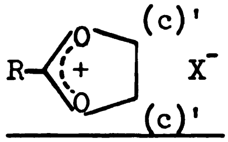
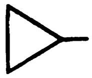
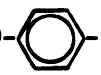
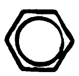
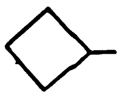


In Table III the proton chemical shifts of the 1,3-dioxolenium cations are listed in order of increased deshielding of the ring protons (c) and are compared to the methylene groups (a) and (b) in the corresponding ester precursors. In FSO_3H the $\Delta\delta$'s for (b) and (c) varied between 0.65-0.95 ppm, whereas in liquid sulfur dioxide $\Delta\delta$ varied between 0.95-1.13 ppm. The trend toward larger $\Delta\delta$'s in going from cation 1 → cation 11 in FSO_3H suggests that the more shielded cations possess 2-substituents which are more effective for delocalization of positive charge and provides at least a qualitative basis for using the cation ring proton chemical shifts as an electron density probe. This criterion has been employed by Olah[6] and Deno[5a,b] in other carbonium ion systems and has been found to provide a quantitative relationship for the 2-aryl-1,3-dioxolenium ions, which will be discussed later.

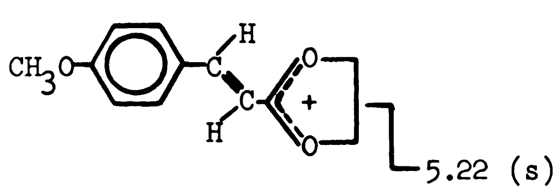
Whereas 2-(p-methoxystyryl)-1,3-dioxolenium fluoroborate gave a brilliant yellow solution and a simple, explicable nmr spectrum in liquid sulfur dioxide, in FSO_3H the cation was immediately decolorized and gave a somewhat more complex spectrum. In the acid medium two groups of appropriate but displaced resonance signals were observed for the cation. This is interpreted as being due to partial protonation of the methoxy group to produce a mixture of the monocation and a dication. The chemical shifts of these two species are shown below:

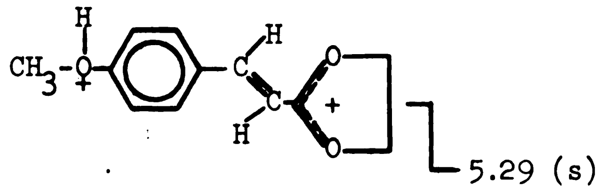
TABLE III

Comparison of Proton Chemical Shifts (δ)
of 2-Bromoethyl Alkyl Ester Precursors (CCl_4)
to 2-Alkyl-1,3-Dioxolenium Cations

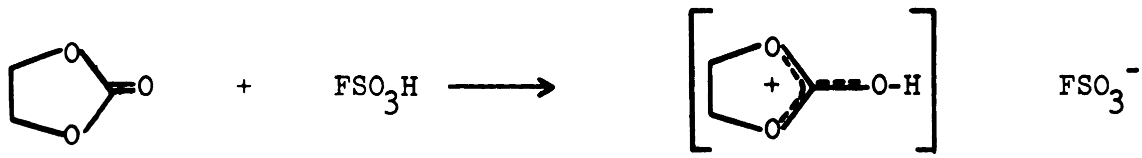
	R	$R\text{-}\overset{O}{\overset{\Vert}{C}}\text{-}O\text{-}\overset{(b)}{CH_2}\text{-}\overset{(a)}{CH_2}Br$ (CCl_4) (a)	(b)	 (FSO_3H, 25°) (c)	Δδ	(SO_2, -20°) (c)'	Δδ
1.	Et_2N-	3.53	4.33	4.98	0.65	—	—
2.		3.50	4.35	5.17	0.82	5.38	1.03
3.	$(CH_3)_2C{=}CH$-	3.48	4.35	5.19	0.84	—	—
4.	CH_3-O--CH=CH-	3.52	4.44	5.22 (5.29)*	0.78	—	—
5.	CH_3-CH=CH-	3.52	4.40	5.23	0.83	5.38	0.98
6.	-CH=CH-	3.53	4.46	5.25	0.79	5.41	0.95
7.		3.49	4.36	5.29	0.93	5.45	1.09
8.	$(CH_3)_3C$-	3.50	4.35	5.30	0.95	5.48	1.13
9.	CH_3-	3.50	4.35	5.30	0.95	5.44	1.09
10.	$CH_2{=}\overset{CH_3}{\overset{\vert}{C}}$-	3.54	4.43	5.34	0.91	5.52	1.09
11.	$CH_2{=}CH$-	3.52	4.44	5.35	0.91	5.52	1.08

*Chemical shift for the methoxy protonated cation

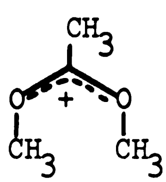




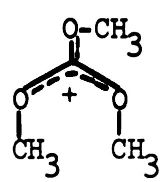
In strong acids such as FSO_3H or $HSbF_6$, ketones and esters have been shown to be protonated to produce hydroxy carbonium ions[5a,b,59,86] and hydroxy-alkoxy carbonium ions,[60] respectively. Protonation of ethylene carbonate in FSO_3H was expected to give 2-hydroxy-1,3-dioxolenium fluorosulfonate. It was surprising to find that the ring protons in this cation (δ = 5.26



ppm singlet) were deshielded more than those in the cyclic dialkoxycarbonium ions 1-6 (Table III), even though one might expect considerable charge delocalization through the resonance structure shown above. A similar observation was reported by Taft and Ramsey[1b,21] for the analogous acyclic series. They found that the methoxy protons were more deshielded in the trimethoxy cation than in the dimethoxy cation shown below. A good explanation for



δ = 5.0 ppm



δ = 5.1 ppm

these observations is not immediately obvious, unless the ethylene carbonate is being protonated on the ether oxygens.

In this investigation, three new methods were discovered for the generation of simple 2-substituted-1,3-dioxolenium cations. It was found that treatment of either a 2-hydroxyethyl, 2-acetoxyethyl or 2-methoxyethyl ester with an excess of FSO_3H resulted in the formation of the dioxolenium cal

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cation and associated protonated species, these depending on which precursor was used. It was further found that the mode of combination of these reactants was very important. Certain interesting protonated ester species could be generated in preference to the 1,3-dioxolenium cations by adding the ester to an excess of FSO_3H. These protonated ester species were gradually converted on standing (i.e. up to 5 months) to the corresponding 1,3-dioxolenium cations. In contrast, by adding the acid to the ester, the 1,3-dioxolenium cations were observed to form immediately as the major species present.

2-Hydroxyethyl esters were the best precursors to the cyclic cations. By adding FSO_3H to 2-hydroxyethyl acetate, 2-methyl-1,3-dioxolenium fluorosulfonate was generated almost quantitatively within 45 minutes (see Figure I). Reversing the order of addition (i.e. adding ester to acid) gave predominately the diprotonated ester (A) which was then gradually converted to the 1,3-dioxolenium cation upon standing at room temperature for several days (see Figure II). These transformations might be represented in the following manner:

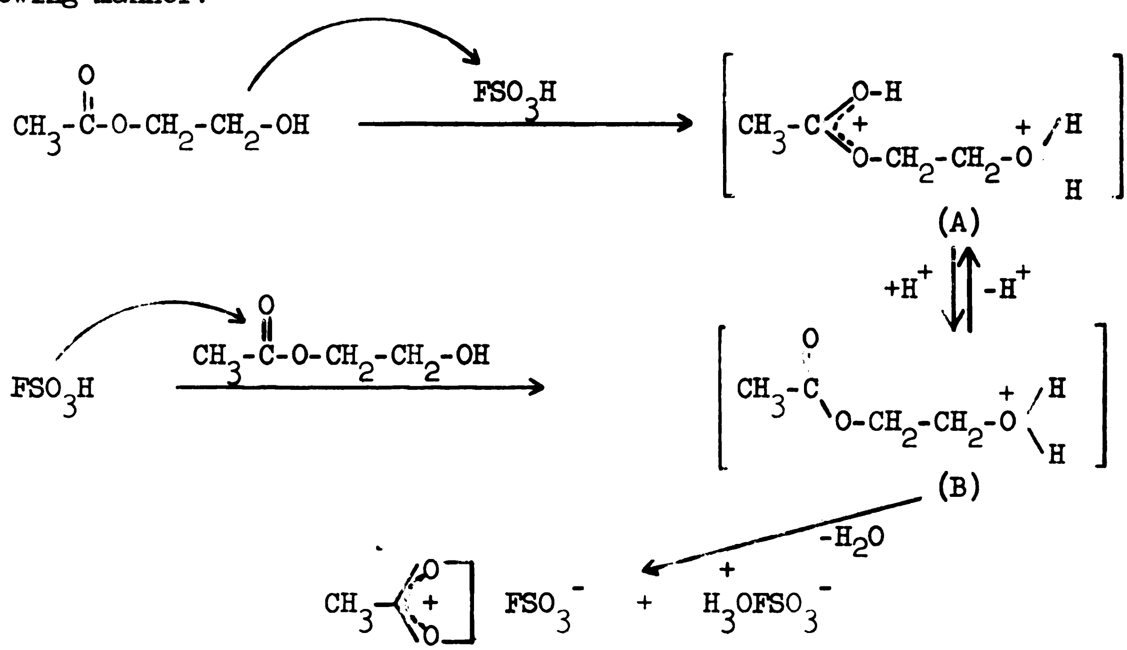
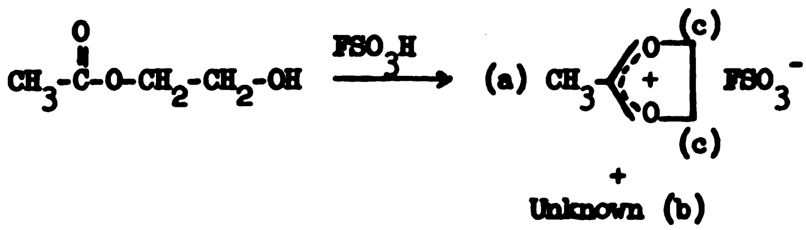
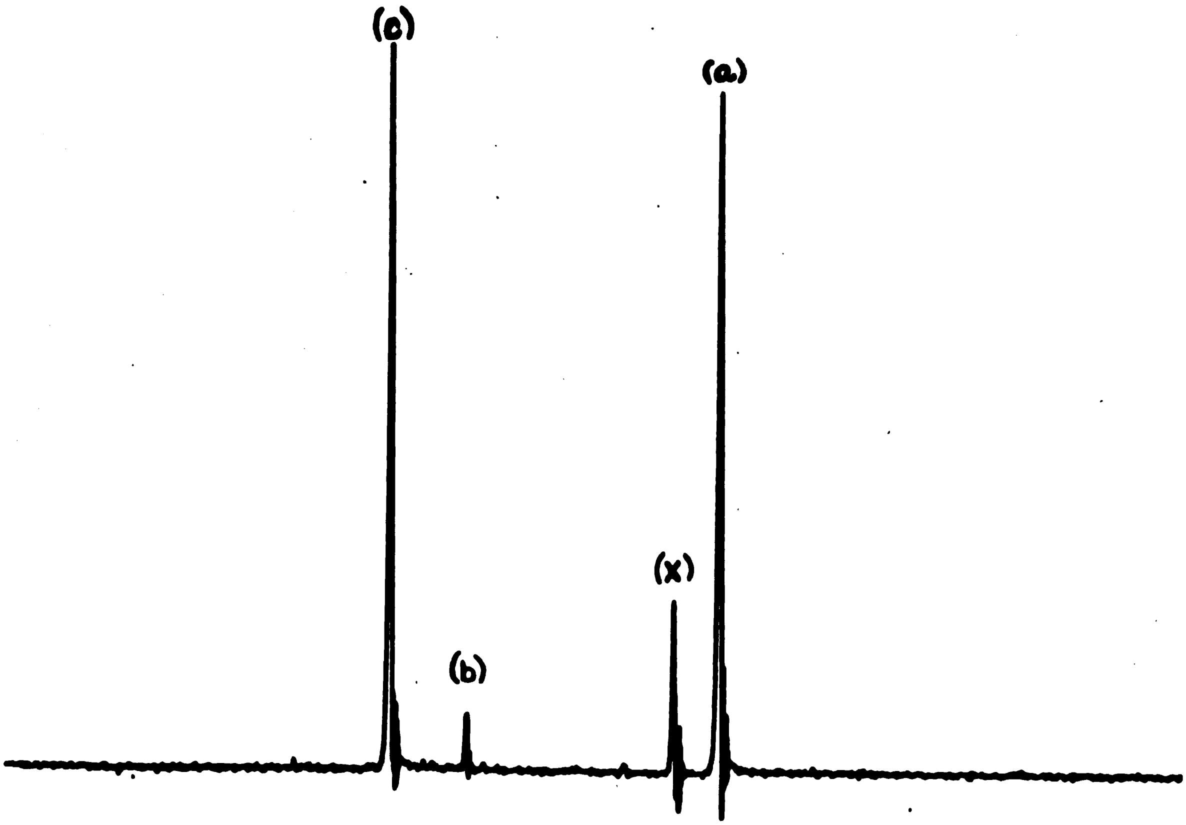


Figure I. Reaction of 2-Hydroxyethyl Acetate with FSO_3H (Addition of Acid to Ester; Reaction Time = 45 minutes)

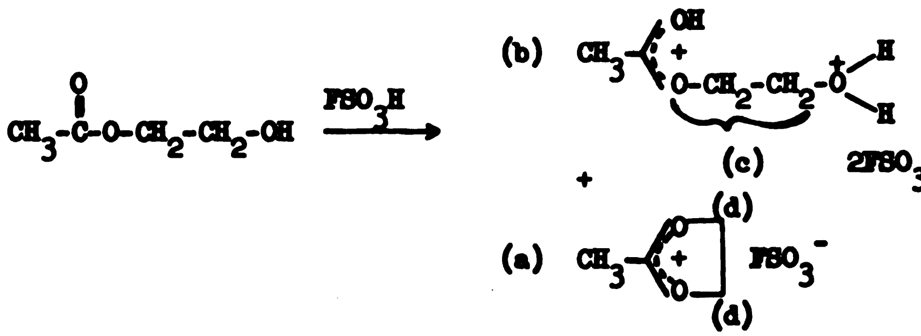


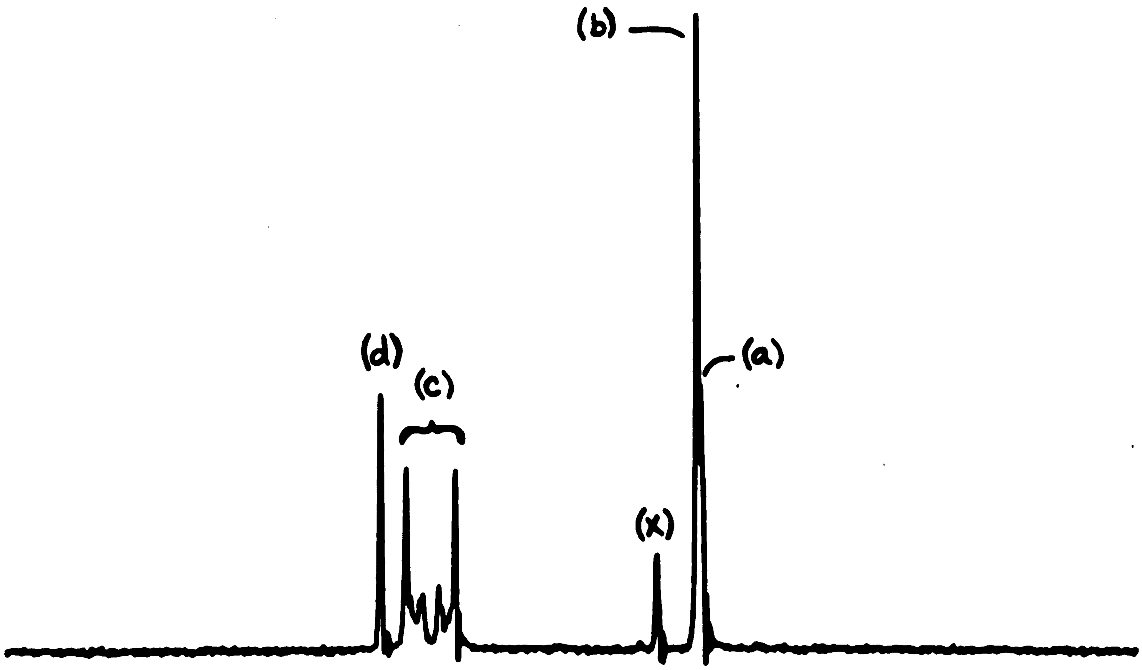


<u>Assignments (δ)</u>

x	3.10 ($TMA \cdot BF_4$)
a	2.75 (s)
b	4.71 (s)
c	5.31 (s)

Figure II. Reaction of 2-Hydroxyethyl Acetate with FSO_3H (Addition of Ester to Acid; Reaction Time = 7 Minutes)





<u>Assignments (δ)</u>

x	3.10 (TMA·BF_4)
a	2.75 (s)
b	2.77 (s)
c	4.91 (q)
d	5.31 (s)
	(c+d):(a+b) = 4:3

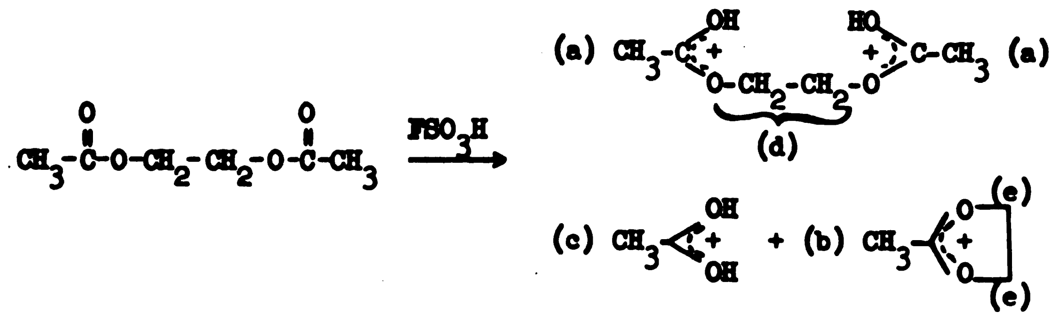
2-Methyl-1,3-dioxolenium cation (Figure I) was identified unequivocally by comparison to an authentic sample which had been prepared according to the method of Meerwein.[22] The identity of the singlet at 4.71 ppm is not readily apparent at this time. It should be mentioned that this same singlet (δ = 4.72 ppm) was observed in the conversion of 2-hydroxyethyl benzoate to 2-phenyl-1,3-dioxolenium fluorosulfonate.

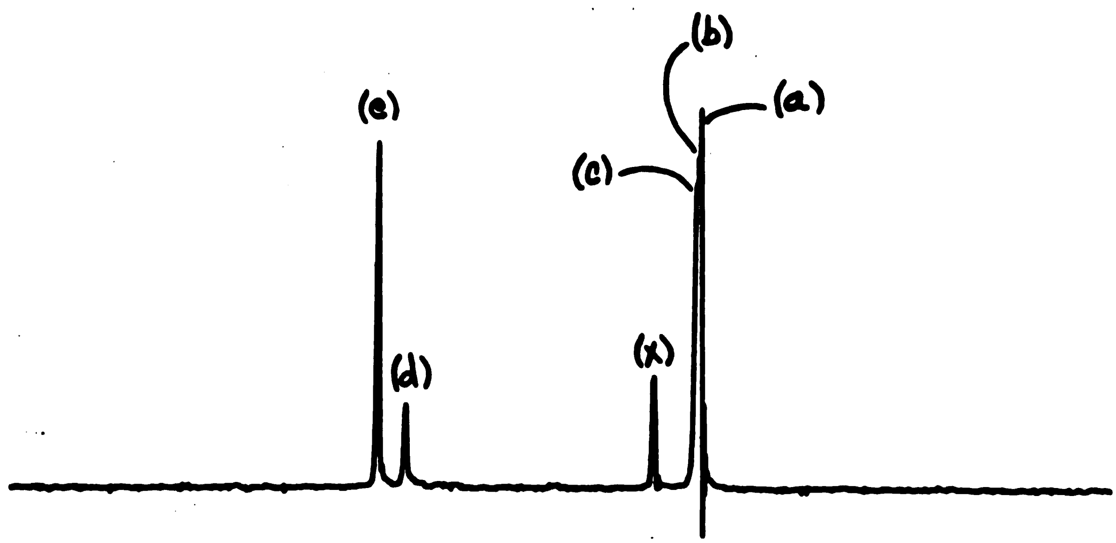
2-Methyl-1,3-dioxolenium cation appeared as the minor product in Figure II with singlets at 2.75 and 5.31 ppm. The major product in Figure II was assigned the diprotonated structure (A). This assignment was consistent with the A_2B_2 pattern at 4.91 ppm and the singlet at 2.77 ppm. Olah reported[60] a value of 2.75 ppm for the corresponding methyl group in protonated ethyl acetate.

The diprotonated species (A) may be longer lived than (B) because the carbonyl group is no longer effective as a nucleophile for backside displacement in this dicationic form. Protonated ester (B), however, can liberate water by intramolecular displacement via the carbonyl group to yield the cyclic cation. The facile conversion of (B) to the cyclic cation presumably precludes observation of (B) under these conditions. Dication (A) was observed to slowly convert to the cyclic cation. This presumably occurs via deprotonation to (B) (the equilibrium between (A) and (B) being overwhelmingly in favor of (A) in FSO_3H) followed by rapid intramolecular cyclization to the 1,3-dioxolenium cation.

By adding FSO_3H to 2-acetoxyethyl acetate, the ester was converted to 2-methyl-1,3-dioxolenium cation within 65 minutes at room temperature (see Figure III). The only other resonance bands extraneous to the cyclic cation were singlets located at 5.10, 2.77 and 2.73 ppm. The bands at 5.10 and 2.73 ppm were assigned to the symmetrical diprotonated diester (C). The

Figure III. Reaction of 2-Acetoxyethyl Acetate with FSO_3H (Addition of Acid to Ester; Reaction Time = 65 Minutes)

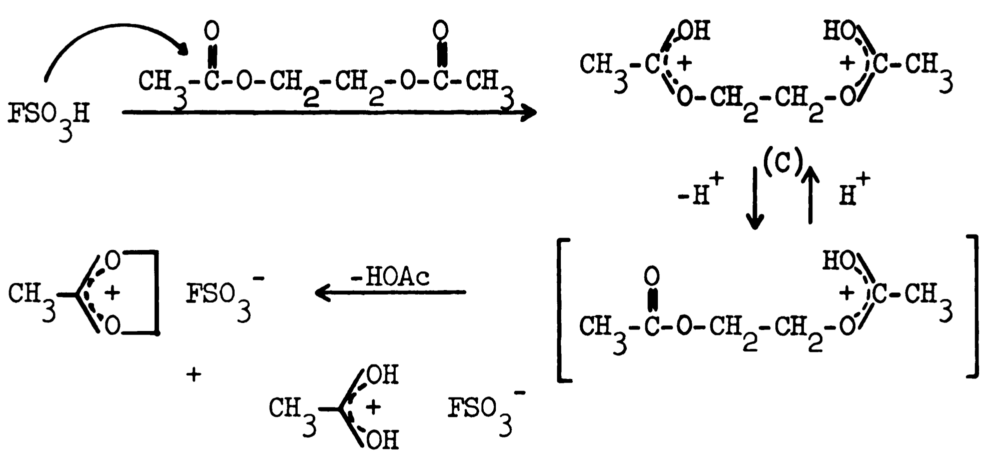




<u>Assignments (δ)</u>

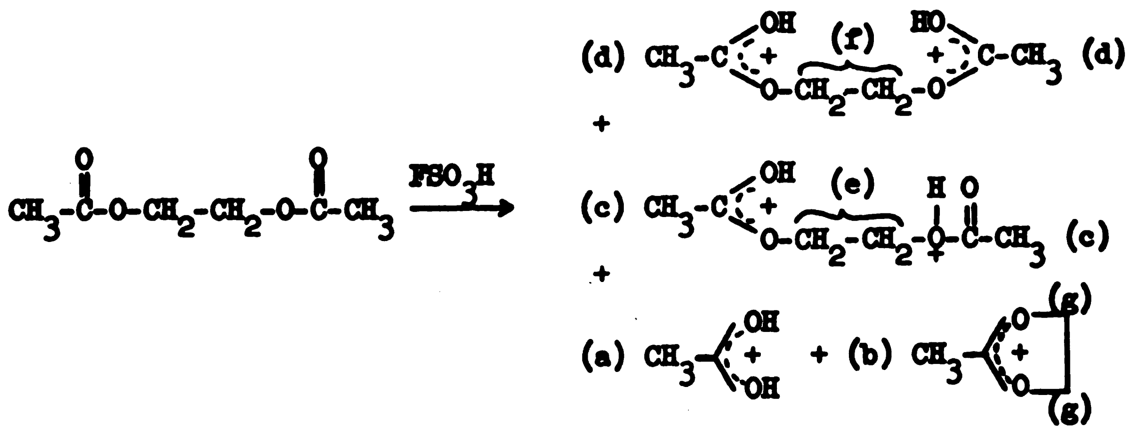
x	3.10 ($TMA \cdot BF_4$)
a	2.73 (s)
b	2.75 (s)
c	2.77 (s)
d	5.10 (s)
e	5.31 (s)

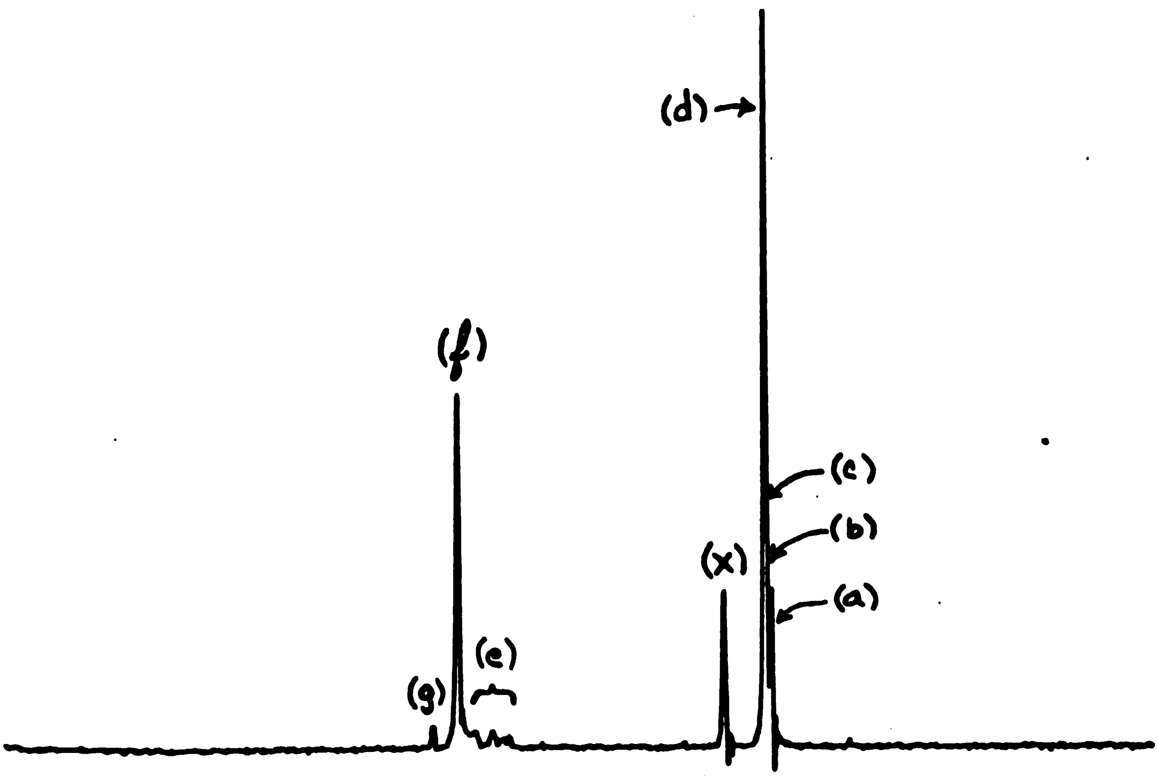
downfield singlet (5.10) would be consistent with the symmetrical protonated dication and has a chemical shift close to that assigned for the A_2B_2 pattern (e.g. 4.91) believed to be due to the methylene protons in the diprotonated 2-hydroxyethyl acetate dication (Figure II). The singlet at 2.73 ppm was assigned to the methyl groups on the dication. The singlet at 2.77 ppm was assigned to protonated acetic acid and was enhanced by the addition of a small amount of acetic acid. The singlets at 5.10 and 2.73 ppm gradually disappeared as the solution remained at room temperature while bands at 5.31, 2.77 and 2.75 increased, eventually giving only three singlets which were unequivocally attributed to a mixture of 2-methyl-1,3-dioxolenium fluorosulfonate and protonated acetic acid. This transformation can be envisioned in the following manner:



A spectrum of the reaction mixture resulting from the addition of 2-acetoxyethyl acetate to FSO_3H (Figure IV) was most revealing. At a reaction time of 15 minutes (25°) only a <u>trace</u> of 2-methyl-1,3-dioxolenium fluorosulfonate had been formed (the amount of cyclic cation formed was a function of addition rate and efficiency of mixing). Resonance bands extraneous to the cyclic cation and protonated acetic acid were as follows; strong singlet at 5.12 ppm, multiplet at 4.93 (presumably a quartet) and a strong singlet at 2.79. The intense singlets at 5.12 ppm and ~2.79, according to our

Figure IV. Reaction of 2-Acetoxyethyl Acetate with FSO_3H (Addition of Ester to Acid; Reaction Time = 15 Minutes)

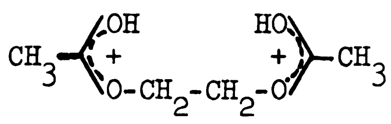




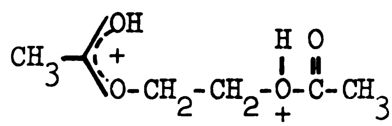
Assignments (δ)

x	3.10 ($TMA \cdot BF_4$)	(d)	~2.79 (s)
(a)	~2.75 (s)	(e)	4.93 (q)
(b)	Between 2.75-2.79 (s)	(f)	5.12 (s)
(c)	Between 2.75-2.79 (s)	(g)	5.31 (s)

argument for Figure III, were assigned to the symmetrically diprotonated ester (C) whereas the partially masked quartet (A_2B_2 pattern ?) at 4.93 was



(C)



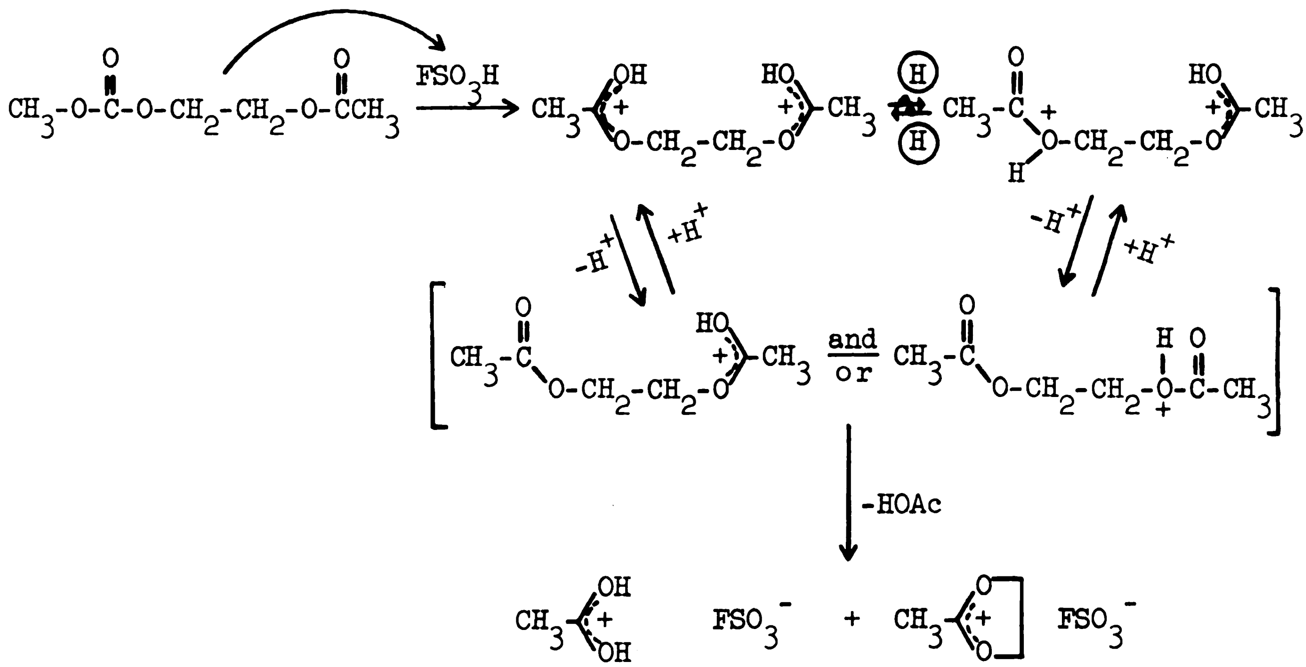
(D)

assigned to the unsymmetrical diprotonated ester (D). Some assurance for this speculation was gained by noting that the ratio of (g + f + e) : (a + b + c + d) was 4:3, thus giving a proton ratio which was consistent with our assignments for (C) and (D). As the mixture stood at room temperature, the singlet at 5.31 ppm due to the ring protons in the cyclic 1,3-dioxolenium cation increased with time, whereas the intensities of the singlet (5.12 ppm) and multiplet (4.93 ppm) decreased a commensurate amount. These changes in intensities were followed in one instance and are as shown below:

Reaction Time	Intensity (e + f) / Intensity (g)
1 hr.	3
2 days	1.69
6 days	1.15
7 days	1.11
9 days	0.89
5 months	0

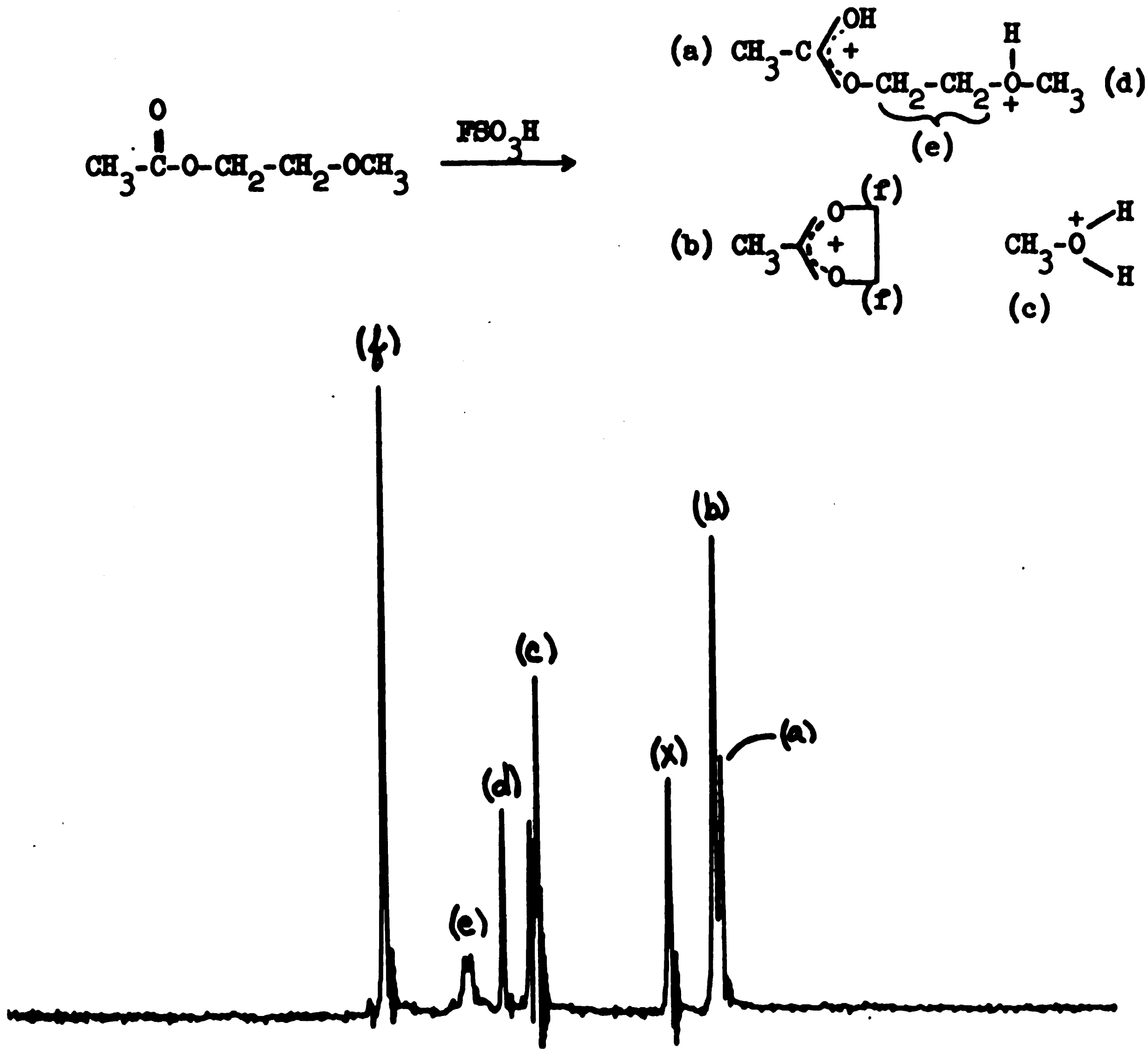
After 5 months the conversion is complete and quantitative to the cyclic cation and protonated acetic acid. After that time the spectrum consists of only three singlets, located at 5.32, 2.84 and 2.76 ppm respectively.

These spectral data may be rationalized according to the following reaction scheme:



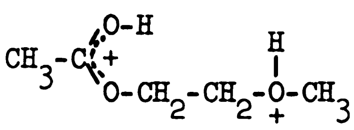
Conversion of 2-methoxyethyl acetate to the cyclic cation by addition of acid to the ester appeared to parallel the previous two examples, in that this mode of combining the reactants also gave the cyclic cation as the major product accompanied by minor amounts of associated protonated species (see Figure V). Resonance signals which were extraneous to those for the cyclic cation were as follows; multiplet at 4.67 ppm, singlet at 4.39 ppm, a multiplet at 4.25 ppm and a singlet at 2.70 ppm. By adding a small amount of methanol, the multiplet at 4.25 ppm was enhanced; thus this peak is assigned to protonated methanol.[62] The signal at 4.67 ppm was assigned to the methylene protons in the diprotonated ester (E) whereas the singlets at 4.39 and 2.70 ppm were assigned to the ethereal and carbonyl methyl groups, respectively in the dication (E). Olah's work[61] supports the assignment at 4.39 ppm in that he reports a δ value of 4.39 ppm for the analogous methyl group in cation (F). Furthermore signals (e) and (d), Figure V, were present in a ratio of approximately 4 : 3 which is consistent with

Figure V. Reaction of 2-Methoxyethyl Acetate with FSO_3H (Addition of Acid to Ester; Reaction Time = 40 Minutes)

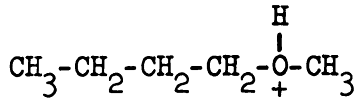


<u>Assignments (δ)</u>

x	3.10 (TMA·BF_4)
a	2.70 (s)
b	2.75 (s)
c	4.25 (m)
d	4.39 (s)
e	4.67 (m)
f	5.31 (s)

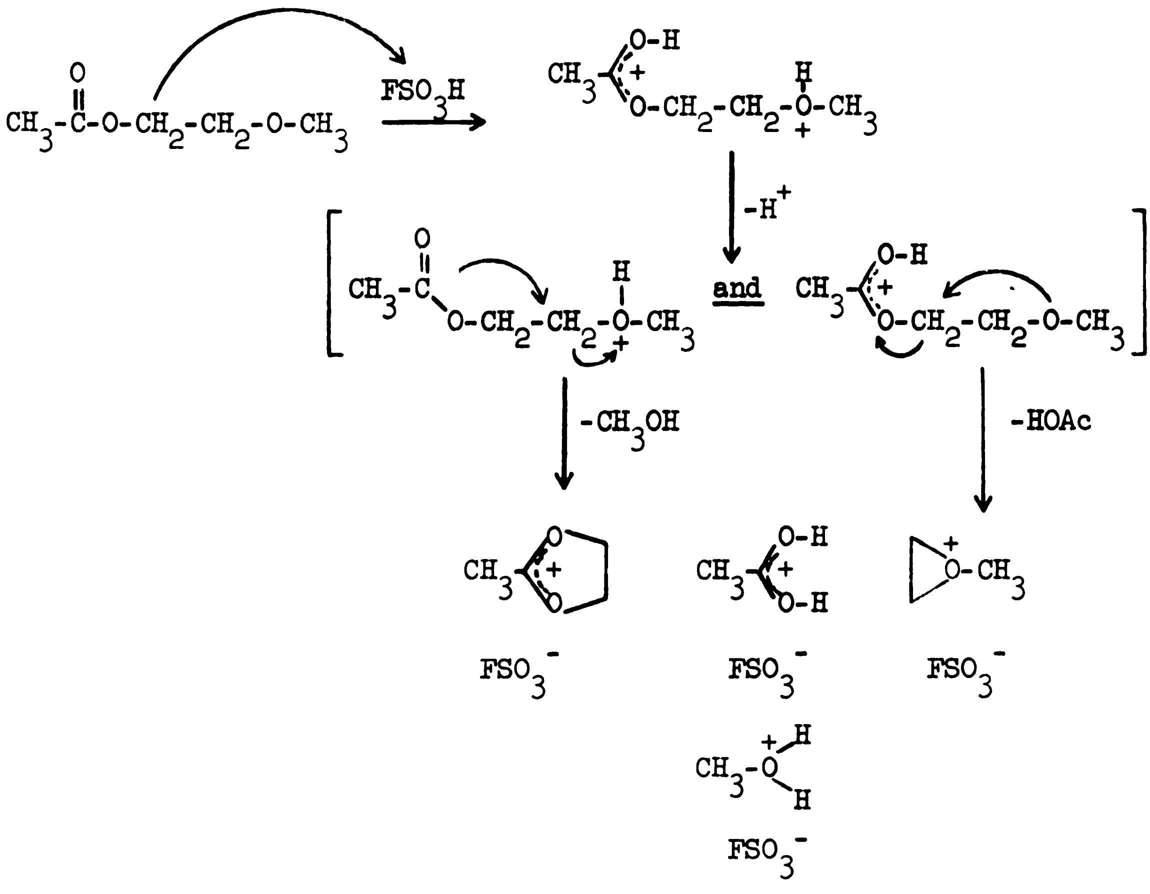


(E)



(F)

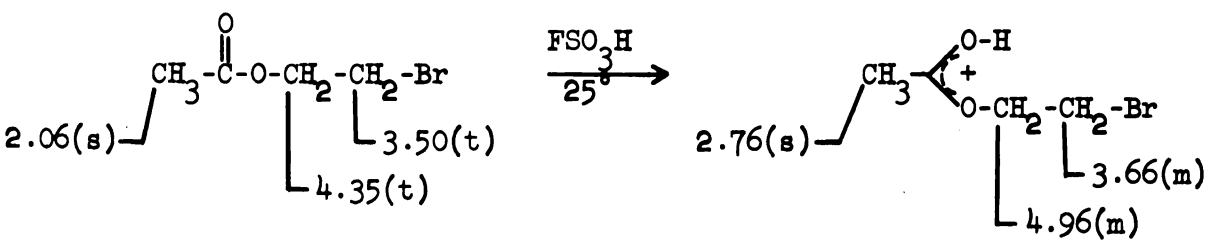
the dication structure (E). Conversion to the cyclic cation was slow and far from complete even after 9 days at room temperature. Protonation of this ester under these conditions is envisioned as proceeding in the following manner:



It should be noted that signals (e) and (d) might alternatively be assigned to the cyclic methyl oxonium cation shown above which could be formed by participation of the methoxy group with concurrent displacement of acetic acid.

The reaction mixture resulting from addition of 2-methoxyethyl acetate to FSO_3H gave a considerably more complex spectrum (see Figure VI). 2-Methyl-1,3-dioxolenium cation and protonated methanol could be unequivocally identified as well as the diprotonated ester seen in Figure V. However, superimposed upon these signals were new resonance bands at 5.05 ppm (h) and at 4.72 ppm (g). The identity of these signals was not readily apparent. These latter two resonance bands appeared to be decreasing in intensity with time (25°) as the 1,3-dioxolenium cation signal (5.31 ppm) increased in intensity.

Intrigued with our success in cyclizing the forementioned acetate esters, it was thought that it might be possible to ionize 2-bromoethyl acetate in FSO_3H to produce 1,3-dioxolenium cations. Nmr analysis indicated that the ester merely underwent carbonyl protonation without loss of bromide ion. This was readily apparent by noting the large downfield shift



($\Delta\delta$ = 0.61 ppm) for the methylene protons attached to the ester oxygen and the carbonyl methyl group ($\Delta\delta$ = 0.70 ppm). Recent work by Olah and coworkers[60] supports these assignments in that carbonyl protonated ethyl acetate was reported to have similar chemical shifts in FSO_3H-SbF_6-SO_2 as shown below:

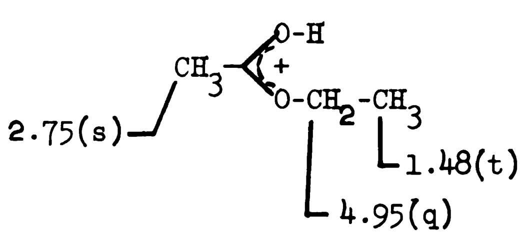
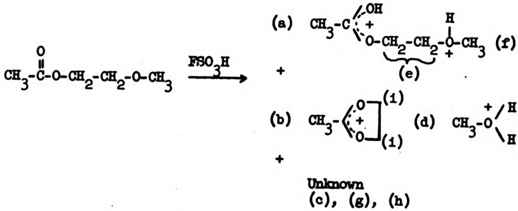
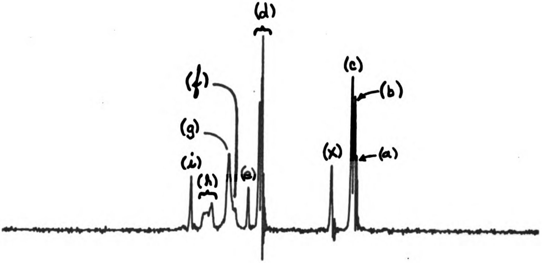


Figure VI. Reaction of 2-Methoxyethyl Acetate with FSO_3H (Addition of Ester to Acid; Reaction Time = 10 minutes)

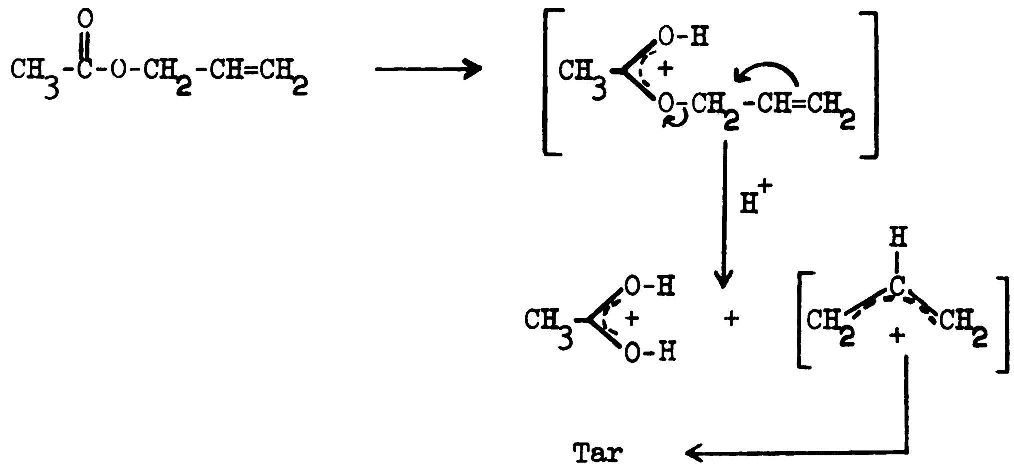




Assignments (δ)

x	3.10 ($TMA \cdot BF_4$)	f	4.68 (m)
a	2.71 (s)	g	4.72 (s)
b	2.74 (s)	h	5.05 (m)
c	2.78 (s)	i	5.30 (s)
d	4.23 (m)		
e	4.41 (s)		

Finally an attempt was made to cyclize allyl acetate with FSO_3H. It was thought that if the olefin's double bond could be protonated in a Markownikoff manner a transient secondary carbonium ion might be generated which could cyclize by participation of the acetoxy group, leading to a 2,4-dimethyl-1,3-dioxolenium cation. Upon combining these reactants, an exothermic reaction ensued leading to a black tar. Nmr analysis of the FSO_3H decantate revealed only a singlet at 2.77 ppm which was identified as protonated acetic acid. It appears as though carbonyl protonation occurs initially, followed by cleavage to acetic acid and the allyl cation.



The latter species does not survive these conditions and converts to the black resin leaving protonated acetic acid as the only identifiable product.

B. 2,2'-Alkylenebis-1,3-Dioxolenium Dications

A recent investigation, by Olah and Comisarow,[13a] of the reaction between dicarboxylic acid fluorides and antimony pentafluoride showed that alkylene dioxodicarbonium ions (acyl dications) were not formed unless the acyl groups were insulated by at least three methylene groups. It was

$$\overset{\oplus}{O}{=}C{\left(CH_2\right)}_n C{=}\overset{\oplus}{O} : n \geq 3$$

considered of interest to investigate the synthesis of a series of 2,2'-alkylenebis-1,3-dioxolenium dications in order to determine whether the charges might be brought closer together and to ascertain how sensitive the dioxolenium ring proton chemical shifts were to charge repulsion as the number of insulating methylene groups was varied.

The 2,2'-alkylenebis-1,3-dioxolenium dications, n=1-6, were prepared according to the method of Meerwein[22] by allowing the appropriate bis-(2-bromoethyl) esters to react with two equivalents of anhydrous silver tetrafluoroborate in methylene chloride. The dications were obtained in high yields either as mixtures with silver bromide or as isolable salts (see

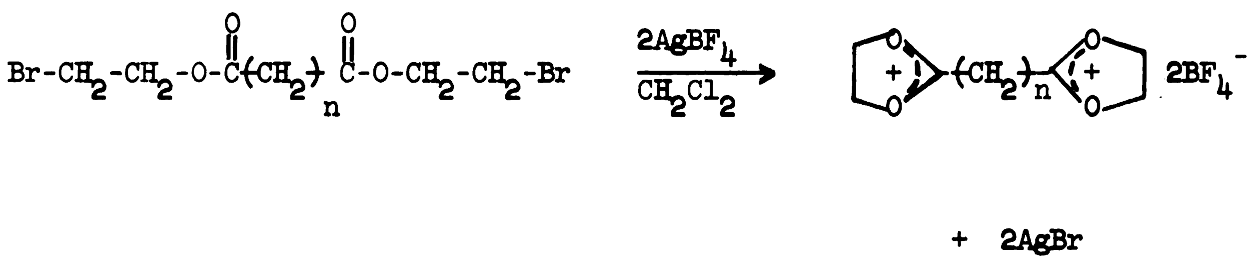
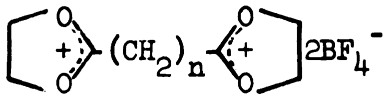


Table IV). Several of the dications, where n = 2, 3 and 4, could not be isolated from the silver bromide due to their insolubility in common polar solvents such as methylene chloride, liquid sulfur dioxide or nitromethane. Interestingly, when n = 1, 5 or 6, the dications were isolable as white crystalline products by repeated extractions of the dication-AgBr mixtures with liquid sulfur dioxide. The dications (n=2,3,4) were, however, fairly soluble in FSO_3H and could be characterized by extracting the silver bromide-dication mixtures with this acid. Satisfactory nmr spectra were obtained by scanning these extracts. (See Spectra 49-54).

Preparation of the dication containing no insulating methylene groups (n=0) between the dioxolenium rings is less straightforward. When bis-(2-bromoethyl) oxalate was allowed to react with $AgBF_4$ or $AgSbF_6$, a silver

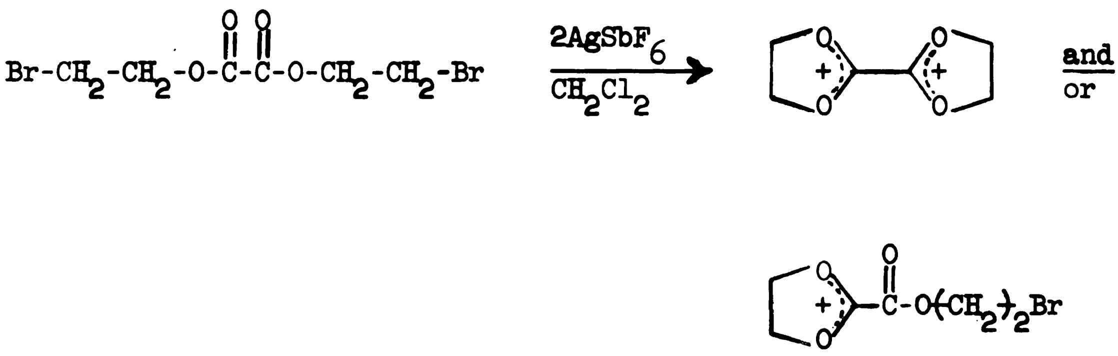
TABLE IV

2,2'-Alkylenebis-1,3-dioxolenium Dications



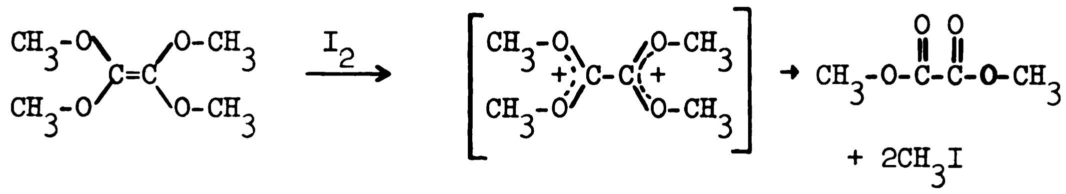
n	Mp, °	Yield,%	Reaction Time, hrs.	Nmr Spectrum
1	208-210	88	8.5	49
2	-	95*	14	50
3	-	77*	3.0	51
4	-	80*	2.5	52
5	173-175	88	2.5	53
6	198-200	91	2.5	54

*Yield calculated for a mixture of the dication and AgBr bromide precipitate appeared after several hours at 25-30°. However, the reaction was not clean and spectral analysis was obscured by a variety of



by-products. This was particularly true of the reaction with $AgBF_4$, which produced an intractable paste. The reaction with $AgSbF_6$ was more promising, but still ambiguous. After a reaction time of 14 hours, a yellow gummy solid was obtained which was characterized by extracting with FSO_3H and examining the resulting extract by nmr spectroscopy. The major resonance signals were a singlet at 5.70 ppm and a multiplet at 4.79-5.07 ppm in a ratio of ~2:3. After a reaction time of 51 hours the reaction product was again analyzed in the same manner. The same signals described above were predominant, accompanied by a weak singlet at 6.00 ppm (see Spectrum 48). It was interesting that the ratio of the singlet at 5.70 ppm and the multiplet at 4.79-5.07 ppm had changed to ~2.3:1 after this longer reaction time. The singlet at 5.70 ppm is certainly appropriate and characteristic for the dioxolenium ring protons, but one cannot be certain whether it is due to the monocation or dication. The multiplet is presumably not due to the bis-(2-bromoethyl) oxalate ester precursor which gave an A_2X_2 pattern at 4.87 and 3.64 ppm in FSO_3H.

Related dications containing no insulating groups between the positive centers have recently been postulated by Hoffmann[63,64] as elusive intermediates in the oxidation of tetramethoxyethylene to dimethyl oxalate.



Bis-(2-bromoethyl) ester precursors were prepared by refluxing the appropriate diacid chlorides with two equivalents of 2-bromoethanol in carbon tetrachloride for 6-25.5 hours (see Table V). Yields were 67-96% and the esters were high-boiling liquids or crystallizable solids. These esters exhibited expected nmr (see Spectra 12-18) and infrared spectra as well as giving suitable elemental analyses.

Fluorosulfonic acid was an excellent medium for obtaining nmr spectra of these dications. The spectra consisted of a characteristic sharp singlet for the equivalent dioxolenium ring protons as well as appropriate resonance signals for the 2-alkylene groups. In all cases integrations of these signals were consistent with the proposed dication structures.

These dications have been arranged in order of increased shielding of the ring protons in Figure VII. This order should reflect the relative amount of charge repulsion which results as the number of insulating methylene groups between the electron deficient centers is decreased. As expected, the magnitude of charge repulsion is inversely related to the number of insulating groups. When n = 6 (ion VI) charge repulsion is at a minimum, and the molecule contains two relatively independent, non-interacting cationic centers. This can be demonstrated by comparing the ring proton chemical shift of the dication (5.32 ppm) with that for the analogous monocation, 2-methyl-1,3-dioxolenium tetrafluoroborate, in which the ring protons have a chemical shift of 5.30 ppm. When n = 1 (ion I) charge repulsion is at a maximum. This is reflected not only by the large deshielding

TABLE V

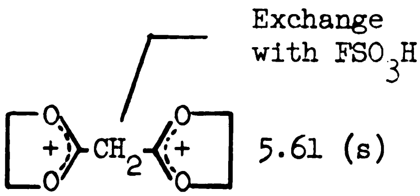
Bis-2-(Bromoethyl) Esters

$$Br\text{-}CH_2\text{-}CH_2\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_n\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}CH_2\text{-}CH_2\text{-}Br$$

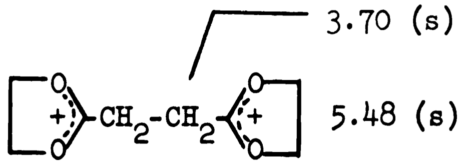
n	Mp or Bp, °	Yield, %	Reaction Time, hrs.	Nmr Spectrum
0	Mp 54.5-56	96	9	12
1	125-6/0.5mm	74	6	13
2	145-147/2mm	67	14	14
3	115-118/2.5mm	74	12	15
4	162-3/0.9mm	79	12	16
5	156-7/2mm	67	8	17
6	Mp 37-38	94	25.5	18

Figure VII

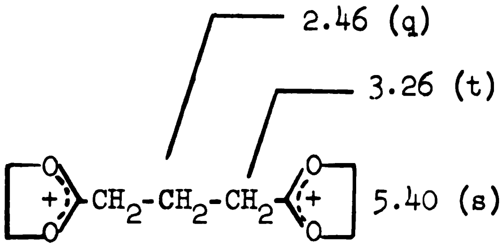
2,2'-Alkylenebis-1,3-dioxolenium Dications
in order of Increased Shielding of Ring Protons



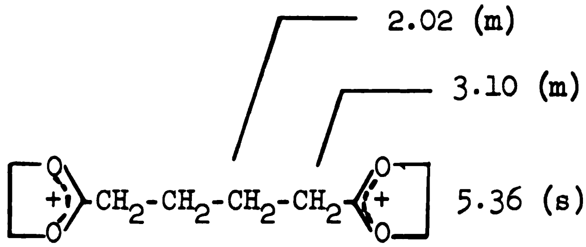
I



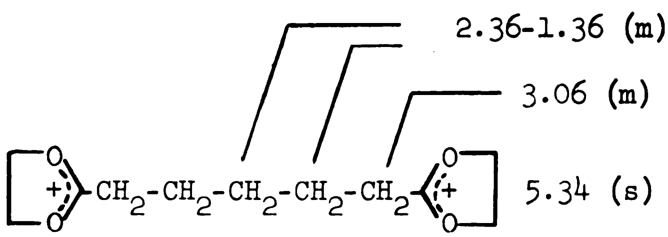
II



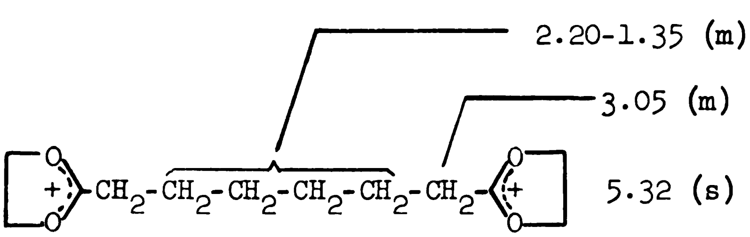
III



IV

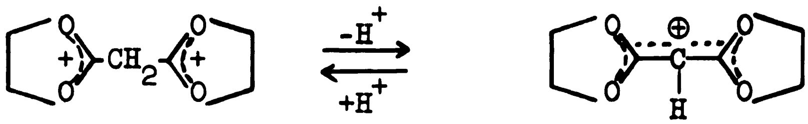


V

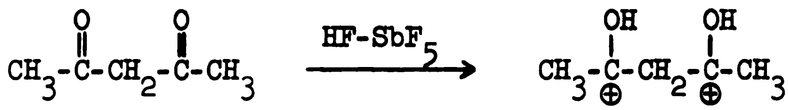


VI

of the ring protons but also by the fact that the insulating methylene protons are so acidic that they exchange readily with the FSO_3H solvent. The exchange probably occurs via the equilibrium shown below. It is



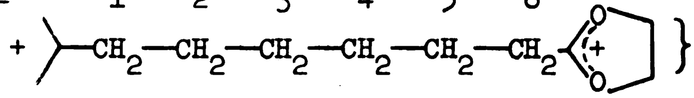
interesting that the methylene group in a 1,3-dihydroxydicarbonium ion reported recently by Brouwer[59] does not exchange very rapidly at -20° to +30° in an HF - SbF_5 medium. The nmr spectrum of this dication consists



of three singlets in a ratio of 1:1:3 which were assigned to the OH, CH_2, and CH_3 groups, respectively.

Recent nmr studies by Dewar[65] and Frankel[66] have reopened the question concerning the roles of inductive and field effects in the transmission of charge in a molecule. These effects have been previously defined by Roberts.[67] The smooth monotonic curve that is obtained by plotting dioxolenium ring proton chemical shifts as a function of charge separation (n), (see Figure VIII) suggests that inductive effects predominate in this system. Successive polarization of σ bonds, as described by Branch and Calvin,[68] accounts for the observed charge repulsions. The charge attenuation per bond in this system appears to be of approximately the same order as that described by these workers, i.e. $\frac{1}{2.8}$. Assuming this value, one would expect charge repulsion to nearly disappear when n = 5-6.

n = 1 2 3 4 5 6



Probe

Chg = 0.36 0.13 .045 .016 .006 .002

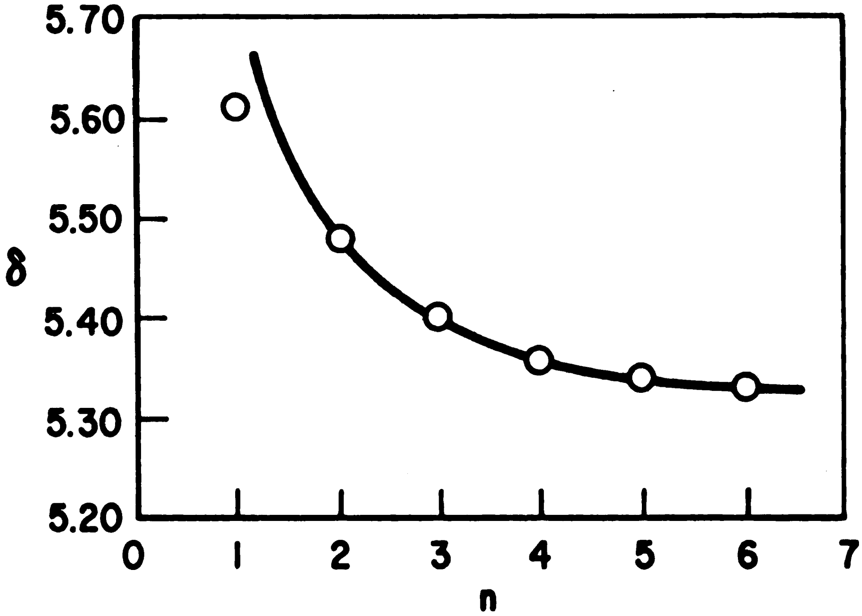


FIGURE VIII DIOXOLENIUM RING PROTON CHEMICAL SHIFT VS NUMBER OF METHYLENE GROUPS

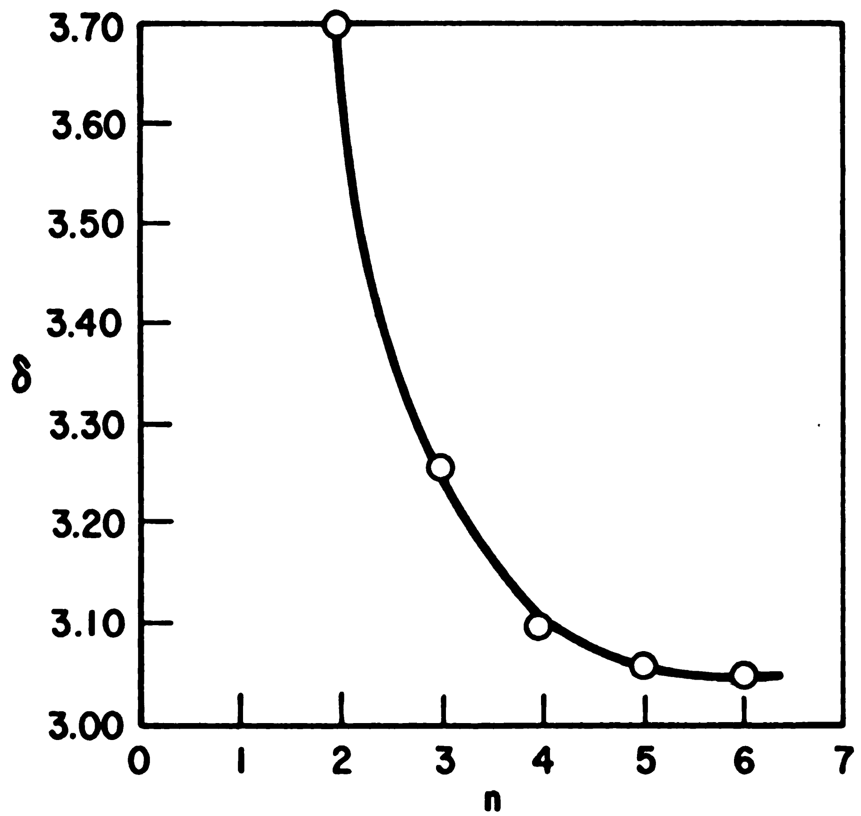


FIGURE IX 2-METHYLENE PROTON CHEMICAL SHIFT VS NUMBER OF METHYLENE GROUPS

This is indeed the case; dication VI, where n = 6, has approximately the same ring proton deshielding value as the monocation, 2-methyl-1,3-dioxolenium tetrafluoroborate.

Further examination of this system showed that these data are fit rather well by the empirically derived equation (1) where 5.30, the limiting value of δ when $n = \infty$, is identical with the chemical shift of the

$$\delta = 5.30 + \frac{1.60}{(n+1)^2} \qquad (1)$$

ring protons in the 2-methyl-1,3-dioxolenium monocation. When n is large, the molecule behaves as if there were no interaction between the cationic centers. Equation (1) obviously fails when n = 0, but attempts to fit the data with an equation using n + 1, $n^2 + 1$, etc. in the denominator of the last term, with appropriate changes in the parameters, were unsuccessful.

The chemical shifts of the methylene protons between the cationic centers provide an even more sensitive probe of charge distribution in these dications. Figure IX shows a plot of the α-methylene proton chemical shifts as a function of n; these data are fit almost precisely by the equation. In Figures VIII and IX, the solid curves are drawn accord-

$$\delta = 2.94 \left(1 + \frac{1}{n^2}\right) \qquad (2)$$

ing to the equations, whereas the points are experimental.

Equation (2) suggests that the chemical shift of the α-methylene protons can be described as the sum of two terms, one of which is constant (i.e., the methylene is always adjacent to and a constant distance from one dioxolenium ring) and one of which varies inversely as the square of n, which may be proportional to the distance from the second cationic center.

An alternative, very simple way of correlating these data is also possible. Each methylene in ion II may be considered to be α to one dioxolenium ring and β to the other. The chemical shift can be expressed as the sum of two parameters, $\delta_{\alpha} + \delta_{\beta}$. Values of these empirical constants which fit the data are: $\delta_{\alpha} = 2.47$, $\delta_{\beta} = 1.23$, $\delta_{\gamma} = 0.79$, $\delta_{\delta} = 0.63$, $\delta_{\epsilon} = 0.59$. The data of Figure VII provide only one independent check on the method, which happens to give a calculated δ that agrees exactly with the observed. However, this method has also been applied to analogous data reported by Olah and coworkers for bis-acylium ions.[13a] The best parameters are $\delta_{\alpha} = 3.60$, $\delta_{\beta} = 1.67$, $\delta_{\gamma} = 0.87$, $\delta_{\delta} = 0.69$, $\delta_{\epsilon} = 0.53$, $\delta_{\zeta} = 0.43$, $\delta_{\eta} = 0.41$. Two examples of the closeness of fit are

$$O{=}\overset{\oplus}{C}-\underset{4.20}{\overset{(4.29)}{C}}-\underset{2.52}{\overset{(2.54)}{C}}-C-C-\overset{\oplus}{C}{=}O$$

and

$$O{=}\overset{\oplus}{C}-\underset{4.00}{\overset{(4.01)}{C}}-\underset{2.10}{\overset{(2.10)}{C}}-\underset{1.40}{\overset{(1.40)}{C}}-\underset{1.29}{\overset{(1.38)}{C}}-C-C-C-\overset{\oplus}{C}{=}O$$

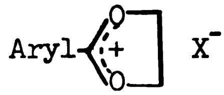
where values in parentheses are calculated, and those below the formulas were observed by Olah and Comisarow.[13a] The parameters for bis-acylium ions are larger than those for bis-dioxolenium ions, due to less charge delocalization in the former.

C. <u>2-Aryl-1,3-dioxolenium Cations</u>:

Using a modified version of Meerwein's method,[22] fifteen 2-(<u>meta</u> and <u>para</u> substituted aryl)-1,3-dioxolenium cations were prepared by reacting equimolar amounts of appropriate 2-bromoethyl esters with anhydrous silver tetrafluoroborate in methylene chloride. Stirring these reactants for 1-2 hours at 25-30° gave 55-96% yields of the white tetrafluoroborate salts (see Table VI). Precautions observed in the workup and storage of these cations were essentially the same as described for the 2-alkyl-1,3-dioxolenium cations. Separation of these cations from silver bromide was

TABLE VI

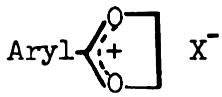
2-Aryl-1,3-Dioxolenium Cations



Aryl Substituent	Mp, °	Yield, %	Reaction Time, hr.	Nmr Spectrum
p-Methoxy	228-230	96	1	55
3,4,5-Trimethoxy	166-167.5	77	2	56
p-Methyl	207-209	81	1	57
m-Methyl	194-196	76	1	58
Phenyl	168-170	81	1	59
p-Fluoro	203-205	63	1	60
p-Chloro	235-237	82	1	61
m-Chloro	173-175	69	1	62
m-Bromo	174.5-176	61	1	63
m-Fluoro	169-171	61	2	64
3,4-Dichloro	218-220	69	1	65
m-Trifluoromethyl	135-137	72	1.5	66
p-Trifluoromethyl	188-189.5	63	4.5	67
m-Nitro	149-151.5	70	1.25	68
p-Nitro	209-211	55	2	69

TABLE VI

2-Aryl-1,3-Dioxolenium Cations



Aryl Substituent	Mp, °	Yield, %	Reaction Time, hr.	Nmr Spectrum
p-Methoxy	228-230	96	1	55
3,4,5-Trimethoxy	166-167.5	77	2	56
p-Methyl	207-209	81	1	57
m-Methyl	194-196	76	1	58
Phenyl	168-170	81	1	59
p-Fluoro	203-205	63	1	60
p-Chloro	235-237	82	1	61
m-Chloro	173-175	69	1	62
m-Bromo	174.5-176	61	1	63
m-Fluoro	169-171	61	2	64
3,4-Dichloro	218-220	69	1	65
m-Trifluoromethyl	135-137	72	1.5	66
p-Trifluoromethyl	188-189.5	63	4.5	67
m-Nitro	149-151.5	70	1.25	68
p-Nitro	209-211	55	2	69

somewhat different, however, since the 2-aryl-1,3-dioxolenium cations were virtually insoluble in methylene chloride. But, these cations were readily extracted with liquid sulfur dioxide or acetonitrile. Purification was generally effected by recrystallization from a mixture of acetonitrile and methylene chloride.

2-Bromoethyl benzoate precursors were prepared by refluxing equivalent amounts of 2-bromoethanol and the appropriate benzoyl chloride in carbon tetrachloride. Reaction times of 6-24 hours gave the esters as colorless high boiling liquids or crystallizable solids in yields of 25-85% (see Table VII). All of the esters gave appropriate infrared and nmr spectra (see Spectra 19-33) as well as suitable elemental analyses.

Nmr spectra of these cations were obtained in liquid sulfur dioxide (-20°) as well as in FSO_3H (25°). A characteristic cation spectrum consists of a sharp singlet for the equivalent dioxolenium ring methylene protons as well as appropriate downfield resonance signals for the corresponding aromatic nuclei (see Spectra 55-59).

Compared to the corresponding 2-aryl-1,3-dioxolanes in CCl_4, the cation ring protons were shifted downfield 1.48-1.62 ppm in FSO_3H and 1.58-1.76 ppm in liquid sulfur dioxide (see Table VIII). In Table VIII the chemical shifts of the dioxolenium cations are listed in order of increased deshielding of the ring protons (b) and are compared to the ring protons in the corresponding dioxolanes (a). An examination of the $\Delta\delta$'s between (a) and (b) in each of these solvents reveals no apparent trends as a function of the electron donating ability of the aromatic substituent. The lack of correlation for the $\Delta\delta$'s may be due to the geometry of the dioxolanes. The tetrahedral (sp^3) geometry at the 2-carbon in the dioxolane ring may force the ring protons to experience considerable and varied anisotropy effects,

TABLE VII

2-Bromoethyl Benzoates

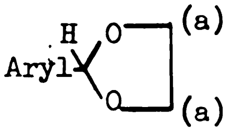
$$\text{Aryl-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-O-}CH_2\text{-}CH_2\text{-Br}$$

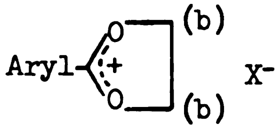
Aryl Substituent	Mp or Bp, °	Yield, %	Reaction Time, hr.	Nmr Spectrum
p-Methoxy	141-2/3mm	44	15	19
3,4,5-Trimethoxy	Mp 56-7	79	10	20
p-Methyl	116-7/4mm	71	12	21
m-Methyl	121-2/3mm	81	12	22
Phenyl	96-7/2mm	69	15	23
p-Fluoro	Mp 41-42.5	41	12	24
p-Chloro	120-1/0.9mm	68	12	25
m-Chloro*	88-9/1.5mm	85	12	26
m-Bromo	118-9/2mm	66	13	27
m-Fluoro	99-100/3mm	65	24	28
3,4-Dichloro	124-5/1mm	38	6	29
m-Trifluoromethyl	93-4/1.9mm	65	24	30
p-Trifluoromethyl	92-3/3mm	72	9	31
m-Nitro	140-2/0.4mm	25	10	32
p-Nitro	Mp 49.5-51	50	9	33

*These data are for 2-chloroethyl *m*-chlorobenzoate.

TABLE VIII

Comparison of Proton Chemical Shifts (δ) of 2-Aryl-1,3-dioxolanes (CCl_4) with 2-Aryl-1,3-dioxolenium Cations





	(CCl_4)	(FSO_3H, 25°)		(SO_2, -20°)	
Aryl Substituent	(a)	(b)	Δδ	(b)	Δδ
p-Methoxy	3.83	5.33	1.50	5.48	1.65
Phenyl	3.83	5.42	1.59	5.57	1.74
p-Fluoro	3.94	5.42	1.48	5.52	1.58
p-Chloro	3.90	5.43	1.53	5.60	1.70
3,4-Dichloro	3.95	5.47	1.52	5.63	1.68
p-Nitro	3.97	5.59	1.62	5.73	1.76

whereas in the dioxolenium cations the sp^2 geometry at that position minimizes this kind of exposure.

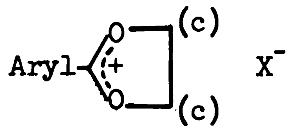
In Table IX the proton chemical shifts of aryl substituted cations are listed in order of increased deshielding of the ring protons (c) and are compared to the methylene groups (a) and (b) in the corresponding ester precursors. In FSO_3H the $\Delta\delta$'s for (b) and (c) varied between 0.81-0.92 ppm, whereas in liquid sulfur dioxide $\Delta\delta$ varied between 0.96-1.06 ppm. Once again, in each of these solvents it is apparent that there is a trend toward larger $\Delta\delta$'s in going from cation 1 → cation 14. Qualitatively this trend seems to parallel the electron donating ability of the meta or para substituents on the aromatic nuclei and suggests the possible use of proton chemical shifts of the dioxolenium ring protons as a probe for assessing charge delocalization from the heterocyclic ring.

In order to test this speculation, chemical shifts of the dioxolenium ring were plotted against Hammett σ and σ^+ values for fifteen 2-(meta and para aryl)-1,3-dioxolenium cations and found to give relatively good linear correlations. A least squares treatment of the σ values as a function of the chemical shifts of the cation ring protons in FSO_3H gave a surprisingly good linear relationship, with a standard error = 0.022, correlation coefficient = 0.966 and ordinate intercept = 5.40 with $\sigma = 0$ (see Figure X). A similar treatment of σ^+ values[81] gave a somewhat less satisfactory correlation (standard error = 0.038, correlation coefficient = 0.940 and ordinate intercept = 5.42). Examination of Figure X shows that this procedure provides an acceptable quantitative correlation of the chemical shifts.

TABLE IX

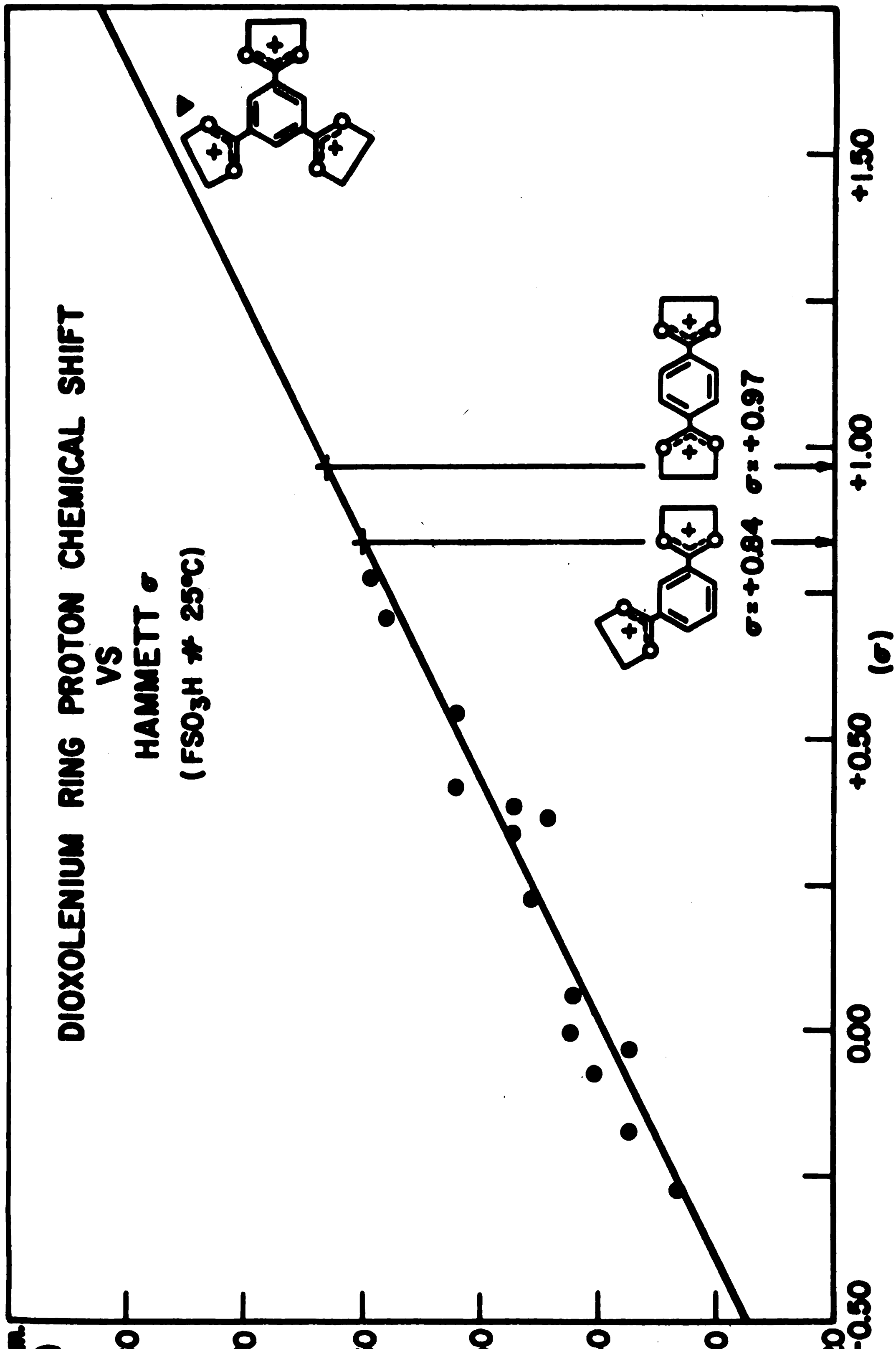
Comparison of Proton Chemical Shifts (δ) of 2-Bromoethyl Benzoate Precursors (CCl_4) to 2-Aryl-1,3-Dioxolenium Cations

$$\text{Aryl-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-O-}\overset{(b)}{\text{CH}_2}\text{-}\overset{(a)}{\text{CH}_2}\text{-Br}$$



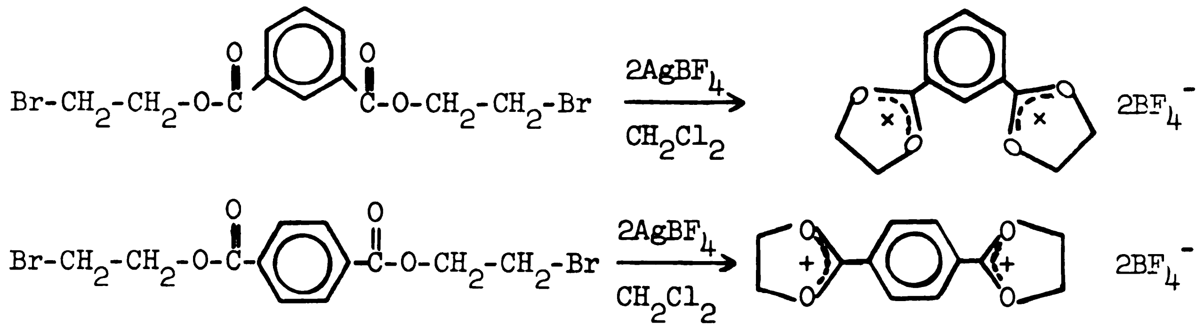
Aryl Substituent		(CCl_4) (a)	(CCl_4) (b)	(FSO_3H, 25°) (c)	(FSO_3H, 25°) Δδ	(SO_2, -20°) (c)	(SO_2, -20°) Δδ
p-Methoxy	1.	3.56	4.52	5.33	0.81	5.48	0.96
3,4,5-Trimethoxy	2.	3.60	4.55	5.37	0.82	5.53	0.98
p-Methyl	3.	3.57	4.53	5.37	0.84	5.53	1.02
m-Methyl	4.	3.57	4.54	5.40	0.86	5.56	1.02
Phenyl	5.	3.58	4.57	5.42	0.85	5.57	1.00
p-Fluoro	6.	3.61	4.60	5.42	0.82	5.52	0.92
p-Chloro	7.	3.60	4.57	5.43	0.86	5.60	1.03
m-Bromo	8.	3.61	4.59	5.47	0.88	5.63	1.04
m-Fluoro	9.	3.52	4.61	5.47	0.86	5.62	1.01
3,4-Dichloro	10.	3.60	4.61	5.47	0.86	5.63	1.02
m-Trifluoro	11.	3.63	4.64	5.52	0.88	5.58	1.04
p-Trifluoro	12.	3.64	4.65	5.52	0.87	5.68	1.03
m-Nitro	13.	3.72	4.70	5.58	0.88	5.70	1.00
p-Nitro	14.	3.68	4.67	5.59	0.92	5.73	1.06

Figure X

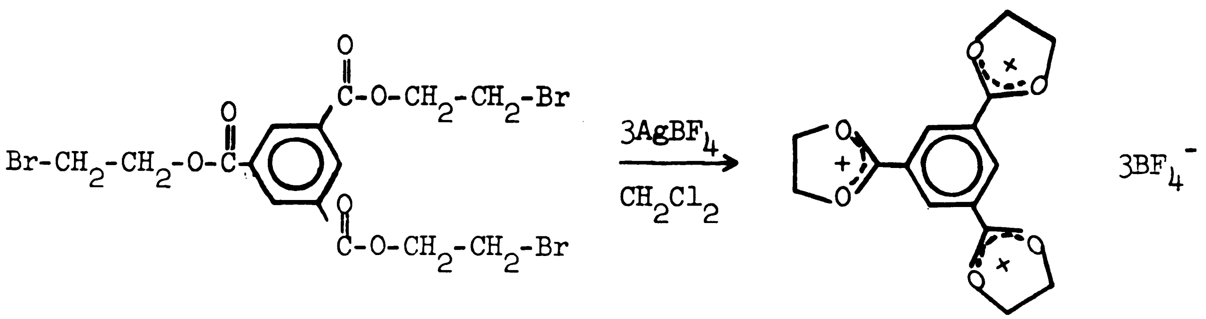

DIOXOLENIUM RING PROTON CHEMICAL SHIFT
VS
HAMMETT σ
(FSO3H # 25°C)
σ = +0.84
σ = +0.97
p.p.m.
(δ)
-5.80
-5.70
-5.60
-5.50
-5.40
-5.30
-5.20
-0.50
0.00
+0.50
+1.00
+1.50
(σ)

D. 2,2' and 2,2',2''-Aryl-1,3-Dioxolenium Dications and Trications

When di- and trisubstituted 2-bromoethyl aryl esters were treated with equivalent amounts of silver tetrafluoroborate in the usual manner, several interesting 1,3-dioxolenium dications and a trication were obtained. 2-Bromoethyl isophthalate and 2-bromoethyl terephthalate gave the corresponding meta and para dications, respectively. Similarly, 2-bromoethyl



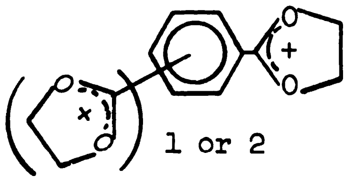
trimesate led to the symmetrical trication. The multications were insoluble



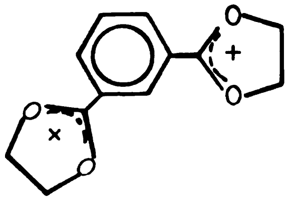
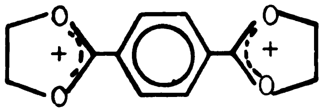
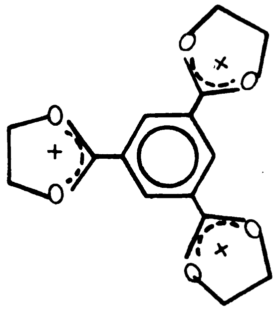
in methylene chloride, liquid sulfur dioxide and thionyl chloride and could be isolated only as mixtures with silver bromide. Identification of these cations was possible, however, by extracting the AgBr-multication mixtures with FSO_3H and filtering through a sintered glass funnel. Satisfactory nmr spectra were obtained by scanning these filtrates. The characteristic A_2X_2 pattern observed for the ester precursors (see Spectra 34-36) were absent in the spectra of the ions, which contained only highly deshielded singlets for the equivalent dioxolenium ring protons accompanied by appropriate resonance signals for the aromatic nuclei (see Spectra 70-72). Chemical shifts of the dioxolenium ring protons were in the expected order as shown in Table X. The electron deficiency of the polycations is reflected not only by the highly deshielded protons of the dioxolenium rings, but also by the low field positions of the aromatic protons.

TABLE X

Nmr Chemical Shifts for 2-Aryl-1,3-Dioxolenium Multications in FSO_3H



1 or 2

Cation		Dioxolenium Ring Protons	Aromatic Protons
	$2X^-$	5.60 (s)	8.03 to 9.26 (m)
	$2X^-$	5.63 (s)	8.72 (s)
	$3X^-$	5.77 (s)	9.58 (s)

These multications serve as excellent models for demonstrating the use of 1,3-dioxolenium ring protons as electron density probes to determine the Hammett σ values of hydrolytically unstable moieties. For example, in the meta-substituted dication one can assume that one of the dioxolenium rings is the probe whereas the other ring is the meta substituent. By extrapolating the Hammett plot for the fifteen meta and para substituted cations (Figure X) until it intersects with the nmr chemical shift for the meta-dication one can obtain a σ value for the 1,3-dioxolenium moiety as a meta substituent. The σ value was found to be +0.84. A similar treatment of the para-substituted dication gave a σ value for the 1,3-dioxolenium moiety, as a para substituent of +0.97. This latter value is the largest positive para σ value thus far reported.

The symmetrical trication provided an excellent model for checking both the accuracy of the determined meta Hammett σ value for the 1,3-dioxolenium ring and the reliability of the linear plot of the fifteen monocations as a function of their σ substituent constants. Using the additivity principle described by Jaffe[69] for multiple meta or para substituted benzenes, it was predicted from the determined meta σ value ($2 \times 0.84 = +1.68$) that the trication dioxolenium ring protons should have a chemical shift (δ) of 5.80 ppm. This value was obtained by intersecting the extrapolated Hammett correlation plot with a line perpendicular to the abscissa at $\sigma = +1.68$. The observed chemical shift for the heterocyclic ring protons of the trication was 5.77 ppm and is designated ▼ on the plot in Figure X. This is in excellent agreement with the predicted value and soundly corroborates the entire correlation.

IV DISCUSSION

The four families of cations which we have examined in the 1,3-dioxolenium ion series can be divided into distinct and distinguishable groups according to the chemical shifts of the ring protons (Figure XI). The chemical shift gradient varies from the most shielded member of the 2-alkyl-1,3-dioxolenium family (i.e. 2-diethylamino-1,3-dioxolenium ion) where $\delta = 4.98$ ppm to the most deshielded member of the aryl multication family (i.e. 2,2',2''-phenylenetris-1,3-dioxolenium trication) where $\delta = 5.77$ ppm. Ignoring anisotropy effects of the 2-substituents, this gradient appears to represent, to the first approximation, the relative order of ground state energies of these alkoxycarbonium ions. In accordance with this hypothesis, the relative order of members of families as well as the order of the families can be rationalized in terms of resonance or inductive interaction of the cation with its 2-substituents. These aspects will be considered in detail according to family.

<u>2-Alkyl-1,3-Dioxolenium Cations</u>:

As shown in Figure XI the 2-alkyl-1,3-dioxolenium cation family is the most shielded group in the series. If one examines the chemical shifts for members of this family (Figure XII) it is apparent that cation I is a special case and should perhaps be thought of as a member of still another cation family which consists of cations containing heteroatoms as 2-substituents. Cation I is presumably the most stabilized member of this entire series due to its ability to delocalize charge from the ring to the nitrogen atom and is perhaps best represented as an immonium ion.

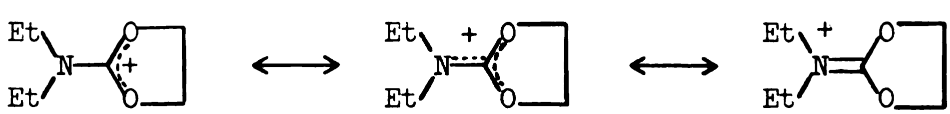


Figure XI

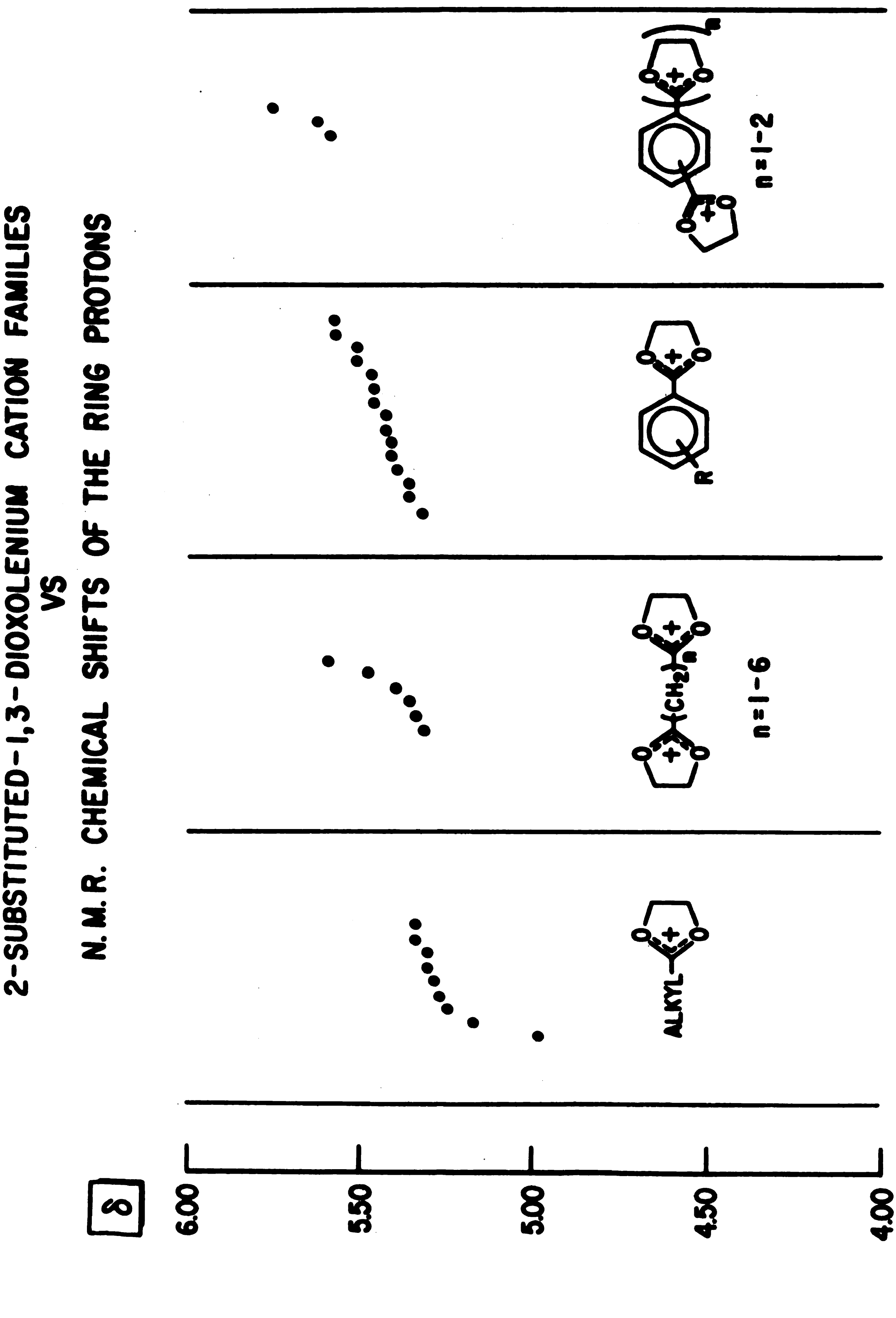
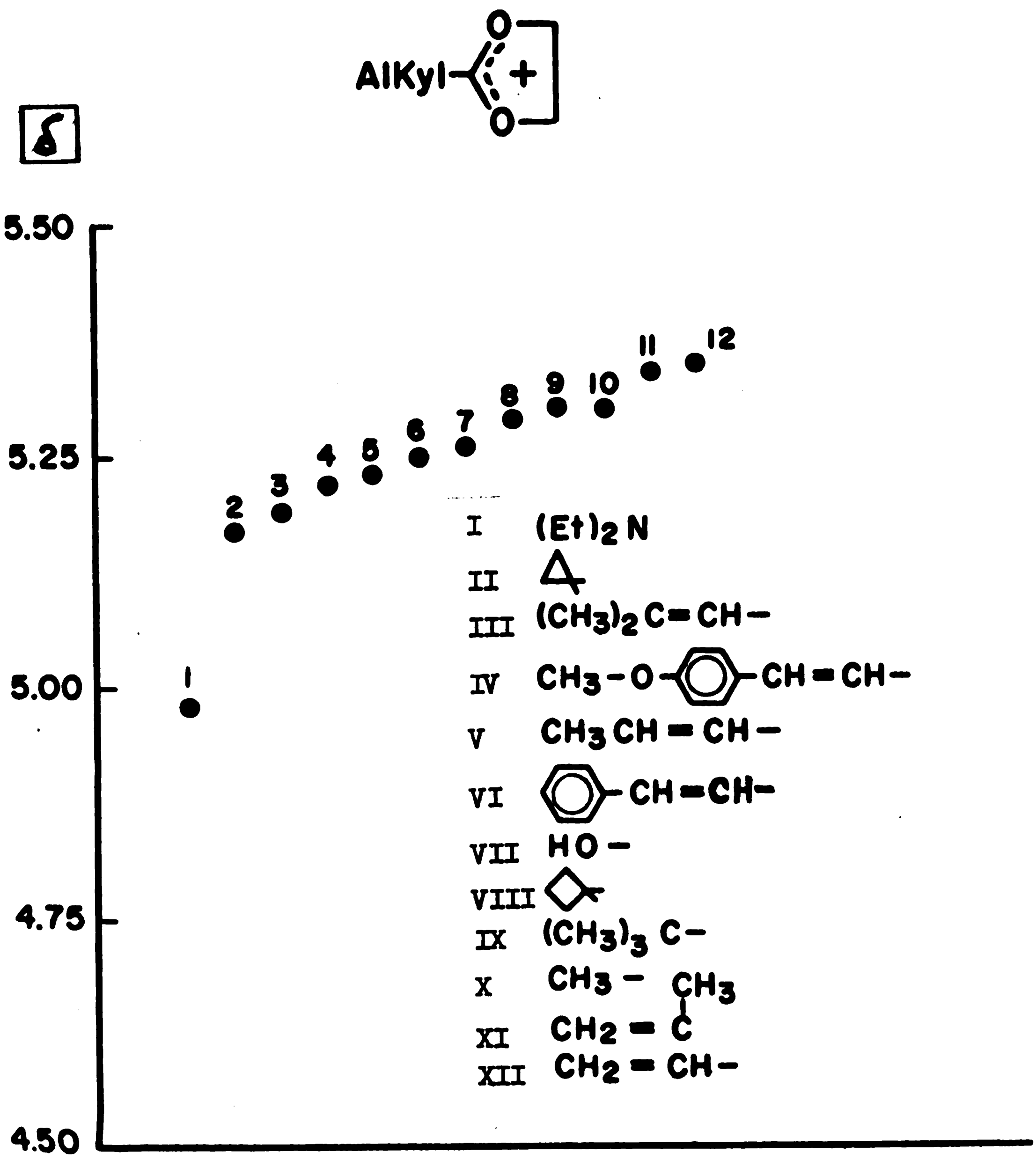
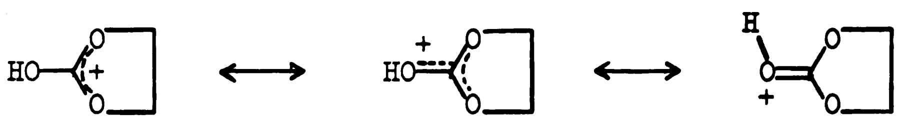

2-SUBSTITUTED-1,3-DIOXOLENIUM CATION FAMILIES
VS
N.M.R. CHEMICAL SHIFTS OF THE RING PROTONS
δ
6.00
5.50
5.00
4.50
4.00
ALKYL
n=1-6
R
n=1-2

FIGURE XII

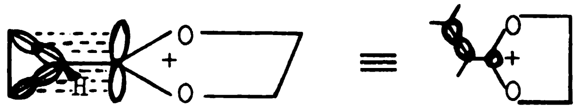

AlKyl
δ
5.50
5.25
5.00
4.75
4.50
1
2
3
4
5
6
7
8
9
10
11
12
I (Et)2N
II
III (CH3)2C=CH–
IV CH3–O–C6H4–CH=CH–
V CH3CH=CH–
VI C6H5–CH=CH–
VII HO–
VIII
IX (CH3)3C–
X CH3–
XI CH2=C(CH3)
XII CH2=CH–

It is not known whether one can as a rule expect this kind of stabilization in analogous systems containing oxygen or sulfur as a 2-substituent. In the case of 2-hydroxy substituted cation (VII), relatively little delocalization of charge from the ring was noted compared to the 2-alkyl substituted cations. Cation (VII) was more deshielded than five of the ten 2-alkyl substituted cations examined in Figure XII. This suggests that the hydroxy oxygen atom contributes very little to delocalization of charge and parallels similar observations made by Taft and Ramsey[21] on analogous acyclic systems. This anomaly may be due to protonation of the ether



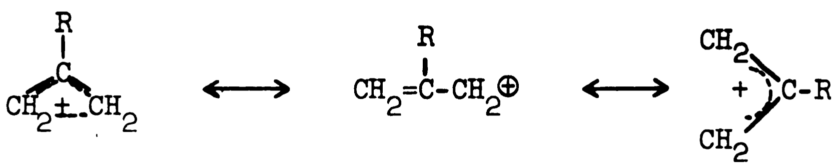
oxygens of the ester whereby charge delocalization would not be possible. This mode of ester protonation has not yet been observed.[60,70]

2-Cyclopropyl-1,3-dioxolenium ion (II), Figure XII, was the most shielded example of this family where the substituent was entirely hydrocarbon. Similarly in Table XI it can be seen that both the α and β-hydrogens of the cyclopropyl groups are deshielded substantially. This demonstrates a large amount of delocalization of charge into the cyclopropane ring. This enhanced delocalization is probably due to interaction of the cyclopropane "bent bonds" with the vacant p-orbital of the cyclic dialkoxy carbonium ion as shown below. This kind of interaction has been invoked by

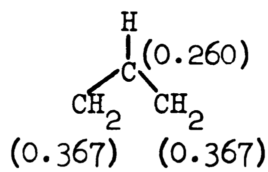


Hart[71], Olah[72] and Deno[73] to account for the unusual stability of other related cyclopropyl carbonium ion systems. Subsequent work by Schleyer[74] and Richey[75] has provided further evidence for the nature of this interaction, which is thought to be best represented by the bisected conformation shown above. It is interesting that the other small ring system in this family, 2-cyclobutyl cation (VIII), was not stabilized much more than the 2-methyl or 2-t-butyl cations, X and IX respectively. Similarly, Table XI shows that relatively little delocalization of charge to the cyclobutane ring has occurred since the α and β protons are deshielded only slightly.

It is generally accepted that in hydrocarbon systems, allylic and methylallylic carbonium ions possess enhanced stability compared to saturated systems because of their ability to delocalize charge.[12f,76] This delocalization has been proposed by Simonetta and Heilbronner[77] to occur



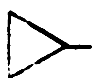
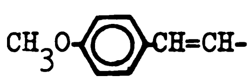
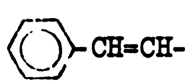
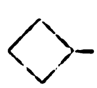
by means of 1,3-π interactions between the terminal centers. Valence bond treatment in this manner gave the following charge distribution. Hirst



and Linnett[78] preferred to invoke the tradional resonance argument and by a simple Hückel treatment of the two odd alternant terminal allyl cations, suggest that the positive charge should reside predominately on the terminal carbon atoms. Large deshielding of the methine proton ($\Delta\delta$ = 4.12 ppm) and the methyl group ($\Delta\delta$ = 2.38 ppm) was observed in the allyl and

TABLE XI

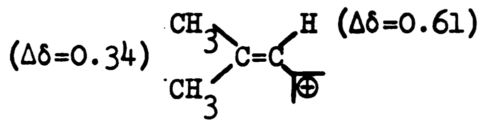
Comparison of Proton Chemical Shifts of 2-Substituents in Ester Precursors (CCl_4) with those in 2-Alkyl-1,3-dioxolenium Cations (FSO_3H)

2-Substituent		Ester	Cation	Δδ
I	$(Et)_2$-N-	a. 1.13(t) b. 3.27(q)	a. 1.32 b. 3.59	0.19 0.32
II		a. 0.73-1.20(m) b. 1.40-1.89(m)	a. 1.75-2.07(m) b. 2.10-2.53(m)	0.70 0.47
III	$(CH_3)_2$C=CH-	a. 2.03(d) b. 5.66 (m)	a. 2.37(d) b. 6.27(m)	0.34 0.61
IV		a. 3.80(s) b. 6.23(d) c. 6.83(d) d. 7.43(d) e. 7.60(d)	a. 4.02(s) b. * c. * d. * e. *	0.22 - - - -
V	CH_3-CH=CH-	a. 1.92(d) b. 5.82(d) c. 7.01(m)	a. 2.27(d) b. 6.44(d) c. 8.22(m)	0.35 0.62 1.21
VI		a. 6.37(d) b. 7.42(m) c. 7.66(d)	a. 6.86(d) b. 7.64(m) c. 8.59(d)	0.49 0.22 0.93
VIII		a. 2.14(m) b. 3.12(q)	a. 2.35(m) b. 3.66(q)	0.21 0.54
IX	$(CH_3)_3$C-	a. 1.20(s)	a. 1.50	0.30
X	CH_3-	a. 2.06(s)	a. 2.75	0.69
XI	CH_2=C(CH_3)-	a. 1.96(s) b. 5.87(d)	a. 2.15(s) b. 6.85(d)	0.19 0.98
XII	CH_2=CH-	a. 5.68-5.99(m) b. 6.12-6.65(m)	a. * b. *	- -

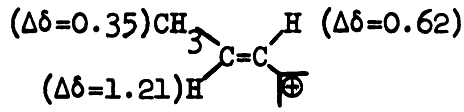
*Spectrum too complex to analyze

methylallyl cations, respectively. This led Olah[12f] to suggest that 1,3-π interactions contribute strongly to the delocalization of charge.

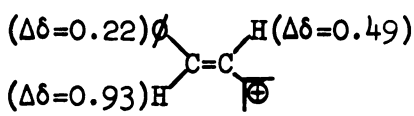
Close examination of related allylic carbonium ions III, V, VI and XI in the dioxolenium series reveals the following trends; hydrogens on the double bond α to the positive center are deshielded from their ester



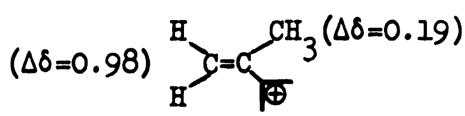
III



V



VI



XI

precursors Δδ=0.49-0.62 ppm (e.g. III,V,VI). The α methyl group, in XI, was deshielded somewhat less, Δδ=0.19 ppm. It is especially noteworthy that protons <u>cis</u> or <u>trans</u> β to the positive center are highly deshielded and are shifted from 0.93-1.21 ppm downfield from their esters (e.g. see V, VI and XI). These protons are deshielded approximately twice as much as their α counterparts. Similarly <u>cis</u> and <u>trans</u> β methyl groups (e.g. III and V) are deshielded 0.34-0.35 ppm from their esters. Again this is about twice as much as is observed for an α methyl group (e.g. XI). If one assumes these deshielding values reflect charge densities and are not due to anisotropy effects, it is tempting to compare these values to the charge densities calculated by Simonetta and Heilbronner[77] for the 1,3-π interaction model. From this model it is predicted, according to the following calculation, that approximately 73% of the charge resides on the

$$\boxed{\begin{array}{l}\text{\% Positive Charge on}\\ \text{Terminal Carbons in}\\ \text{1,3-}\pi\text{ Interaction Model}\end{array}} = \frac{(2)(0.367)}{(2)(0.367)+(0.266)}\,10^2 = \underline{73\%}$$

terminal carbons and 27% on the internal carbon. Using deshielding values ($\Delta\delta$) for the α and β-proton probes in Cation V it is calculated, as shown below, that approximately 80% of the charge is on the terminal carbon and ~20% on the internal carbon. Similar treatment of the values for α and β

$$\boxed{\begin{array}{l}\text{\% Positive Charge on}\\ \text{Terminal Carbons}\\ \text{in Cation V}\end{array}} = \frac{2(\Delta\delta \text{ for } \beta\text{-H})}{2(\Delta\delta \text{ for } \beta\text{-H})+(\Delta\delta \text{ for } \alpha\text{-H})}\,10^2 =$$

$$\frac{(2)(1.21)}{(2)(1.21)+(0.62)}\,10^2 = \underline{80\%}$$

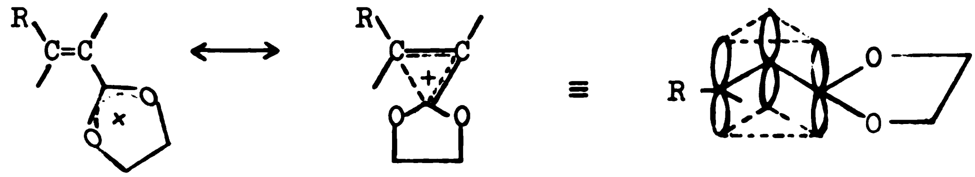
protons in cation VI predicts the same values. Using the $\Delta\delta$ value for the

$$\boxed{\begin{array}{l}\text{\% Positive Charge on}\\ \text{Terminal Carbons in}\\ \text{Cation VI}\end{array}} = \frac{(2)(0.93)}{(2)(0.93)+(0.49)}\,10^2 = \underline{80\%}$$

α-methyl group in cation XI and the $\Delta\delta$ value for the β-methyl groups in either cation III or V one obtains almost the same value for charge delocalization in these cations. A comparison of these crude delocalization

$$\boxed{\begin{array}{l}\text{\% Positive Charge on}\\ \text{Terminal Carbons in}\\ \text{Cations III, V and XI}\end{array}} = \frac{(2)(0.35)}{(2)(0.35)+(0.19)}\,10^2 = \underline{79\%}$$

data to the value obtained from the Simonetta-Heilbronner model provides supporting evidence for such 1,3-π interactions in the vinyl, propenyl, isopropenyl and styryl-1,3-dioxolenium cations. This interaction might be represented as follows:



In view of the possibility of this kind of delocalization it was rather surprising to find that the dioxolenium ring protons in the 2-vinyl and 2-isopropenyl-1,3-dioxolenium cations were deshielded from saturated systems such as 2-methyl and 2-t-butyl cations (see Figure XII). However, when the unsaturated substituent contains a terminal group which is capable of stabilizing positive charge, the cations such as III, IV, V and VI appear to resume their predicted ability to delocalize charge from the dioxolenium ring. According to the deshielding of the dioxolenium ring protons the unsaturated cations fall in the following order:

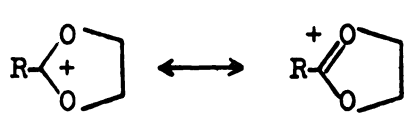
$(CH_3)_2$-C=CH- $\langle$ p-CH_3O-ϕ-CH=CH- $\langle$ CH_3-CH=CH- $\langle$ ϕ-CH=CH- $\langle$

III IV V VI

Saturated Cations VIII, IX, X $\langle$ CH_2=C(CH_3)- $\langle$ CH_2=CH-

XI XII

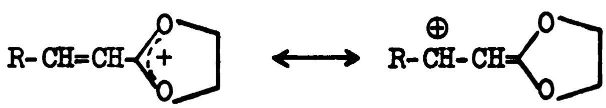
In order to rationalize the relative order of these cations one must consider the dual oxonium-carbonium ion character of these systems. The anomalous order of the two unsaturated cations XI and XII may reflect the high order of their oxonium ion character (b); such structures would be stabil-



(a) (b)

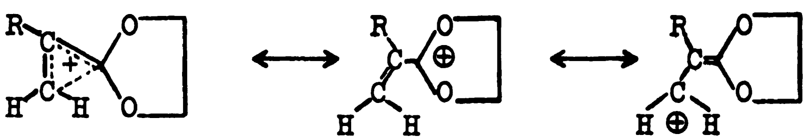
ized by conjugation with the carbon-carbon double bond. The higher electronegativity of the sp^2 hydridized carbon substituent and the predominate oxonium ion character of XI and XII may account for the fact that the ring protons in these cations are more deshielded than in the saturated cations VIII-X.

In the case of the terminal substituted unsaturated cations III, IV, V and VI more interaction of the double bond with the positive charge occurs since the cation resulting from allylic type resonance can be stabilized by methyl or phenyl groups.



; R=CH_3, ∅ or p-CH_3-O-∅-

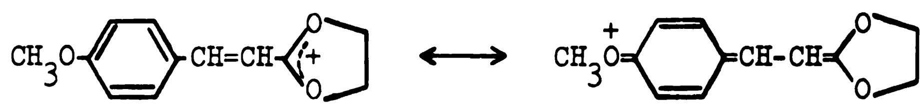
Alternatively and in keeping with the postulated 1,3-π interactions described above, the 2-vinyl and 2-isopropenyl-1,3-dioxolenium cations may possess comparable carbonium ion character but merely be distinguished from the terminal substituted unsaturated systems by their inability to delocalize charge from the 1,3-π interaction site which of course involves the dioxolenium ring and essentially amounts to back donation of positive charge; see (a). Because of this, charge may not actually be removed from the dioxolenium ring in the classical sense as shown by (b) and lead to



(a) (b)

ground state energies for XI and XII which are fortuitously higher than those for the methyl (X) and t-butyl (IX) cations. In the case of the terminal substituted unsaturated systems, decreases in ground state energies of the cations may result by their ability to delocalize charge from the 1,3-π interaction site. In the case of the terminal methyl substituted cations V and III it may reflect more efficient neutralization of charge in a 1,3-π interaction situation and would be in keeping with the Simonetta-Heilbronner model which predicts highest charge density at the terminal position.

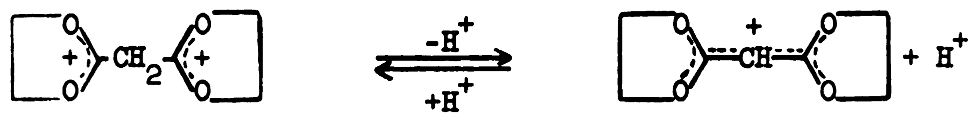
In either case increased stability of the cations is noted when conventional carbonium ion stabilizing groups are substituted in the terminal position of the allylic group. Cation stability responds not only to the kind of group but also to the number of such groups substituted. For example two terminal methyl groups stabilize the cation somewhat better than one. Likewise a p-methoxyphenyl terminal group gives enhanced stability compared to a phenyl group. In fact, strong interaction of the <u>para</u>-methoxy group with the cationic center in the p-methoxystyryl-1,3-dioxolenium ion may account for why this cation is a brilliant canary yellow, and is the only colored cation observed in this entire series. In a classical sense this interaction may be represented in the following manner:



<u>2,2'-Alkylenebis-1,3-Dioxolenium Dications</u>:

Ring proton chemical shifts for members of this family where n = 5 or 6 (δ = 5.32-5.34) do not differ much from the saturated members of the monocation (δ = 5.30) family. This clearly indicates that these dications are relieved of charge repulsion interactions and probably have ground state energies which are quite similar to the monocations. Decreasing the number of insulating groups between the positive centers dramatically increases charge repulsion, especially when n = 1 or 2. This is well illustrated in

Figures VIII and IX. In fact when n = 1 the charge repulsion is so great that the α protons are acidic and exchange readily in acid solution. Exchange by means of the monocation shown below provides relief from these



repulsion interactions. Although exchange of α protons was not observed for n = 2-6 in fluorosulfonic acid, the acidity of these protons probably increases as n decreases from 6 → 2. This may account for the unusual sensitivity that the α protons display when utilized as a probe (see Figure IX).

This dication system provides a unique model for examining the effects of charge repulsion as a function of separation and nmr spectroscopy provides an excellent tool for assessing these parameters. Using the empirically derived equation (2), presented in the Results section, it is possible

$$\delta = 2.94\ (1 + \frac{1}{n^2})$$

to obtain an excellent correlation of α-proton chemical shifts with charge separation both in our system as well as Olah's bisacylium dication series.[13a] Examination of this equation reveals its similarity to the well known Coulomb law[79] which defines the force between two charges as follows:

$$\text{Force} = \frac{(\text{Charge})(\text{Charge})'}{(\text{Dielectric Constant})(\text{distance})^2} = \frac{QQ'}{Kn^2}$$

By simple mathematical operations on these two equations it is possible to derive an equation which will allow the calculation of repulsion forces in these dication systems by merely knowing the chemical shift of the α-protons and the dielectric constant of the medium separating the charges. The derivation is as follows:

Dividing empirical equation by 2.94 gives:

$$\frac{\delta}{2.94} = 1 + \frac{1}{n^2} \qquad (1)$$

Solving for $\frac{1}{n^2}$, one obtains:

$$\frac{1}{n^2} = \frac{\delta}{2.94} - 1 \qquad (2)$$

The Coulomb equation is reduced to a more simple form with the following assumptions:

The dication charges are equal, therefore:

$$F = \frac{Q^2}{Kn^2} \qquad (3)$$

Multiplying equation (3) by $\frac{K}{Q^2}$:

$$\frac{FK}{Q^2} = \frac{1}{n^2} \qquad (4)$$

Equating $\frac{1}{n^2}$ in equations (2) and (4) one obtains:

$$\frac{FK}{Q^2} = \frac{\delta}{2.94} - 1 \qquad (5)$$

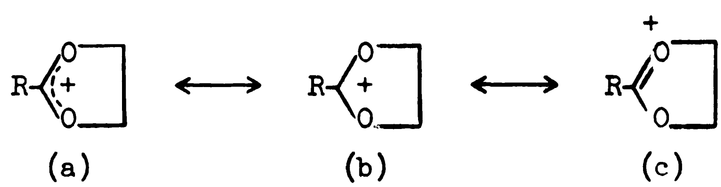
Solving for F one obtains an equation for calculating the repulsion forces in these dications which only requires knowledge of the chemical shift of the α-protons, magnitude of the charge and the dielectric constant of the medium separating the charges. The equation is as follows:

$$\boxed{\text{Repulsion Force} = \frac{Q^2}{K}\left(\frac{\delta}{2.94} - 1\right)} \qquad (6)$$

This treatment should be applicable to other dicarbonium ion series such as those reported by Olah and coworkers.[13a,80] Such an examination could provide further insight as to the relative ground state energies of these dicarbonium ion systems.

2-Aryl-1,3-Dioxolenium Cations:

As shown in the Results section, 2-(meta and para substituted) aryl-1,3-dioxolenium ions exhibit a very good linear free energy relationship in their nmr correlation with Hammett σ values. In view of the possible carbonium ion character of the dioxolenium ring, it was at first surprising that Brown σ^+ values[81] gave a much poorer correlation. However, hydrolysis studies on p-substituted methyl orthobenzoates also show a better correlation with Hammett σ values than with σ^+ values.[81] These reactions have since been shown to involve related acyclic dialkoxy carbonium ions. These observations suggest that resonance interactions between electron-supplying substituents and the electron deficient 1,3-dioxolenium moiety are not strong. This may indicate that the oxonium form (c) is an important



contributor to the resonance hybrid (a).

Nevertheless, delocalization of charge to the para position of the phenyl ring is apparent if one examines the relative amounts of deshielding of the meta and para-methoxy groups in the 3,4,5-trimethoxy phenyl-1,3-dioxolenium cation compared to their ester precursor. In 2-(bromoethyl)-3,4,5-trimethoxybenzoate the meta-methoxy group is exhibited as a singlet at 3.87 ppm and the para is found at 3.81 ppm (see Spectrum 20). An nmr spectrum of the corresponding cation in liquid SO_2 reveals that the down-field order of the para and meta chemical shifts is reversed and the para now shows a chemical shift at 4.05 ppm ($\Delta\delta$ = 0.24), whereas the meta is found at 3.94 ppm ($\Delta\delta$ = 0.07). This apparent para methoxy interaction is also corroborated by the fact that the p-methoxyphenyl-1,3-dioxolenium cation is not protonated and only the meta-methoxy groups in the trimethoxy cation exhibit any tendency to be protonated (i.e., produce polycations).

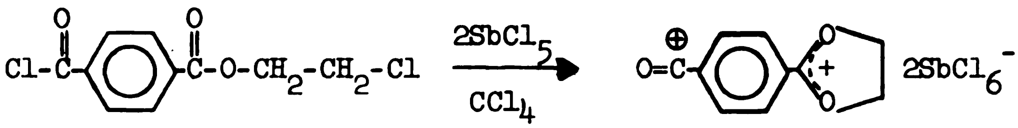
A comparison of the meta and para-methylphenyl-1,3-dioxolenium cations shows the same trend, but less dramatically. The meta-methyl cation is deshielded 0.10 ppm, whereas the para-methyl cation is shifted 0.16 ppm downfield compared to their respective ester precursors.

Since the chemical shifts (δ's) of the dioxolenium ring are directly related to Hammett σ values, they should also be proportional to log $\frac{k}{k_o}$. This relationship should allow prediction of ring opening reaction rate

$$\delta \propto \sigma = \rho \log \frac{k}{k_o}$$

constants for any of the members of this family by merely knowing the δ for the particular member and the ring opening reaction rate for the 2-phenyl-1,3-dioxolenium cation for a specific set of conditions.

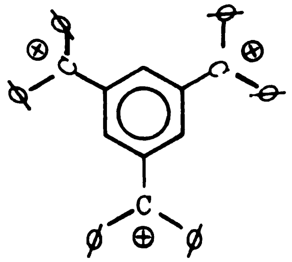
In the Results section it was shown how this linear free energy correlation was used to obtain Hammett δ values for the dioxolenium ring. Determination of these values by usual methods would be very difficult if not impossible because of the solvolytic instability of the dioxolenium moiety. In view of the ease with which the dioxolenium ring can be synthesized this technique could be used to determine Hammett σ values for even higher energy carbonium ions by merely synthesizing a suitable model which contained the carbonium ion site either meta or para to the dioxolenium ring probe. For example, a model for determining the σ values for the oxocarbonium ion moiety could be synthesized in the following manner:



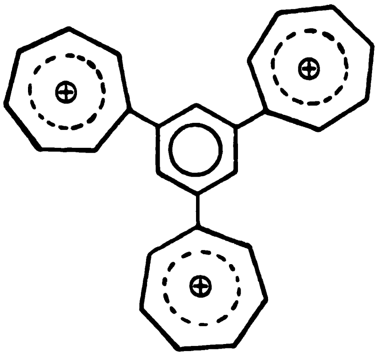
Volz[82] has reported the facile conversion of aroyl chlorides to oxocarbonium ions with $SbCl_5$ whereas Meerwein[35] has observed that 2-chloroethyl benzoates cyclize readily to the 1,3-dioxolenium cation. By merely determining the δ for this dication, the σ value for $-\overset{\oplus}{C}=O$ could be obtained by referring to Figure X.

<u>2,2' and 2,2',2"-Aryl-1,3-dioxolenium Dications and Trications</u>:

This family is the most deshielded group in this series and is of particular interest in that it allows one the opportunity to examine in a systematic manner the intramolecular interaction of multiple charge in a closed conjugated polyene system. The trication described herein is the first reported example in the literature.[83] More recently Volz[84] succeeded in synthesizing trication (A) whereas Murray and Kaplan[85] reported the preparation of tricarbonium ion (B). In each case substantial delocalization into the



(A)



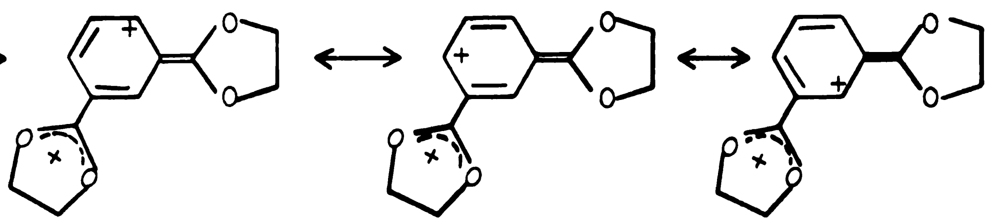
(B)

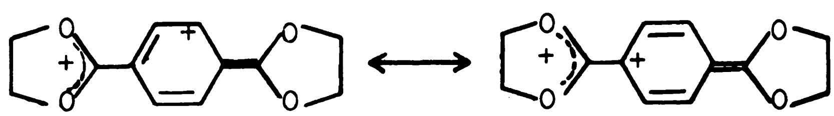
central aromatic nucleus was observed accompanied by strong charge repulsion interactions.

In order to gain further insight to the question of whether the cyclic dialkoxy carbonium ion moiety (dioxolenium ring) possesses predominately carbonium or oxonium ion character, analogous phenyl substituted mono-, di- and tri-dioxolenium cations (see Figure XIII) were examined by nmr spectroscopy. The chemical shifts for the dioxolenium ring protons were in the predicted order one might expect for both accumulation as well as location of charge on the central aromatic ring. The relative order of deshielding:

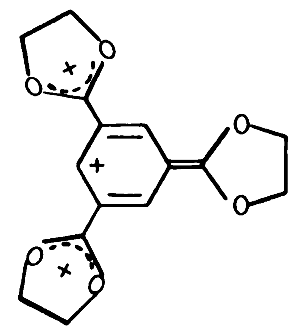
Cation:	I	$<$	II	$<$	III	$<$	IV
δ :	(5.42 ppm)		(5.60 ppm)		(5.63 ppm)		(5.77 ppm)

In the case of the meta-dication (II), delocalization of charge into the aromatic nucleus can lead to three non-equivalent contributors to the resonance hybrid, where positive charges can be separated by at least one to three carbon atoms. Interaction of the para-dication with the aromatic nucleus results in only two non-equivalent contributors, where in one case

II $\leftrightarrow$ 

III $\leftrightarrow$ 

the positive charges are on adjacent carbons. From these classical resonance representations it is apparent that, based on charge interaction, III should have a higher ground state energy than II. Similar delocalization of charge in the trication, III, can lead to only one contributor as shown below:

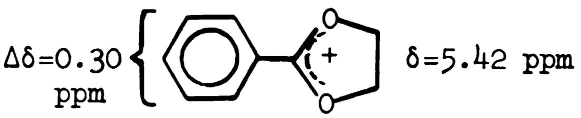


The greater accumulated formal charge in the trication undoubtedly gives this cation the highest ground state energy of the entire series.

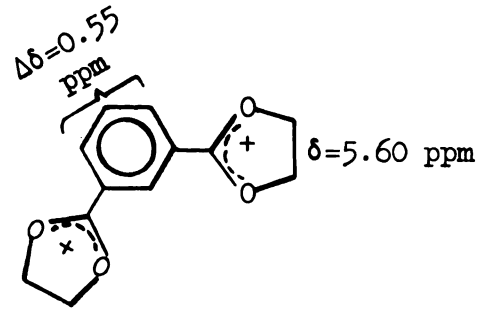
As shown in Figure XIII the deshielding parameters ($\Delta\delta$) for the aromatic nuclei in each case parallel the relative ground state energies predicted for the members of this family and are consistent with the conjectured delocalization and charge interactions described above.

FIGURE XIII

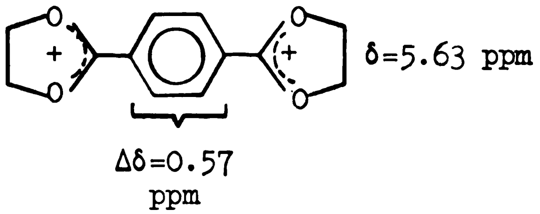
Deshielding Parameters ($\Delta\delta$) for Mono-, Di- and Tri-Dioxolenium Cations (FSO_3H) Compared to their Ester Precursors (CCl_4)



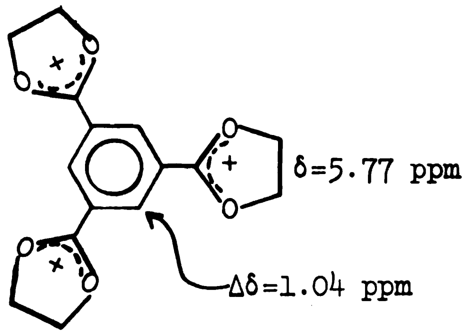
I



II



III



IV

V. EXPERIMENTAL

A. General

1. Melting Points: Melting points were measured on a Thomas-Hoover melting point apparatus and are uncorrected unless otherwise specified.

2. Microanalyses: Elemental analyses were carried out by Mr. L. E. Swim, Analytical Laboratories, The Dow Chemical Company, Midland, Michigan.

3. Nuclear Magnetic Resonance Spectra: Spectra were scanned on a Varian Model A-60 instrument using either tetramethylsilane or tetramethylammonium tetrafluoroborate, as specified, for an internal standard. The chemical shift for tetramethylammonium tetrafluoroborate was taken as 3.10 ppm. All chemical shifts are reported as δ values in ppm.

4. Infrared Spectra: Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrometer either on NaCl or KBr plates, as indicated.

5. Solvents: Anhydrous methylene chloride and acetonitrile were prepared by distilling these solvents from phosphorous pentoxide; they were then stored over silica gel (Grace Chemical Company). Anhydrous diethyl ether (Mallinckrodt) was used as it was received without further treatment.

6. Miscellaneous: All recrystallizations and manipulations of the moisture sensitive cations were carried out in a Labconco dry box containing several (6 x 12 in.) beds of phosphorous pentoxide. Bottled cation samples were always stored in a desiccator over anhydrous calcium chloride.

B. Precursors to 2-Alkyl-1,3-dioxolenium Cations

1. 2-Bromoethyl Acetate: This material was obtained from the Eastman Kodak Company. Redistillation through a 1/2 x 21" Vigreux column gave a colorless liquid, bp 160-161° (Nmr: Spectrum 9).

2. 2-Bromoethyl Acrylate: This compound was obtained from the Bordon Chemical Company as a tan liquid. Using N,N-diphenyl phenylene

diamine (DPPD) as an inhibitor, both in the distillation pot and receiver, this product was redistilled through a 1/2 x 21" Vigreux column to give a colorless liquid, bp 52-53°/5 mm (Nmr: Spectrum 11).

3. <u>2-Bromoethyl Methacrylate</u>: This was obtained from the Borden Chemical Company. This material was redistilled (inhibited with DPPD) through a 1/2 x 21" Vigreux column to give a colorless liquid, bp 46-49°/ 2.7 mm. (Nmr: Spectrum 10).

4. <u>2-Methoxyethyl Acetate</u>: This material was obtained from the Eastman Kodak Company. Redistillation through a 1/2 x 21" Vigreux column yielded a colorless, sweet smelling liquid boiling at 141-143°.

5. <u>2-Hydroxyethyl Acetate</u>: This material was obtained from the Eastman Kodak Company. It was redistilled through a 1/2 x 12" Vigreux column. A colorless fraction boiling at 185-188° was collected.

6. <u>1,2-Diacetoxyethane</u>: This material was obtained from the Eastman Kodak Company and was redistilled through a 1/2 x 12" Vigreux column. A colorless fraction boiling at 190-192° was collected.

7. <u>Preparation of 2-Bromoethyl-N,N-Diethyl Carbamic Acid Ester</u>: N,N-Diethylcarbamoyl chloride (Eastman, 27.12 g, 0.2 mole) and 2-bromoethanol (25 g, 0.2 mole) were combined with 50 ml of carbon tetrachloride and refluxed for 20 hours. Solvent was removed from the dark brown reaction mixture with a rotating evaporator (Büchi). The amber liquid residue was distilled through a 1/2 x 21" Vigreux to give a major colorless fraction boiling at 77-79°/1.5 mm. The product weighed 25.3 g (56%).

<u>Anal</u>: Calculated for $C_7H_{14}BrNO_2$: C, 37.5; H, 6.30; N, 6.25. Found: C, 37.8; H, 6.15; N, 6.04.

<u>Infrared</u>: $\nu_{C=O}$, 1713 cm^{-1} (s), (neat).

<u>Nmr</u>: Spectrum 1.

8. Preparation of 2-Bromoethyl Cyclopropanecarboxylate: Cyclopropanecarbonyl chloride (Aldrich, 20.9 g, 0.2 mole) in 25 ml of carbon tetrachloride was charged into a 250 ml three-necked flask equipped with a condenser, stirrer and addition funnel. A solution of 2-bromoethanol (Eastman) in 25 ml of carbon tetrachloride was added with stirring, dropwise over a period of 30 minutes. A slight exothermic reaction was noted during the addition. Continued stirring while under reflux for five hours produced an amber reaction mixture. Removal of the solvent on a Büchi rotating evaporator gave a tan liquid residue which was distilled through a 1/2 x 21" Vigreux column. A major colorless fraction boiling at 81-82°/10 mm was collected as the product. Wt. 33.5 g (87%).

Anal: Calculated for $C_6H_9BrO_2$: C, 37.3; H, 4.70. Found: C, 37.4; H, 4.87.

Infrared: $\gamma_{>C=O}$, 1738 cm^{-1} (s), (neat).

Nmr: Spectrum 2.

9. Preparation of 3,3-Dimethylacrylyl Chloride: Into a 500 ml, three-necked round-bottomed flask equipped with a stirrer, condenser and addition funnel was charged 100 g (1.0 mole) of 3,3-dimethylacrylic acid (Aldrich). Thionyl chloride (357 g, 3.0 moles) was added dropwise with stirring, producing at first an endothermic reaction followed by an exothermic reaction which was maintained at 40° during the rest of the addition. After completing the addition the reaction mixture was refluxed for 4 hours, then distilled. The product came over as a light tan liquid (bp 77-80°/105 mm) which weighed 64 g (54%).

10. Preparation of 2-Bromoethyl-3,3-Dimethylacrylate: 2-Bromoethanol (Eastman, 24.9 g, 0.2 mole) was added to a solution of 3,3-dimethylacrylyl chloride (23.7 g, 0.2 mole) in 75 ml of carbon tetrachloride

contained in a 250-ml round-bottomed flask equipped with a reflux condenser. The reaction mixture was refluxed for 10 hours, after which the solvent was removed on a rotating evaporator (Büchi). Distillation of the tan liquid residue gave 38.9 g of a sweet-smelling colorless liquid boiling at 68-73°/5 mm. Redistillation of this fraction through a 1/2 x 21" Vigreux column yielded 30.1 g (73%) of product boiling at 78-79°/4 mm.

Anal: Calculated for $C_7H_{11}BrO_2$: C, 40.6; H, 5.36; Br, 38.6. Found: C, 40.7; H, 5.20; Br, 38.8.

Infrared: $\gamma_{>C=O}$, 1724 (s); $\gamma_{>C=C<}$, 1659 cm^{-1} (m) (neat).

Nmr: Spectrum 3.

11. Preparation of p-Methoxycinnamoyl Chloride: p-Methoxycinnamic acid (Aldrich, 50 g, 0.28 mole) was stirred in a 500-ml, three-necked round-bottomed flask equipped with a condenser and addition funnel as 200 g (1.68 mole) of thionyl chloride was added dropwise over a period of 30 minutes. The reaction was not exothermic. The reaction mixture was then refluxed, while stirring for 1 hour. Excess thionyl chloride was removed on a rotating evaporator (Büchi), leaving a dark brown oily residue. Upon transferring this residue it suddenly solidified into a yellow-amber mass which weighed 54.3 g (100%) and melted at 48-51°. This material was used without further purification for preparation of the ester.

12. Preparation of 2-Bromoethyl p-Methoxycinnamate: 2-Bromoethanol (Eastman, 35 g, 0.28 mole), was added to a solution of p-methoxycinnamoyl chloride (54 g, 0.28 mole) in 50 ml of carbon tetrachloride contained in a 250 ml flask equipped with a reflux condenser. The reaction mixture was refluxed for 3 hours after which the solvent was removed on a rotating evaporator (Büchi), leaving an amber colored oil. This oil was distilled

through 1/2 x 12" Vigreux column giving a major cut boiling at 150-180°/1 mm. The distillate solidified into a white mass, mp 47-51°, which weighed 66.8 g (84%). Recrystallization from petroleum ether (30-60°) gave white crystals melting at 50-51.5°.

Anal: Calculated for $C_{12}H_{13}BrO_3$: C, 50.5; H, 4.59. Found: C, 50.5; H, 4.43.

Infrared: $\nu_{>C=O}$, 1728 cm^{-1} (Fluorolube).

Nmr: Spectrum 5.

13. Preparation of 2-Bromoethyl Crotonate: 2-Bromoethanol (40.25 g, 0.5 mole) was added over a period of 5-10 minutes to 52 g (0.5 mole) of crotonyl chloride which was being stirred in a 250 ml three-necked flask equipped with a condenser, stirrer and addition funnel. After the addition was complete, an exothermic reaction set in and was accompanied by the evolution of copious amounts of hydrogen chloride. The tan reaction mixture was maintained at reflux, while stirring for 4 hours. During that time the mixture became dark brown. The crude product was distilled through a 1/2 x 21" Vigreux column giving a colorless, major fraction boiling at 110-117°/39 mm which weighed 49.5 g. This material was redistilled to give a colorless, major fraction boiling at 118-119°/40 mm.

Anal: Calculated for $C_6H_9BrO_2$: C, 37.3; H, 4.70. Found: C, 37.3; H, 4.57.

Infrared: $\nu_{>C=O}$, 1735 cm^{-1}; $\nu_{>C=C<}$, 1668 cm^{-1} (neat).

Nmr: Spectrum 4.

14. Preparation of 2-Bromoethyl Cinnamate: Cinnamoyl chloride (Eastman, 49.9 g, 0.3 mole) and 2-bromoethanol were combined with 75 ml of carbon tetrachloride in a 250 ml round-bottomed flask equipped with a reflux condenser. The reaction mixture was refluxed for 24 hours and

the solvent was removed on a Büchi rotating evaporator to give a viscous, tan liquid residue. Distillation of this material through a 1/2 x 12" Vigreux column yielded a major fraction boiling at 120-123°/2 mm which was very prone to solidify in the condenser and receiver. The crude, white solid product (49.5 g, 62%) melted at 41-45° and was very soluble in diethyl ether, acetone and carbon tetrachloride. Recrystallization from diethyl ether using a Dry Ice®-methylene chloride cooling bath produced nice white needles melting at 43-46°. The melting point was improved to 44.5-46° by placing the product in a vacuum desiccator over paraffin shavings and evacuating to 2 mm.

<u>Anal</u>: Calculated for $C_{11}H_{11}BrO_2$: C, 51.8; H, 4.35. Found: C, 52.1; H, 4.63.

<u>Infrared</u>: $\gamma_{\gt C=O}$, 1719 cm^{-1} (Fluorolube).

<u>Nmr</u>: Spectrum 6.

15. <u>Preparation of 2-Bromoethyl Pivalate</u>: Pivaloyl chloride (Eastman, 36.18 g, 0.3 mole) and 2-bromoethanol (37.5 g, 0.3 mole) were combined with 50 ml of carbon tetrachloride in a 250 ml round-bottomed flask equipped with a reflux condenser. The reaction mixture was refluxed for 10 hours after which the solvent was removed on a Büchi rotating evaporator to yield a light yellow oil residue. This crude product was distilled through a 1/2 x 12" Vigreux column to give a fraction boiling at 75-85°/33 mm which was found by nmr spectroscopy to be predominately the desired product. Redistillation through a 1/2 x 21" Vigreux column gave 15.6 g (25%) of colorless product boiling at 94-95°/34 mm.

Anal: Calculated for $C_7H_{13}BrO_2$: C, 40.2; H, 6.27. Found: C, C, 40.0; H, 6.18.

<u>Infrared</u>: $\gamma_{\gt C=O}$, 1738 cm^{-1} (neat).

<u>Nmr</u>: Spectrum 8

16. Preparation of 2-Bromoethyl Cyclobutanecarboxylate: A solution of cyclobutanecarbonyl chloride (Kaplop Labs, 26.9 g, 0.2 mole) in 25 ml of carbon tetrachloride was charged into a 250 ml three-necked flask equipped with a stirrer, condenser, and addition funnel. A solution of 2-bromoethanol (Eastman)(25 g, 0.2 mole) in 25 ml of carbon tetrachloride was added dropwise with stirring over a period of 20 minutes. The reaction mixture was stirred while refluxing for 15 hours. Removal of the solvent on a Büchi rotating evaporator gave a sweet-smelling liquid residue which was distilled through a 1/2 x 21" Vigreux column. A water white product boiling at 79-80°/5 mm was obtained (31.3 g, 77%).

Anal: Calculated for $C_7H_{11}BrO_2$: C, 40.6; H, 5.36. Found: C, 40.4; H, 5.27.

Infrared: $\gamma_{\rangle C=O}$, 1740 cm^{-1} (neat)

Nmr: Spectrum 7

C. Precursors to 2-Aryl-1,3-dioxolenium Cations:

1. Preparation of 2-Bromoethyl p-Methoxybenzoate: p-Methoxybenzoyl chloride (Aldrich, 51.2 g, 0.3 mole) and 2-bromoethanol (37.5 g, 0.3 mole) were combined in 50 ml of carbon tetrachloride and refluxed for 15 hours. When the mixture was cooled to room temperature, some white crystalline material fell out of solution and was filtered off and identified as 4-methoxybenzoic acid. Solvent was removed from the syrupy filtrate on a rotating evaporator leaving a dark brown, viscous residue which was distilled through a 1/2 x 21" Vigreux column. A major fraction came over at 109-110°/3 mm (39.1 g, 44%).

Anal: Calculated for $C_{10}H_{11}BrO_3$: C, 46.4; H, 4.28. Found: C, 46.4; H, 4.35.

Infrared: $\gamma_{\rangle C=O}$, 1722 cm^{-1} (neat)

Nmr: Spectrum 19

2. Preparation of 2-Bromoethyl 3,4,5-Trimethoxybenzoate: 3,4,5-trimethoxybenzoyl chloride (Aldrich, 69.2 g, 0.3 mole) and 2-bromoethanol (37.5 g, 0.3 mole) were combined in 50 ml of carbon tetrachloride and the orange-red reaction mixture was refluxed for 10 hours. Solvent was removed on a rotating evaporator to give an amber oil that slowly solidified into an off-white mass. Recrystallization of this crude material from n-hexane gave a white fluffy material melting at 56.5-59° (75.95 g, 79%). Recrystallization from diethyl ether gave white crystals melting at 56-57°.

Anal: Calculated for $C_{12}H_{15}O_5Br$: C, 45.2; H, 4.74. Found: C, 45.5; H, 4.93.

Infrared: $\gamma_{>C=O}$, 1715 cm^{-1} (Fluorolube)

Nmr: Spectrum 20

3. Preparation of 2-Bromoethyl p-Methylbenzoate: p-Methylbenzoyl chloride (Aldrich, 35.7 g, 0.2 mole) and 2-bromoethanol (25.0 g, 0.2 mole) were combined with 40 ml of carbon tetrachloride and refluxed for 12 hours. The solvent was removed on a rotating evaporator leaving an amber colored liquid residue. Fractionation of this residue through a 1/2 x 21" Vigreux column gave a colorless major cut boiling at 116-117°/4 mm (35.1 g, 71%).

Anal: Calculated for $C_{10}H_{11}BrO_2$: C, 49.4; H, 4.56. Found: C, 49.6; H, 4.69.

Infrared: $\gamma_{>C=O}$, 1725 cm^{-1} (neat)

Nmr: Spectrum 21

4. <u>Preparation of 2-Bromoethyl m-Methylbenzoate</u>: m-Methylbenzoyl chloride (Research Organic Company, 31.1 g, 0.2 mole) and 2-bromoethanol (25 g, 0.2 mole) were combined in 30 ml of carbon tetrachloride and refluxed for 12 hours. Removal of the solvent on a rotating evaporator and distillation of the liquid residue gave a colorless major fraction boiling at 115-116°/2 mm (39.85 g, 81%).

<u>Anal</u>: Calculated for $C_{10}H_{11}BrO_2$: C, 49.4; H, 4.56. Found: C, 49.3; H, 4.44.

<u>Infrared</u>: $\gamma_{>C=O}$, 1730 cm^{-1} (neat)

<u>Nmr</u>: Spectrum 22

5. <u>Preparation of 2-Bromoethyl Benzoate</u>:

(a) Benzoyl chloride (Heyden Chemical Company, 28.2 g, 0.2 mole) and 2-bromoethanol (25 g, 0.2 mole) were combined in 50 ml of carbon tetrachloride contained in a 250 ml three-necked flask equipped with a condenser and stirrer. The reaction mixture was maintained at reflux while stirring for 19 hours. Solvent was removed on a rotating evaporator (Büchi) yielding a light amber oil which weighed 44.5 g (97%). This crude product was distilled through a 1/2 x 21" Vigreux column giving a major cut of colorless product boiling at 96-97°/2 mm which weighed 31.4 g (69%).

<u>Anal</u>: Calculated for $C_9H_9BrO_2$: C, 47.2; H, 3.96. Found: C, 47.2; H, 4.09.

<u>Infrared</u>: $\gamma_{>C=O}$, 1731 cm^{-1} (neat).

<u>Nmr</u>: Spectrum 23

(b) Approximately 300 mg of 2-phenyl-1,3-dioxolane were dissolved in 1 ml of bromotrichloromethane (Dow) contained in an nmr tube. This sample was immersed in a constant temperature bath maintained at 18°

and irradiated with a sunlamp (General Electric, lamp to sample distance = 3") for 3 hours. After this time the sample was then scanned on an nmr spectrometer and found to be quantitatively converted to 2-bromoethyl benzoate. The spectra for this sample were found to be identical in every respect to the infrared and nmr spectra obtained for the authentic product obtained according to method (a).

6. Preparation of 2-Bromoethyl p-Fluorobenzoate: p-Fluorobenzoyl chloride (Aldrich, 31.8 g, 0.2 mole) and 2-bromoethanol (25 g, 0.2 mole) were combined in 40 ml of carbon tetrachloride to give a light yellow, homogenous reaction mixture. This was refluxed for 12 hours, after which the solvent was removed on a rotating evaporator (Büchi). Distillation of the liquid residue through a 1/2 x 12" Vigreux column gave a major fraction boiling 95-100°/2 mm. Upon standing this distillate crystallized to an off-white solid, mp 38-43°. Redistillation of this crude product gave 20.22 g (41%) of purified material which melted at 41-42.5°.

Anal: Calculated for $C_9H_8BrFO_2$: C, 43.8; H, 3.26. Found: C, 44.0; H, 3.38.

Infrared: $\gamma_{\gt C=O}$, 1720 cm^{-1} (Fluorolube)

Nmr: Spectrum 24

7. Preparation of 2-Bromoethyl p-Chlorobenzoate: Into a 250 ml round-bottomed flask equipped with a reflux condenser was charged 52.5 g (0.3 mole) of p-chlorobenzoyl chloride (Hooker Chemical) and 37.5 g (0.3 mole) of 2-bromoethanol. While being stirred with a magnetic stirrer, the reaction mixture was heated at 100-125° for 12 hours. During this time the slightly viscous reaction mixture turned dark brown. After the mixture was filtered to remove some suspended solid material, the filtrate was distilled through a 1/2 x 21" Vigreux column to give a major colorless

fraction coming over at 120-121°/0.9 mm or 99-100°/0.2 mm which was prone to crystallize in the condenser and receiver (33.3 g, 68%, mp 28-32°). This product was recrystallized from diethyl ether, using a Dry Ice®-methylene chloride cooling bath, to give a fine white powder, mp 32.5-33.5°.

Anal: Calculated for $C_9H_8BrClO_2$: C, 41.0; H, 3.06. Found: C, 41.3; H, 3.16.

Infrared: $\gamma_{\rangle C=O}$, 1732 cm^{-1} (neat)

Nmr: Spectrum 25

8. Preparation of 2-Chloroethyl m-Chlorobenzoate: m-Chlorobenzoyl chloride (Hooker Chemical Company, 52.5 g, 0.3 mole) and 2-chloroethanol (24.15 g, 0.3 mole) were combined in a 150 ml round-bottomed flask equipped with a reflux condenser. The reaction mixture was stirred with a magnetic stirrer as the temperature was gradually increased. At a temperature of 85-100°, the evolution of hydrogen chloride was detected. The temperature of the reaction mixture was maintained at 100-110°, with stirring, for 12 hours. Distillation of this material through a 1/2 x 21" Vigreux column gave a water-white, major fraction boiling at 88-89°/1.5 mm. The product weighed 55.5 g (85%).

Anal: Calculated for $C_9H_8Cl_2O_2$: C, 49.3; H, 3.68. Found: C, 49.2; H, 3.86.

Infrared: $\gamma_{\rangle C=O}$, 1730 cm^{-1} (neat)

Nmr: Spectrum 26

9. Preparation of 2-Bromoethyl m-Bromobenzoate: m-Bromobenzoyl chloride (Eastman, 43.9 g, 0.20 mole) and 2-bromoethanol (25 g, 0.20 mole) were combined in 50 ml of carbon tetrachloride and refluxed for 13 hours. Solvent was removed at reduced pressure on a rotating evaporator (Büchi)

leaving an amber liquid residue which weighed 58.9 g (96%). This crude material was distilled through a 1/2 x 12" Vigreux column giving a major cut (colorless) which boiled at 113-120°/2 mm and weighed 40.75 g (66%). This fraction was redistilled to give an analytically pure sample which boiled at 118-119°/2 mm.

<u>Anal</u>: Calculated for $C_9H_8Br_2O_2$: C, 35.1; H, 2.62. Found: C, 35.2; H, 2.52.

<u>Infrared</u>: $\gamma_{\gt C=O}$, 1738 cm^{-1} (neat)

<u>Nmr</u>: Spectrum 27

10. <u>Preparation of 2-Bromoethyl *m*-Fluorobenzoate</u>: *m*-Fluorobenzoyl chloride (Columbia, 11.9 g, 0.075 mole) and 2-bromoethanol (9.4 g, 0.075 mole) were combined in 15 ml of carbon tetrachloride contained in a 50 ml round-bottomed flask equipped with a reflux condenser. The reaction mixture was refluxed for 18 hours during which time it darkened. Solvent was removed from the mixture on a rotating evaporator (Büchi) to yield a dark brown oily residue. This material was distilled through a 1/2 x 12" Vigreux column to give a major cut boiling at 89.5-90°/2 mm (14.3 g, 77%).

<u>Anal</u>: Calculated for $C_9H_8BrO_2F$: C, 43.8; H, 3.26. Found: C, 43.6; H, 3.17.

<u>Infrared</u>: $\gamma_{\gt C=O}$, 1736 cm^{-1} (neat)

<u>Nmr</u>: Spectrum 28

11. <u>Preparation of 2-Bromoethyl 3,4-Dichlorobenzoate</u>: 3,4-Dichlorobenzoyl chloride (Heyden, 62.9 g, 0.3 mole) and 2-bromoethanol (37.5 g, 0.3 mole) were combined in 50 ml of carbon tetrachloride and refluxed for 6 hours. The reaction mixture was cooled to ice temperature and filtered free of some suspended solid material. Solvent was removed on a

rotating evaporator (Büchi) to give a liquid residue (80.5 g) which was distilled through a 1/2 x 21" Vigreux column. The distillate came over as a mixture of a colorless liquid and a white solid, bp 120-125°/1 mm. The distillate solidified to a white mass in the receiver, mp 46-49°. Recrystallization from a mixture of n-hexane and diethyl ether using a Dry Ice®-methylene chloride cooling bath, gave a white crystalline product, mp 48-49.5°.

Anal: Calculated for $C_9H_7BrCl_2O_2$: C, 36.3; H, 2.37. Found: C, 36.1; H, 2.30.

Infrared: $\nu_{>C=O}$, 1737 cm^{-1} (Fluorolube)

Nmr: Spectrum 29

12. Preparation of 2-Bromoethyl *m*-Trifluoromethylbenzoate: *m*-Trifluoromethylbenzoyl chloride (Columbia, 10.4 g, 0.05 mole) and 2-bromoethanol (6.25 g, 0.05 mole) was combined with 15 ml of carbon tetrachloride in a 50 ml round-bottomed flask equipped with reflux condenser. The reaction mixture was refluxed for 24 hours after which the solvent was removed on a rotating evaporator (Büchi). A dark brown residual oil was obtained and fractionated through a 1/2 x 12" Vigreux column. A major cut, boiling at 82-88°/2 mm was collected and redistilled to give 9.65 g (65%) of a colorless product boiling at 87-88°/2 mm.

Anal: Calculated for $C_{10}H_8BrF_3O_2$: C, 40.3; H, 3.04; Br, 26.8. Found: C, 40.6; H, 2.95; Br, 26.6.

Infrared: $\nu_{>C=O}$, 1736 cm^{-1} (neat)

Nmr: Spectrum 30

13. Preparation of 2-Bromoethyl p-Trifluoromethylbenzoate: p-Trifluoromethylbenzoyl chloride (Columbia, 10.4 g, 0.05 mole) and 2-bromoethanol (6.25 g, 0.05 mole) were combined with 30 ml of carbon tetrachloride in a 50 ml round-bottomed flask equipped with a reflux condenser. The reactants were refluxed for 9 hours and the solvent was then removed on a rotating evaporator (Büchi) to leave an amber liquid residue. Distillation of this material through a 1/2 x 12" Vigreux column gave a major fraction boiling at 86-87°/1.5 mm (10.7 g, 72%).

Anal: Calculated for $C_{10}H_8BrF_3O_2$: C, 40.4; H, 2.71. Found: C, 40.5; H, 2.97.

Infrared: $\gamma_{>C=O}$, 1740 cm^{-1} (neat)

Nmr: Spectrum 31

14. Preparation of 2-Bromoethyl m-Nitrobenzoate: m-Nitrobenzoyl chloride (Eastman, 55.7 g, 0.3 mole) and 2-bromoethanol (37.5 g, 0.3 mole) were combined in 50 ml of carbon tetrachloride to give a deep red reaction mixture which was refluxed for 10 hours. When the mixture was cooled to room temperature, a red-yellow solid fell out of solution and was filtered. Solvent was removed from the filtrate on a rotating evaporator (Büchi) to give a viscous yellow-red liquid residue. The liquid was fractionated through a 1/2 x 21" Vigreux column. A cut boiling at 130-135°/2.5 mm was identified as the desired ester by nmr spectroscopy. Redistillation of this crude product gave a major fraction at 133-135°/2.5 mm (20.75 g, 25%).

Anal: Calculated for $C_9H_8BrNO_4$: C, 39.4; H, 2.94. Found: C, 39.7; H, 2.78.

Infrared: $\gamma_{>C=O}$, 1735 cm^{-1} (neat)

Nmr: Spectrum 32

15. Preparation of 2-Bromoethyl p-Nitrobenzoate: p-Nitrobenzoyl chloride (Eastman, 55.68 g, 0.30 mole) and 2-bromoethanol (37.5 g, 0.30 mole) were combined in 50 ml of carbon tetrachloride and refluxed for 9 hours. The gray reaction mixture was cooled to room temperature and filtered free of some suspended solid material which was identified as 4-nitrobenzoic acid. Solvent was removed from the filtrate on a rotating evaporator (Büchi) to yield a gray solid product melting at 50-53° (46.45 g, 50%). Recrystallization from diethyl ether, using a Dry Ice®-methylene chloride cooling bath, gave a white powdery product melting at 49.5-51°.

Anal: Calculated for $C_9H_8BrNO_4$: C, 39.4; H, 2.94. Found: C, 39.6; H, 3.07.

Infrared: $\gamma_{C=O}$, 1730 cm^{-1} (Fluorolube)

Nmr: Spectrum 33

16. Preparation of 2-Bromoethyl Isophthalate: Isophthaloyl chloride (Eastman, 60.9 g, 0.3 mole) and 2-bromoethanol (75.0 g, 0.6 mole) were combined with 50 ml of carbon tetrachloride and refluxed for 19 hours. After the mixture was cooled to room temperature, some white solid crystallized out of solution and was filtered. It was identified as isophthalic acid. Solvent was removed from the filtrate on a rotating evaporator (Büchi) to yield a tan oily residue. This residue partially crystallized after standing in a stoppered flask for several days and was filtered, and washed with 20 ml of cold ether. The crude tan solid product weighed 45.13 g (39%) and melted at 50-56°. Recrystallization from a mixture of n-hexane and diethyl ether gave a nice white powder which melted at 51-54°. The melting point was improved to 54-56° by placing the material in a vacuum desiccator over paraffin shavings and evacuating to 2 mm.

Anal: Calculated for $C_{12}H_{12}Br_2O_4$: C, 37.9; H, 3.18. Found: C, 38.1; H, 3.19.

Infrared: $\gamma_{\supset C=O}$, 1730 cm^{-1} (Fluorolube)

Nmr: Spectrum 34

17. Preparation of 2-Bromoethyl Terephthalate: Terephthaloyl chloride (Eastman, 60.9 g, 0.3 mole) and 2-bromoethanol (75 g, 0.6 mole) were combined in 50 ml of carbon tetrachloride and refluxed for 5 hours. While the reaction mixture was being filtered to remove a small amount of suspended solid material, it solidified to a gray slushy mass. After it was cooled in an ice bath, the crude gray diester was filtered and found to weigh 80.9 g (71%), mp 90-94°. Several recrystallizations from diethyl ether gave a fluffy white product melting at 95-96°.

Anal: Calculated for $C_{12}H_{12}Br_2O_4$: C, 37.9; H, 3.18; Br, 42.1. Found: C, 38.0; H, 3.11; Br, 41.7.

Infrared: $\gamma_{\supset C=O}$, 1733 cm^{-1} (Fluorolube)

Nmr: Spectrum 35

18. Preparation of Tris(2-bromoethyl) Trimesate: Trimesoyl chloride (Frinton Labs, 26.55 g, 0.1 mole) and 2-bromoethanol (37.5 g, 0.3 moles) were combined in 50 ml of carbon tetrachloride. The homogeneous reaction mixture was refluxed for 12 hours, after which the solvent was removed at reduced pressure on a rotating evaporator (Büchi). A viscous, tan oil remained which could not be induced to crystallize. An attempt to distill this material at a pot temperature of 175° at 2 mm was unsuccessful. A small amount of volatile material was collected, but the main portion would not distill under these conditions. The above treatment converted the material into a dark brown syrup which was soluble in diethyl ether and carbon tetrachloride but not in n-hexane. Adding

n-hexane to an ether solution of the syrup gave a white crystalline material which weighed 35.7 g (67%) and melted at 86-91°. Recrystallization from diethyl ether (Dry Ice®-methylene chloride cooling bath) gave glittering white crystals melting at 94.5-96.5°. The melting point was increased to 95.5-96.5° by placing the material in a vacuum desiccator over paraffin shavings and evacuating to 5 mm.

Anal: Calculated for $C_{15}H_{15}Br_3O_6$: C, 33.9; H, 2.85. Found: C, 33.7; H, 2.61. Infrared: $\gamma_{>C=O}$, 1745 cm^{-1} (Fluorolube)

Nmr: Spectrum 36

D. Precursors to 2,2'-Alkylene-1,3-dioxolenium Dications

1. Preparation of Bis(2-bromoethyl) Oxalate: A solution of oxalyl chloride (Eastman, 25 g, 0.20 mole) in 50 ml of carbon tetrachloride was added dropwise with stirring over a period of 30 minutes to a solution of 2-bromoethanol (49.3 g, 0.39 mole) in 50 ml of carbon tetrachloride. The reaction was not exothermic. While being stirred the reaction mixture was refluxed for 9 hours, after which the solvent was removed on a rotating evaporator (Büchi). A viscous oily residue remained. Allowing this oil to stand in the hood draft caused some crystals to form on the walls of the evaporating dish. When these crystals were added to the oil and scratched, crystallization to a mass of gray platelets occurred. This crude material was recrystallized once from n-hexane to give 58.1 g (96%) of a glittering white crystalline product which melted at 54.5-56°. Cort and Pearson[55] reported a melting point of 55-55.5°.

Anal: Calculated for $C_6H_8Br_2O_4$: C, 23.7; H, 2.65. Found: C, 23.9; H, 2.65.

Infrared: $\gamma_{>C=O}$, 1770, 1745 cm^{-1} (Fluorolube)

Nmr: Spectrum 12

2. <u>Preparation of Bis-(2-bromoethyl) Malonate</u>: 2-Bromoethanol (50 g, 0.4 mole) in 75 ml of carbon tetrachloride was added dropwise to a stirred solution of malonyl chloride (28.2 g, 0.2 mole) in 75 ml of carbon tetrachloride over a period of 30 minutes. A moderately exothermic reaction was observed. The reaction mixture was then refluxed, with stirring, for 6 hours, after which the solvent was removed at reduced pressure on a rotating evaporator (Büchi). The dark brown, viscous residue was distilled through a 1/2 x 12" Vigreux column giving a major colorless fraction boiling at 125-126°/0.5 mm and weighing 47 g (74%).

<u>Anal</u>: Calculated for $C_7H_{10}Br_2O_4$: C, 26.4; H, 3.17. Found: C, 26.4; H, 3.13.

<u>Infrared</u>: $\nu_{\rangle C=O}$, 1761 cm^{-1} (neat)

<u>Nmr</u>: Spectrum 13

3. <u>Preparation of Bis(2-bromoethyl) Succinate:</u> Succinyl chloride (Eastman, 26.5 g, 0.17 mole) and 2-bromoethanol (42.5 g, 0.34 mole) were combined in 75 ml of carbon tetrachloride and refluxed for 14 hours. Solvent was removed at reduced pressure on a rotating evaporator (Büchi) leaving a tan liquid residue which weighed 55.2 g (97%). The crude ester was taken up in 50 ml of carbon tetrachloride and washed with 125 ml of a saturated solution of sodium bicarbonate. The aqueous phase was extracted with carbon tetrachloride (2 x 25 ml). The combined extracts were washed with water (2 x 100 ml) and dried over anhydrous calcium sulfate. Solvent was removed at reduced pressure on a rotating evaporator (Büchi), leaving a nearly colorless liquid residue which weighed 37.8 g (67%). This material was distilled through a 1/2 x 12" Vigreux column, yielding a colorless, major fraction which boiled at 145-147°/2 mm and

weighed 27.3 g (48%).

Anal: Calculated for $C_8H_{12}Br_2O_4$: C, 28.9; H, 3.64. Found: C, 29.2; H, 3.92.

Infrared: $\gamma_{>C=O}$, 1740 cm^{-1} (neat)

Nmr: Spectrum 14

4. Preparation of Bis-(2-bromoethyl) Glutarate: Glutaryl chloride (Aldrich, 33.8 g, 0.2 mole) and 2-bromoethanol (50.0 g, 0.4 mole) were combined in 75 ml of carbon tetrachloride and refluxed for 12 hours. Solvent was removed on a rotating evaporator (Büchi). The residue was distilled through a 1/2 x 12" Vigreux column and collected as a fraction boiling at 113-123°/2.5 mm. Weight of the crude product was 51.2 g (74%). Redistillation of the crude product gave an analytical sample boiling at 115-118°/2.5 mm.

Anal: Calculated for $C_9H_{14}Br_2O_4$: C, 31.2; H, 4.08. Found: C, 31.3; H, 3.85.

Infrared: $\gamma_{>C=O}$, 1749 cm^{-1} (neat)

Nmr: Spectrum 15

5. Preparation of Bis-(2-bromoethyl) Adipate: 2-Bromoethanol (50 g, 0.4 mole) in 50 ml of carbon tetrachloride was added dropwise to a stirred solution of adipyl chloride (36.6 g, 0.2 mole) in 50 ml of the same solvent over a period of 30 minutes. A slight rise in temperature was noted (to 35°). The reaction mixture was stirred while at reflux for 17 hours, after which the solvent was removed at reduced pressure on a rotating evaporator (Büchi). A light tan liquid residue was obtained which weighed 70 g (97%). This residue was distilled through a 1/2 x 12" Vigreux column, giving a colorless major fraction which boiled at 162-163°/0.9 mm and

weighed 52.80 g (73%).

Anal: Calculated for $C_{10}H_{16}Br_2O_4$: C, 33.4; H, 4.48. Found: C, 33.3; H, 4.48.

Infrared: $\nu_{C=O}$, 1749 cm^{-1} (neat)

Nmr: Spectrum 16

6. Preparation of Bis(2-bromoethyl) Pimelate: Pimelyl chloride (Frinton Labs, 19.7 g, 0.10 mole) and 2-bromoethanol (12.5 g, 0.10 mole) were combined in 75 ml of carbon tetrachloride and refluxed for 8 hours. Solvent was removed on a rotating evaporator, to give a dark brown oil weighing 35.7 g (95%). This crude product was distilled through a 1/2 x 12" Vigreux column, yielding a light tan liquid as a major fraction which weighed 25.0 g (67%) and boiled at 150-159°/2 mm. This material was redistilled to give a pure product which boiled at 156-159°/2 mm.

Anal: Calculated for $C_{11}H_{18}Br_2O_4$: C, 35.3; H, 4.85. Found: C, 35.5; H, 4.86.

Infrared: $\nu_{C=O}$, 1750 cm^{-1} (neat)

Nmr: Spectrum 17

7. Preparation of Bis(2-bromoethyl) Suberate: Suberyl chloride (Frinton Labs, 21.1 g, 0.10 mole) and 2-bromoethanol (24.9 g, 0.20 mole) were combined in 75 ml of carbon tetrachloride. A vigorous reaction accompanied by a copious evolution of HCl was observed shortly after addition. The reaction mixture was refluxed for 25 hours, after which the solvent was removed at reduced pressure on a rotating evaporator (Büchi). A heavy, tan liquid residue remained and crystallized into a tan solid upon standing overnight at room temperature. The crude product weighed 26.4 g (94%) and melted at 31-35°. Recrystallization from

n-hexane gave glittering white plates which melted at 37-38°.

Anal: Calculated for $C_{12}H_{20}Br_2O_4$: C, 37.1; H, 5.19. Found: C, 37.3; H, 5.21.

Infrared: $\nu_{C=O}$, 1750 cm^{-1} (Fluorolube)

Nmr: Spectrum 18

E. 2-Alkyl-1,3-dioxolenium Cations:

1. Preparation of 2-(N,N-Diethylamino)-1,3-dioxolenium Tetrafluoroborate: Under anhydrous conditions, powdered silver tetrafluoroborate (1.93 g, 0.01 mole) was added in one portion to a stirred solution of 2-bromoethyl N,N-diethylcarbamate (1.96 g, 0.01 mole) in 20 ml of dry methylene chloride. An exothermic reaction sufficient to cause the solvent to reflux slightly was observed and was accompanied by the formation of a yellow precipitate. The reaction mixture was stirred at 25-30° for 1 hour after which the insoluble material was filtered, washed with methylene chloride (2 x 10 ml) and found to weigh 1.64 g (88%, assuming it is only silver bromide). Reduction of the filtrate to one-half its original volume and addition of diethyl ether caused a colorless oil (lower phase) to separate. This layer could not be induced to crystallize until it was cooled in a Dry Ice®-methylene chloride cooling bath and scratched. After some effort, a white crystalline material formed and was filtered. It weighed 1.6 g (69%), mp 46-51°. Recrystallization of this crude material from methylene chloride (Dry Ice® cooling) yielded fine white crystals melting at 53-54.5°.

Anal: Calculated for $C_7H_{14}NO_2 \cdot BF_4$: C, 36.4; H, 6.11. Found: C, 36.4; H, 6.29.

Nmr: Spectrum 37

2. <u>Preparation of 2-(Cyclopropyl)-1,3-dioxolenium Tetrafluoroborate</u>: Under anhydrous conditions, powdered silver tetrafluoroborate (1.93 g, 0.01 mole) was added in one portion to a stirred solution of 2-bromoethyl cyclopropanecarboxylate (1.93 g, 0.01 mole) in 20 ml of dry methylene chloride. An immediate precipitation of a yellow cream-colored solid accompanied the slightly exothermic reaction. After the reaction mixture was stirred for 2 hours at 25-30° with a magnetic stirrer, the suspended solid was filtered and washed with methylene chloride (2 x 10 ml). The yellow-gray filter cake weighed 3.30 g (85%, assuming it consists of cation and silver bromide). Reducing the filtrate to half the original volume and adding 10 ml of diethyl ether gave 0.05 g (2.5%) of the cation salt as a white crystalline product which melted at 123-125.5°. The above filter cake was slurried in 10 ml of liquid sulfur dioxide, filtered and then washed with liquid sulfur dioxide (2 x 5 ml). A yellow-gray filter cake of silver bromide remained which weighed 1.55 g (83%). Evaporation of the filtrate yielded 1.25 g (63%) of a white crystalline product. This material was recrystallized from a mixture of acetonitrile and methylene chloride (Dry Ice ®-methylene chloride cooling bath) to give fine white crystals melting at 124.5-126°.

<u>Anal</u>: Calculated for $C_6H_9O_2 \cdot BF_4$: C, 36.0; H, 4.54. Found: C, 35.8; H, 4.34.

<u>Nmr</u>: Spectrum 38

3. <u>Preparation of 2-(2-Methylpropenyl)-1,3-dioxolenium Tetrafluoroborate</u>: Anhydrous powdered silver tetrafluoroborate (1.93 g, 0.01 mole) was added in one portion to a stirred solution of 2-bromoethyl 3,3-dimethylacrylate (2.07 g, 0.01 mole) in 20 ml of dry methylene chloride while under anhydrous conditions. The reaction was mildly exothermic and accompanied

by the formation of a cream-yellow precipitate. The reaction mixture was allowed to stir for 2 hours at 25-30°. After this time the precipitate was filtered and washed with methylene chloride (2 x 10 ml). The filtrate was reduced to dryness leaving a slushy gray solid. This residue was dissolved in 5-10 ml of methylene chloride and filtered. Anhydrous diethyl ether was added; this caused the product to precipitate. The crude product was filtered and found to weigh 1.4 g (65%), mp 57-61°. Recrystallization from a mixture of diethyl ether and methylene chloride (Dry Ice® cooling) gave a fine white crystalline product melting at 61-62°.

<u>Anal</u>: Calculated for $C_7H_{11}O_2 \cdot BF_4$: C, 39.3; H, 5.18. Found: C, 39.0; H, 5.03.

<u>Nmr</u>: Spectrum 39

4. <u>Preparation of 2-(p-Methoxystyryl)-1,3-dioxolenium Tetrafluoroborate</u>: 2-Bromoethyl 4-methoxycinnamate (2.85 g, 0.01 mole) in 20 ml of methylene chloride was charged into a 50 ml erlenmeyer flask equipped with a magnetic stirrer. In a dry box, (1.93 g, 0.01 mole) of powdered silver tetrafluoroborate (Alfa Inorg) was added in one portion to the stirred ester solution. A precipitate formed immediately and the solution became a brilliant canary yellow. The reaction mixture was stirred for 1 hour at 25-30°, after which the yellow precipitate was filtered (3.4 g, 71% assuming it consists of the cation and silver bromide). Trituration of the precipitate with 10 ml of liquid sulfur dioxide followed by filtration and washing the filter cake with liquid sulfur dioxide (2 x 10 ml) left a cream-colored filter cake of silver bromide (1.65 g) and a brilliant yellow filtrate. Evaporation of the sulfur dioxide yielded a yellow solid which weighed 2.08 g (71%). This material turned dark at ~130-140° and decomposed at 185-195°. Recrystallization from a mixture of acetonitrile

and methylene chloride using a Dry Ice®-methylene chloride bath, gave a brilliant yellow powder which darkened at ~210° and decomposed to a black resin at 220-223°. This product gave a canary yellow solution in liquid sulfur dioxide, methylene chloride or acetonitrile but was rapidly decolorized in FSO_3H or water.

Anal: Calculated for $C_{12}H_{13}O_3 \cdot BF_4$: C, 49.5; H, 4.30. Found: C, 49.5; H, 4.45.

Nmr: Spectrum 41

5. Preparation of trans-2-(Propenyl)-1,3-dioxolenium Tetrafluoroborate: Under anhydrous conditions, powdered silver tetrafluoroborate (1.93 g, 0.01 mole) was added in one portion to a stirred solution of 2-bromoethyl crotonate (1.93 g, 0.01 mole) in 20 ml of anhydrous methylene chloride. A yellow precipitate formed shortly after the addition. The reaction mixture was stirred for 1 hour at 25-30° after which time the insoluble material was filtered and washed with methylene chloride (2 x 10 ml). The yellow-gray filter cake weighed 3.38 g. This represents a yield of 87%, assuming it consists of cation salt and silver bromide. This filter cake was slurried in 10 ml of liquid sulfur dioxide, filtered and washed twice with 5-ml portions of this solvent. The silver bromide remaining on the filter weighed 1.38 g (94%). Reducing the filtrate to dryness gave 1.58 g (79%) of a fine crystalline material melting at 140-147°. Recrystallization from a mixture of acetonitrile and methylene chloride gave an analytical sample of glittering white crystals melting at 150-152°.

Anal: Calculated for $C_6H_9O_2 \cdot BF_4$: C, 36.0; H, 4.54. Found: C, 36.3; H, 4.41.

Nmr: Spectrum 40

6. Preparation of 2-(Styryl)-1,3-dioxolenium Tetrafluoroborate: Powdered silver tetrafluoroborate (1.93 g, 0.01 mole) was added in one portion to a stirred solution of 2-bromoethyl cinnamate (2.65 g, 0.01 mole) in 20 ml of methylene chloride under anhydrous conditions. The reaction mixture was stirred for 1.75 hours, filtered, then washed with methylene chloride (2 x 10 ml). The yellow gray filter cake weighed 3.2 g (77%, assuming it consists of silver bromide and cation salt). This filter cake was slurried in 10 ml of liquid sulfur dioxide, filtered and washed twice with 5 ml portions of the solvent. A filter cake of silver bromide remained which weighed 1.7 g (92%). The sulfur dioxide filtrate was reduced to dryness, to yield 1.45 g (67%) of an off-white solid product which melted at 173-176°. Recrystallization of this crude material from a mixture of acetonitrile and methylene chloride (Dry Ice® cooling) gave glittering white crystals which melted at 178-179.5°.

Anal: Calculated for $C_{11}H_{11}O_2 \cdot BF_4$: C, 50.4; H, 4.23. Found: C, 50.1; H, 4.34.

Nmr: Spectrum 42

7. Preparation of 2-(*t*-Butyl)-1,3-Dioxolenium Tetrafluoroborate: Under anhydrous conditions powdered silver tetrafluoroborate (Alfa Inorganic, 1.93 g, 0.01 mole), was added in one portion to a solution of 2-bromoethyl pivalate (2.09 g, 0.01 mole) and 15 ml of anhydrous methylene chloride contained in a 50 ml erlenmeyer flask equipped with a magnetic stirrer. An immediate exothermic reaction was observed accompanied by the formation of light yellow precipitate. The flask was stoppered and the reaction mixture was stirred for 2 hours at 25-30°. After the silver bromide was filtered and washed with methylene chloride (2 x 10 ml), the filter cake

weighed 1.8 g (96% of theory for AgBr). When the filtrate was cooled, some product crystallized out, but addition of a small amount of diethyl ether caused more complete crystallization. The product was filtered as a white fluffy solid melting at 148-151° (1.55 g, 72%). An analytical sample was obtained by dissolving the product in a 5:1 methylene chloride:acetonitrile mixture and adding a small amount of diethyl ether. Cooling in a Dry Ice® bath gave fine white needles, melting at 151.5-152.5°.

Anal: Calculated for $C_7H_{13}O_2 \cdot BF_4$: C, 38.9; H, 6.07. Found: C, 38.9; H, 6.12.

Nmr: Spectrum 44

8. Preparation of 2-(Cyclobutyl)-1,3-dioxolenium Tetrafluoroborate: Under anhydrous conditions, powdered silver tetrafluoroborate (Alfa Inorganic, 1.93 g, 0.01 mole) was added in one portion to a stirred solution of 2-bromoethyl cyclobutanecarboxylate (2.07 g, 0.01 mole) in 15 ml of anhydrous methylene chloride. Although the immediate formation of a light yellow precipitate was observed, the reaction did not appear to be exothermic. The reaction mixture was stirred for 1 hour at 25-30°. The suspended silver bromide was filtered and washed twice with 10-ml portions of methylene chloride. The weight of filter cake was 1.85 g (99%). The colorless filtrate was reduced to 1/2 its original volume under reduced pressure and then anhydrous diethyl ether was added until a colorless oil separated from the solution. The two-phase system was cooled in a Dry Ice®-methylene chloride bath and scratched. After some effort, the oil finally crystallized to a white fluffy solid which was filtered, washed with 10 ml of ether and found to weigh 1.20 g (56%), mp 28-31°. Recrystallization from a mixture of methylene chloride and diethyl ether (Dry Ice® cooling)

gave a white powdery product which melted at 31-32°.

Anal: Calculated for $C_7H_{11}O_2 \cdot BF_4$: C, 39.3; H, 5.18. Found: C, 39.4; H, 5.11.

Nmr: Spectrum 43

9. Preparation of 2-(Methyl)-1,3-dioxolenium Tetrafluoroborate: In a dry box, powdered anhydrous silver tetrafluoroborate (1.93 g, 0.01 mole) was added in one portion to a stirred solution of 2-bromoethyl acetate (1.67 g, 0.01 mole) in 20 ml of methylene chloride. A yellow precipitate formed shortly after the addition. After the reaction mixture was allowed to stir for 1 hour, the insoluble material was filtered, washed with methylene chloride (2 x 10 ml) and found to weigh 3.45 g (96%, assuming it consists of cation salt and silver bromide). This filter cake was slurried in 10 ml of liquid sulfur dioxide, filtered, and washed twice with 5 ml portions of this solvent. The silver bromide left on the filter weighed 1.85 g (99%). Reduction of the filtrate to dryness gave 1.45 g (83%) of a white powdery material which melted at 148-157°. Recrystallization from a mixture of acetonitrile and methylene chloride (Dry Ice® cooling) gave glittering fine white crystals melting at 170-172°. Meerwein[22] reported a melting point of 164-166°.

Anal: Calculated for $C_4H_7O_2 \cdot BF_4$: C, 27.6; H, 4.06. Found: C, 27.7; H, 3.80.

Nmr: Spectrum 45

10. Preparation of 2-(Isopropenyl)-1,3-dioxolenium Tetrafluoroborate: Under anhydrous conditions, powdered silver tetrafluoroborate (Alfa Inorganic, 1.93 g. 0.01 mole), was added in one portion to a stirred solution of 2-bromoethyl methacrylate (1.93 g, 0.01 mole) in 15 ml of dry methylene chloride contained in a 50 ml erlenmeyer flask. An immediate, mild

exothermic reaction accompanied by the formation of a light yellow precipitate was observed. The reaction mixture was allowed to stir with a magnetic stirrer (25-30°) for 2 hours. The insoluble material was then filtered from the red-brown solution (3.5 g). The insoluble material was suspended in 15 ml of liquid sulfur dioxide, filtered, and then washed twice with 10-ml portions of liquid sulfur dioxide. The red-brown filtrate was evaporated to dryness under reduced pressure leaving a brown solid residue. This residue was slurried in 20 ml of anhydrous diethyl ether, filtered and then washed with ether (2 x 20 ml). The tan solid product weighed 1.45 g (81%) and melted at 150-153°. Recrystallization from a mixture of acetonitrile and methylene chloride, using a Dry Ice®-methylene chloride cooling bath, gave fine white crystals, mp 155-156.5°.

<u>Anal</u>: Calculated for $C_6H_9O_2 \cdot BF_4$: C, 36.1; H, 4.54. Found: C, 36.2; H, 4.28.

<u>Nmr</u>: Spectrum 46

11. <u>Preparation of 2-(Vinyl)-1,3-dioxolenium Tetrafluoroborate</u>: Under anhydrous conditions, powdered silver tetrafluoroborate (1.93 g, 0.01 mole) was added in one portion to a stirred solution of 2-bromoethyl acrylate (1.79 g, 0.01 mole) in 20 ml of dry methylene chloride. A yellow creamy precipitate formed immediately. The reaction mixture was stirred for 4.5 hours at 25-30° after which the insoluble material was filtered and washed twice with 10 ml-portions of methylene chloride. This precipitate weighed 2.70 g (73%, assuming it consists of cation salt and silver bromide). The filter cake was slurried in 10 ml of liquid sulfur dioxide, followed by washing twice with 10-ml portions of the same solvent. A filter cake of silver bromide remained which weighed 1.45 g (78%). Reducing the filtrate to dryness gave a dark, brown sticky residue which

was slurried in anhydrous diethyl ether and filtered. The crude product weighed 0.8 g (43%). Recrystallization from a mixture of acetonitrile and methylene chloride (Dry Ice® cooling) gave a fine white powder which melted at 151-152.5°.

Anal: Calculated for $C_5H_7O_2 \cdot BF_4$: C, 32.3; H, 3.80. Found: C, 32.5; H, 3.90.

Nmr: Spectrum 47

12. Preparation of 2-(Hydroxy)-1,3-dioxolenium Fluorosulfonate: Ethylene carbonate (Eastman, 4 drops) was added to an nmr tube containing approximately 1 ml of fluorosulfonic acid (Allied) and a small amount of tetramethylammonium tetrafluoroborate. The addition was slightly exothermic but the sample did not change noticeably in appearance. The nmr spectrum, which was scanned 2.5 hours after the addition, consisted of only a sharp singlet at 5.26 ppm.

F. 2-Aryl-1,3-dioxolenium Cations:

1. Preparation of 2-(p-Methoxyphenyl)-1,3-dioxolenium Tetrafluoroborate: 2-Bromoethyl 4-methoxybenzoate (2.95 g, 0.01 mole) in 20 ml of anhydrous methylene chloride was charged into a 50 ml erlenmeyer flask equipped with a magnetic stirrer. Under anhydrous conditions, powdered silver tetrafluoroborate (1.93 g, 0.01 mole) was added in one portion to the stirred ester solution. A yellow-cream colored precipitate formed immediately. After the reaction mixture was allowed to stir at 25-30° for 1 hour, the precipitate was filtered and found to weigh 3.95 g (81%, assuming it consists of cation salt and silver bromide). The filter cake was slurried in 10 ml of liquid sulfur dioxide and filtered, then further

washed twice with 5-ml portions of liquid sulfur dioxide. The weight of the silver bromide filter cake was 1.7 g (91%). Evaporation of the filtrate gave 2.0 g (96%) of white powdery product which melted at 221-224°. Recrystallization from acetonitrile using a Dry Ice®-methylene chloride cooling bath gave glittering white crystals melting at 228-230° (decomposition to a black melt).

<u>Anal</u>: Calculated for $C_{10}H_{11}O_3 \cdot BF_4$: C, 45.2; H, 4.17. Found: C, 45.3; H, 4.18.

<u>Nmr</u>: Spectrum 55

2. <u>Preparation of 2-(3,4,5-Trimethoxyphenyl)-1,3-dioxolenium Tetrafluoroborate</u>: Under anhydrous conditions, powdered silver tetrafluoroborate (1.93 g, 0.01 mole) was added in one portion to a stirred solution of 2-bromoethyl 3,4,5-trimethoxybenzoate (3.19 g, 0.01 mole) in 30 ml of methylene chloride. The addition produced a mildly exothermic reaction and a yellow precipitate. After the reaction mixture was stirred at 25-30° for 2 hours, the precipitate was filtered and washed with methylene chloride (2 x 10 ml). The gray-yellow filter cake of silver bromide weighed 1.7 g (91%). Evaporation of the filtrate gave 2.5 g (77%) of a white crystalline product, mp 158-165°. Recrystallization from a mixture of acetonitrile and methylene chloride (Dry Ice® cooling) yielded silky white needles which melted at 166-167.5°.

<u>Anal</u>: Calculated for $C_{12}H_{15}O_5 \cdot BF_4$: C, 44.2; H, 4.64. Found: C, 44.3; H, 4.65.

<u>Nmr</u>: Spectrum 56

3. Preparation of 2-(p-Methylphenyl)-1,3-dioxolenium Tetrafluoroborate: 2-Bromoethyl 4-methylbenzoate (2.67 g, 0.01 mole) in 20 ml of dry methylene chloride was charged into a 50 ml erlenmeyer flask equipped with a magnetic stirrer. In a dry box, powdered silver tetrafluoroborate (Alfa, 1.93 g, 0.01 mole) was added in one portion. A yellow-cream colored precipitate appeared shortly after the addition. The reaction mixture was stirred for 1 hour at 25-30° after which the precipitate was filtered. The filter cake was slurried in 10 ml of liquid sulfur dioxide, filtered, then washed with liquid sulfur dioxide (2 x 5 ml). The silver bromide filter cake weighed 1.7 g (91%). Evaporation of the filtrate gave 2.20 g (81%) of a white powder which melted at 203-206°. Recrystallization from acetonitrile using a Dry Ice®-methylene chloride cooling bath gave a white crystalline material melting at 207-209° (decomposition to a brown melt).

Anal: Calculated for $C_{10}H_{11}O_2 \cdot BF_4$: C, 48.0; H, 4.44. Found: C, 48.2; H, 4.34.

Nmr: Spectrum 57

4. Preparation of 2-(m-Methylphenyl)-1,3-dioxolenium Tetrafluoroborate: 2-Bromoethyl 3-methylbenzoate (2.44 g, 0.01 mole) in 20 ml of anhydrous methylene chloride was charged into a 50 ml erlenmeyer flask equipped with a magnetic stirrer. Under anhydrous conditions, powdered silver tetrafluoroborate (1.93 g, 0.01 mole) was added in one portion to the stirred ester. A yellow cream-colored precipitate formed almost immediately. The reaction mixture was allowed to stir for 1 hour at 25-30°, then filtered. The filter cake was washed twice with 10-ml portions of methylene chloride and found to weigh 3.65 g (84%, assuming it consists of cation salt and silver bromide). Reducing the volume of the filtrate and cooling gave 0.2 g (8%) of the cation salt which melted at 183-187° (dec).

The above filter cake was slurried in 10 ml of liquid sulfur dioxide and filtered, then washed twice with 5-ml portions of liquid sulfur dioxide. The silver bromide filter cake weighed 1.7 g (91%) whereas 1.7 g (68%) of product was obtained upon evaporation of the filtrate. Total yield 1.9 g (76%), mp 187-190°. Recrystallization of the crude material from a mixture of acetonitrile and methylene chloride (Dry Ice®-methylene chloride cooling bath) gave a white crystalline product melting at 194-196°.

Anal: Calculated for $C_{10}H_{11}O_2 \cdot BF_4$: C, 48.0; H, 4.44. Found: C, 48.0; H, 4.58.

Nmr: Spectrum 58

5. Preparation of 2-(Phenyl)-1,3-dioxolenium Tetrafluoroborate: Powdered silver tetrafluoroborate (1.93 g, 0.01 mole) was added in one portion to a stirred solution of 2-bromoethyl benzoate (2.29 g, 0.01 mole) in 20 ml of dry methylene chloride under anhydrous conditions. A yellow-gray precipitate formed shortly after the addition. After the reaction mixture was allowed to stir for 1 hour at 25-30°, the insoluble material was filtered and washed with methylene chloride (2 x 10 ml). The filter cake was then slurried in 10 ml of liquid sulfur dioxide, filtered, and washed with two 5-ml portions of this solvent. A residue of silver bromide remained on the filter and weighed 1.75 g (94%). Evaporation of the filtrate yielded 1.9 g (81%) of a white powdery product which melted at 160-166°. Recrystallization of this material from a mixture of acetonitrile and methylene chloride (Dry Ice® cooling) gave glittering white crystals melting with decomposition at 168-170°. Meerwein reported a decomposition temperature of 166°.[22]

Anal: Calculated for $C_9H_9O_2 \cdot BF_4$: C, 45.8; H, 3.84. Found: C, 45.8; H, 3.97.

Nmr: Spectrum 59

6. Preparation of 2-(p-Fluorophenyl)-1,3-dioxolenium Tetrafluoroborate: 2-Bromoethyl 4-fluorobenzoate (2.47 g, 0.01 mole) in 20 ml of anhydrous methylene chloride, was charged into an erlenmeyer flask (50 ml) equipped with a magnetic stirrer. In a dry box, silver tetrafluoroborate (Alfa Inorg, 1.93 g, 0.01 mole) was added in one portion to the stirred ester solution. A yellow-white precipitate formed immediately. The reaction mixture was allowed to stir at 25-30° for 1.0 hour, then filtered. After the filter cake was washed with 2 x10-ml portions of methylene chloride the filter cake weighed 3.55 g (81%, based on the assumption that the precipitate consists of cation salt and silver bromide). This filter cake was slurried in 10 ml of liquid sulfur dioxide, filtered and washed with two 5-ml portions of liquid sulfur dioxide. The AgBr residue weighed 1.55 g (83%). Evaporation of the filtrate gave 1.6 g (63%) of the white crystalline cation salt which decomposed to a black melt at 195-200°. Recrystallization from a mixture of acetonitrile and methylene chloride (using Dry Ice®-methylene chloride as a cooling bath) gave a white crystalline product which decomposed to a black melt at 203-205°.

Anal: Calculated for $C_9H_8FO_2 \cdot BF_4$: C, 42.6; H, 3.17. Found: C, 42.5; H, 3.23.

Nmr: Spectrum 60

7. Preparation of 2-(p-Chlorophenyl)-1,3-dioxolenium Tetrafluoroborate: Under anhydrous conditions, anhydrous powdered silver tetrafluoroborate (1.93 g, 0.01 mole) was added in one portion with stirring to a solution of 2-bromoethyl p-chlorobenzoate (2.19 g, 0.01 mole) in 20 ml of dry methylene chloride. A yellow-white precipitate appeared immediately after the addition. The reaction mixture was stirred with a magnetic stirrer for 1 hour at 25-30°, then filtered and washed twice with 10-ml

portions of methylene chloride. This yellow-gray filter cake was slurried in 10 ml of liquid sulfur dioxide, filtered and then washed twice again with 5-ml portions of liquid sulfur dioxide. The filter cake of silver bromide weighed 1.35 g (72%). Evaporation of the sulfur dioxide filtrate yielded 1.85 g (82%) of a gray powdery product which melted at 175-185°. Recrystallization of this crude material from a mixture of acetonitrile and methylene chloride gave fine white crystals melting at 235-237° (decomposition to a black melt).

Anal: Calculated for $C_9H_8ClO_2 \cdot BF_4$: C, 40.0; H, 2.98. Found: C, 40.2; H, 3.16.

Nmr: Spectrum 61

8. Preparation of 2-(m-Chlorophenyl)-1,3-dioxolenium Tetrafluoroborate: 2-Chloroethyl m-chlorobenzoate (2.19 g, 0.01 mole) was charged into a 50 ml erlenmeyer flask containing 20 ml of dry methylene chloride and equipped with a magnetic stirrer. Under anhydrous conditions, powdered silver tetrafluoroborate (1.93 g, 0.01 mole) was added in one portion to the ester solution. The reaction mixture was stirred at 25-30° for 1 hour during which time a considerable amount of white precipitate fell out of solution. This precipitate was filtered, washed with two 10-ml portions of methylene chloride and found to weigh 2.7 g (66%, assuming it consists of silver bromide and cation salt). Reduction of the filtrate to dryness under reduced pressure yielded 0.4 g (18%) of the cation salt as a white powder melting at 158-164°. The filter cake was slurried in 10 ml of liquid sulfur dioxide, filtered and washed with two 5-ml portions of the same solvent. A silver chloride filter cake weighing 1.20 g (81%) was obtained. Evaporation of the sulfur dioxide yielded a white powdery product weighing 1.55 g (69%) and melting at 168-171°. Recrystallization

from a mixture of acetonitrile and methylene chloride (Dry Ice® cooling) gave silky, white plates which decomposed to a brown melt at 173-175°.

Anal: Calculated for $C_9H_8ClO_2 \cdot BF_4$: C, 40.0; H, 2.98. Found: C, 40.0; H, 2.97.

Nmr: Spectrum 62.

9. Preparation of 2-(*m*-Bromophenyl)-1,3-dioxolenium Tetrafluoroborate: Powdered, anhydrous silver tetrafluoroborate (1.93 g, 0.01 mole) was added in one portion to a stirred solution of 2-bromoethyl *m*-bromobenzoate (3.08 g, 0.01 mole) in 20 ml of dry methylene chloride under anhydrous conditions. A yellow-white precipitate appeared shortly after the addition and during the hour that the reaction mixture was allowed to stir at 25-30°. The insoluble material was filtered, washed with methylene chloride (2 x 10 ml) and found to weigh 3.95 g (79%, assuming it consists of cation salt and silver bromide). This insoluble material was then slurried in 10 ml of liquid sulfur dioxide, filtered and washed with two 5-ml portions of the same solvent. The silver bromide filter cake weighed 1.75 g(94%). Evaporation of the filtrate yielded 1.92 g (61%) of a white solid, mp 168-175°. Recrystallization from a mixture of methylene chloride and acetonitrile (Dry Ice®-cooling bath) gave fine white crystals, mp 174.5-176°.

Anal: Calculated for $C_9H_8BrO_2 \cdot BF_4$: C, 34.3; H, 2.56. Found: C, 34.4; H, 2.51.

Nmr: Spectrum 63

10. Preparation of 2-(*m*-Fluorophenyl)-1,3-dioxolenium Tetrafluoroborate: Powdered silver tetrafluoroborate (1.93 g, 0.01 mole) was added in one portion to a stirred solution of 2-(bromoethyl) *m*-fluorobenzoate (2.47 g, 0.01 mole) in 20 ml of methylene chloride under anhydrous

conditions. The reaction mixture was allowed to stir for 2 hours at 25-30° during which time a substantial amount of yellow-gray precipitate formed. This insoluble material was filtered, washed with methylene chloride (2 x 10 ml), and found to weigh 3.87 g (88%, assuming it consisted of silver bromide and cation salt). Reducing the filtrate to half the original volume gave 0.1 g of the cation salt which melted at 153-160°. The filter cake was slurried in 10 ml of liquid sulfur dioxide, filtered, then washed twice with 5 ml of this solvent. The weight of the silver bromide filter cake was 1.65 g (88%). Solvent was removed from the filtrate to yield 1.55 g (61%) of a white crystalline product melting at 158-165°. Recrystallization from a mixture of acetonitrile and methylene chloride (Dry Ice® cooling) gave a fine white crystalline product which melted at 169-171°.

Anal: Calculated for $C_9H_8O_2F \cdot BF_4$: C, 42.6; H, 3.17. Found: C, 42.5; H, 3.28.

Nmr: Spectrum 64

11. Preparation of 2-(3,4-Dichlorophenyl)-1,3-dioxolenium Tetrafluoroborate: Under anhydrous conditions, powdered silver tetrafluoroborate (1.93 g, 0.01 mole) was added in one portion to a stirred solution of 2-(bromoethyl) 3,4-dichlorobenzoate (2.1 g, 0.01 mole) in 20 ml of dry methylene chloride. A creamy yellow precipitate formed almost immediately. After the reaction mixture was stirred at 25-30° for 1 hour the insoluble material was filtered and washed with methylene chloride (2 x 10 ml). The solid weighed 2.80 g (69%, assuming it consists of silver bromide and cation salt). The filter cake was slurried in 10 ml of liquid sulfur dioxide, then washed with two 5-ml portions of liquid sulfur dioxide, leaving a silver bromide residue on the filter of 1.2 g (64%). Evaporation

of the filtrate gave 1.5 g (69%) of a white powdery material which melted at 200-208°. Recrystallization from acetonitrile (Dry Ice® cooling bath) yielded fine white crystals which decomposed to a black melt at 218-220°.

Anal: Calculated for $C_9H_7Cl_2O_2 \cdot BF_4$: C, 35.5; H, 2.32. Found: C, 35.6; H, 2.51.

Nmr: Spectrum 65

12. Preparation of 2-(m-Trifluoromethylphenyl)-1,3-dioxolenium Tetrafluoroborate: In a dry box, powdered anhydrous silver tetrafluoroborate (1.93 g, 0.01 mole) was added in one portion to a stirred solution of 2-bromoethyl m-trifluoromethylbenzoate (2.97 g, 0.01 mole) in 20 ml of anhydrous methylene chloride. The reaction mixture was allowed to stir for 1.5 hours at 25-30°, during which time a substantial amount of yellow-gray precipitate formed. The insoluble material was filtered, washed with two 10-ml portions of methylene chloride and found to weigh 3.77 g (77%, assuming it consists of cation salt and silver bromide). Reducing the filtrate to 1/3 original volume and cooling yielded 0.2 g (7%) of the cation salt. The filter cake was slurried in 10 ml of liquid sulfur dioxide, filtered and washed with two 5-ml portions of this solvent. A yellow-gray filter cake of silver bromide was obtained which weighed 1.75 g (94%). Evaporation of the filtrate to dryness yielded a white fluffy solid which weighed 2.05 (68%) and melted at 129-134°. The total crude yield was 2.25 g (72%). Recrystallization from a mixture of acetonitrile, methylene chloride and diethyl ether gave a white fluffy product which melted at 135-137°.

Anal: Calculated for $C_{10}H_8F_3O_2 \cdot BF_4$: C, 39.5; H, 2.65. Found: C, 39.7; H, 2.76.

Nmr: Sprectrum 66

13. Preparation of 2-(p-Trifluoromethylphenyl)-1,3-dioxolenium Tetrafluoroborate: Powdered silver tetrafluoroborate (1.93 g, 0.01 mole) was added in one portion to a stirred solution of 2-bromoethyl p-trifluoromethylbenzoate (2.97 g, 0.01 mole) in 20 ml of anhydrous methylene chloride. The reaction mixture was allowed to stir for 4.5 hours at 25-30°, during which time a substantial amount of yellow-gray precipitate formed. The insoluble material was filtered, washed with two 10-ml portions of methylene chloride and found to weigh 3.47 g (71%, assuming it consists of cation salt and silver bromide). The filter cake was slurried in 10 ml of liquid sulfur dioxide, filtered and washed with two 5-ml portions of this solvent. A yellow-gray filter cake of silver bromide was obtained which weighed 1.55 g (83%). Evaporation of the filtrate to dryness yielded a white solid which weighed 1.89 g (63%) and melted at 178-183°. Recrystallization from a mixture of acetonitrile, methylene chloride and diethyl ether gave a fine white powder which melted at 188-189.5°.

Anal: Calculated for $C_{10}H_8F_3O_2 \cdot BF_4$: C, 39.5; H, 2.65. Found: C, 39.3; H, 2.74.

Nmr: Spectrum 67

14. Preparation of 2-(m-Nitrophenyl)-1,3-dioxolenium Tetrafluoroborate: Under anhydrous conditions, powdered silver tetrafluoroborate (1.93 g, 0.01 mole) was added in one portion to a stirred solution of 2-(bromoethyl) m-nitrobenzoate (2.74 g, 0.01 mole) in 20 ml of dry methylene chloride. The reaction mixture was stirred with a magnetic stirrer for 1.25 hours. A gray-yellow precipitate which formed during this time was filtered and found to weigh 3.75 g (80%, assuming it consists of silver bromide and cation salt). This material was slurried in 10 ml of liquid

sulfur dioxide, filtered and washed with two 5-ml portions of the solvent. A filter cake of silver bromide was obtained which weighed 1.65 g (87%). The filtrate was reduced to dryness to yield 1.97 g (70%) of a light yellow product melting at 145-149°. Recrystallization from a mixture of acetonitrile and methylene chloride (Dry Ice® cooling) gave white crystals melting at 149-151.5°.

Anal: Calculated for $C_9H_8NO_4 \cdot BF_4$: C, 38.5; H, 2.87. Found: C, 38.2; H, 2.93:

Nmr: Spectrum 68

15. Preparation of 2-(p-Nitrophenyl-1,3-dioxolenium Tetrafluoroborate: Powdered silver tetrafluoroborate (1.93 g, 0.01 mole) was added in one portion to a stirred solution of 2-bromoethyl p-nitrobenzoate (3.17 g, 0.01 mole) under anhydrous conditions in a dry box. The reaction mixture was stirred for 2 hours after which the insoluble material was filtered and washed with methylene chloride (2 x 10 ml). The yellow-gray filter cake was slurried in 10 ml of liquid sulfur dioxide, filtered, then washed with two 5-ml portions of liquid sulfur dioxide. A filter cake of silver bromide remained which weighed 1.20 g (64%). The sulfur dioxide filtrate was evaporated to dryness to give 1.75 g (55%) of tan, slightly clingy product which melted at 201-204°. This material was recrystallized from a mixture of acetonitrile and methylene chloride, using a Dry Ice®-methylene chloride cooling bath, to yield a cream-colored product which melted at 209-211° (decomposition to a black melt).

Anal: Calculated for $C_9H_8NO_4$: C, 38.5; H, 2.87. Found: C, 38.6; H, 3.15.

Nmr: Spectrum 69

G. 2,2'-Alkylene-1,3-dioxolenium Dications

1. Attempted Preparation of Bis-2,2'-dioxolenium Dication:

(a) With Silver Tetrafluoroborate:

Under anhydrous conditions, powdered anhydrous silver tetrafluoroborate (1.93 g, 0.01 mole) was added in one portion to a stirred solution of bis-2-bromoethyl oxalate (1.52 g, 0.005 mole) in 25 ml of dry methylene chloride. A creamy-yellow, clingy precipitate appeared with 2-3 minutes after the addition. After being stirred for 40 minutes at 25-30°, the reaction mixture had transformed into a gray-yellow, gummy mass. Stirring was continued under these conditions for a total of 2 hours. The solvent was decanted and found to fume profusely when exposed to the atmosphere. Nmr analysis showed that it contained only small amounts of unconverted ester. (The fuming suggested the presence of fluoroboric acid or boron trifluoride.) The residue from the above decantate was a stringy, gummy, intractable paste which resisted further workup.

(b) With Silver Hexafluoroantimonate:

Under anhydrous conditions, 1.72 g (0.005 mole) of silver hexafluoroantimonate (Alfa) were added in one portion to a stirred solution of bis-2-bromoethyl oxalate (0.77 g, 0.0025 mole) in 25 ml of dry methylene chloride. The reaction mixture was then allowed to stir at 25-30°. During the first 3 hours, a substantial amount of a nice yellow precipitate appeared. After stirring under these conditions for 12 hours, the insoluble material transformed into a gummy, cream colored mass. The reaction mixture was stirred under these conditions for a total of 51 hours. Solvent was removed from the insoluble mass, washed with two 10-ml portions of methylene chloride and then dried. The gummy mass was slurried in ~4 ml of FSO_3H and filtered through a sintered glass funnel. Nmr analysis

of the amber colored filtrate gave a spectrum which consisted of a multiplet at 4.79-5.07 ppm, a strong singlet at 5.70 ppm and a weak singlet at 6.00 ppm. The multiplet and strong singlet were present in a ratio of ~2.1:1. (See Nmr Spectrum 48).

2. <u>Preparation of 2,2'-Methylenebis-1,3-dioxolenium Tetrafluoroborate</u>: Powdered, anhydrous silver tetrafluoroborate (3.86 g, 0.02 mole) was added in one portion to a solution of bis-2-bromoethyl malonate (3.18 g, 0.01 mole) in 25 ml of dry methylene chloride under anhydrous conditions. The reaction mixture was allowed to stir for 8.5 hours at 25-30°, during which time a considerable amount of gray-white precipitate was formed. This insoluble material was filtered, washed with two 10-ml portions of methylene chloride and found to weigh 6.2 g (88% assuming it consists of silver bromide and dication salt). An nmr spectrum of this dication was obtained by slurrying approximately 800 mg of the above filter cake in 3 ml of FSO_3H. The slurry was filtered through a sintered glass funnel and the filtrate was scanned. Alternatively, the filter cake was extracted with three 10-ml portions of liquid sulfur dioxide. Solvent was evaporated from the combined extracts to give a cream colored solid, mp 204-208°. Recrystallization from a mixture of methylene chloride and acetonitrile gave cream colored crystals melting at 208-210°.

<u>Nmr</u>: Spectrum 49

3. <u>Preparation of 2,2'-Ethylenebis-1,3-dioxolenium Tetrafluoroborate</u>: Under anhydrous conditions, powdered silver tetrafluoroborate (3.86 g, 0.02 mole) was added in one portion to a solution of bis(2-bromoethyl) succinate (4.05 g, 0.01 mole) in 20 ml of dry methylene chloride. A yellow, curdy precipitate formed immediately after the addition. The reaction mixture was stirred for 14 hours at 25-30°, during which time

substantially more precipitate was formed. The light yellow-gray material was filtered, washed with two 10-ml portions of methylene chloride and found to weigh 7.4 g (95%, assuming it consisted of cation salt and silver bromide). This precipitate was slurried in 10 ml of liquid sulfur dioxide and filtered. The filtrate yielded only a small amount of unconverted ester upon evaporation. The dication salt did not appear to be soluble in liquid sulfur dioxide. Nmr samples of the dication were prepared by slurrying a small amount (~500 mg) of the above precipitate in 2-3 ml of fluorosulfonic acid (Allied Chemical Company), followed by filtration through a sintered glass funnel. The filtrate was analyzed by nmr spectroscopy using tetramethylammonium tetrafluoroborate as the internal standard.

Nmr: Spectrum 50

4. Preparation of 2,2'-Trimethylenebis-1,3-dioxolenium Tetrafluoroborate: Under anhydrous conditions, powdered anhydrous silver tetrafluoroborate (1.93 g, 0.01 mole) was added in one portion to a stirred solution of bis-2-bromoethyl glutarate (1.73 g, 0.005 mole) in 20 ml of dry methylene chloride. The reaction mixture was stirred at 25-30° for 3 hours during which time a substantial amount of gray-yellow precipitate was formed. This insoluble material was filtered, washed with methylene chloride (2 x 10 ml) and found to weigh 3.50 g (96%, assuming it consists of silver bromide and dication salt). The filter cake was slurried in 10 ml of liquid sulfur dioxide, filtered and then washed with two 10-ml portions of the same solvent. The dication salt was only slightly soluble in liquid sulfur dioxide and remained in the filter cake which now weighed 2.78 g (77%, assuming it consists of silver bromide and dication salt). Removal of sulfur dioxide from the filtrate yielded a small amount of white,

tacky unworkable gum. An nmr spectrum of this dication was obtained by slurrying approximately 800 mg of the above filter cake in 3 ml of FSO_3H. The slurry was filtered through a sintered glass funnel and the filtrate was scanned.

Nmr: Spectrum 51

5. Preparation of 2,2'-Tetramethylenebis-1,3-dioxolenium Tetrafluoroborate: Under anhydrous conditions, powdered anhydrous silver tetrafluoroborate (1.93 g, 0.01 mole) was added in one portion to a stirred solution of bis-2-bromoethyl adipate (1.8 g, 0.005 mole) in 20 ml of dry methylene chloride. The reaction mixture was stirred at 25-30° for 2.5 hours during which time a substantial amount of gray-yellow precipitate was formed. This insoluble material was filtered, washed with methylene chloride (2 x 10 ml) and found to weigh 3.68 g (99%, assuming it consists of silver bromide and dication salt). The filter cake was slurried in 10 ml of liquid sulfur dioxide, filtered and then washed with two 10-ml portions of the same solvent. The filter cake now weighed 3.00 g (80%, assuming it consists of silver bromide and dication salt). Reducing the filtrate to dryness gave 0.5 g of a white, sticky paste which was not further characterized. An nmr spectrum of this dication was obtained by slurrying approximately 800 mg of the above filter cake in 3 ml of FSO_3H. The slurry was filtered through a sintered glass funnel and the filtrate was scanned.

Nmr: Spectrum 52

6. Preparation of 2,2'-Pentamethylenebis-1,3-dioxolenium Tetrafluoroborate: Powdered, anhydrous silver tetrafluoroborate (1.93 g, 0.01 mole) was added in one portion to a solution of bis-2-bromoethyl pimelate (1.87 g, 0.005 mole) in 25 ml of dry methylene chloride under anhydrous

conditions. A light yellow precipitate formed shortly after the addition and during the 2.5 hours that the reaction mixture was allowed to stir at 25-30°. The precipitate was filtered, washed with two 10-ml portions of methylene chloride and found to weigh 3.55 g (93%, assuming it consists of silver bromide and dication salt). This insoluble material was slurried in 10 ml of liquid sulfur dioxide, filtered and washed twice with 10-ml portions of the same solvent. The silver bromide filter cake weighed 1.65 g (88%). Upon reducing the filtrate to dryness, 1.70 g (88%) of a white solid was obtained which melted at 158-164°. Several recrystallizations from a mixture of acetonitrile and methylene chloride (Dry Ice® cooling) gave fine, glittering white crystals which melted at 173-175°.

<u>Anal</u>: Calculated for $C_{11}H_{18}O_4 \cdot B_2F_8$: C, 34.1; H, 4.68. Found: C, 34.2; H, 4.91.

<u>Nmr</u>: Spectrum 53

7. <u>Preparation of 2,2'-Hexamethylenebis-1,3-dioxolenium Tetrafluoroborate</u>: Under anhydrous conditions, powdered anhydrous silver tetrafluoroborate (1.93 g, 0.01 mole) was added in one portion to a solution of bis-2-bromoethyl suberate (1.94 g, 0.005 mole) in 20 ml of dry methylene chloride. A light yellow precipitate formed shortly after the addition and during the 2.5 hours that the reaction mixture was allowed to stir at 25-30°. The precipitate was filtered, washed with methylene chloride (2 x 10 ml) and found to weigh 3.78 g (98%, assuming it consists of silver bromide and dication salt). This material was then slurried in 10 ml of liquid sulfur dioxide, filtered and washed with two 5-ml portions of the same solvent. The silver bromide filter cake weighed 1.80 g (96%). Evaporation of the filtrate gave 1.82 g (91%) of an off-white solid which

melted at 175-185°. Several recrystallizations from a mixture of acetonitrile and methylene chloride (Dry Ice® cooling) gave fine, glittering white crystals which melted at 198-200° (amber colored melt).

Anal: Calculated for $C_{12}H_{20}O_4 \cdot B_2F_8$: C, 35.9; H, 5.02. Found: C, 35.9; H, 4.97.

Nmr: Spectrum 54

H. 2,2' and 2,2',2"-Aryl-1,3-dioxolenium Dications and Trications

1. Preparation of 2,2'-m-Phenylenebis-1,3-dioxolenium Tetrafluoroborate: Under anhydrous conditions, powdered anhydrous silver tetrafluoroborate (1.93 g, 0.01 mole) was added in one portion to a solution of 2-bromoethyl isophthalate (1.90 g, 0.005 mole) in 20 ml of dry methylene chloride. A yellow precipitate formed shortly after the addition. The reaction mixture was stirred for 3 hours and then allowed to stand overnight at 25-30°. The gray precipitate was filtered, washed with methylene chloride (2 x 10 ml) and found to weigh 3.60 g (94%, assuming it consists of silver bromide and dication salt). This material was then slurried in 10 ml of liquid sulfur dioxide, filtered and washed with two 5-ml portions of the same solvent. The dication salt was virtually insoluble in this solvent. An nmr spectrum of this dication was obtained by slurrying approximately 800 mg of the above filter cake in 3 ml of FSO_3H. The slurry was filtered through a sintered glass funnel and the filtrate was scanned.

Nmr: Spectrum 70

2. Preparation of 2,2'-p-Phenylenebis-1,3-dioxolenium Tetrafluoroborate: Powdered anhydrous silver tetrafluoroborate (1.93 g, 0.01 mole) was added in one portion to a stirred solution of 2-bromoethyl terephthalate (1.90 g, 0.005 mole) in 20 ml of dry methylene chloride under anhydrous

conditions. A yellow precipitate formed shortly after the addition. The reaction mixture was stirred for 1 hour and then allowed to stand for 31 hours at 25-30°. A substantial amount of precipitate formed during that time. This insoluble material was filtered, washed with methylene chloride (2 x 10 ml) and found to weigh 3.6 g (94%, assuming it consists of silver bromide and dication salt). The filter cake was slurried in 10 ml of liquid sulfur dioxide and filtered. The dication salt was virtually insoluble in this solvent. An nmr spectrum of this dication was obtained by slurrying approximately 1 g of the above filter cake in ~5 ml of FSO_3H. The slurry was filtered through a sintered glass funnel and the filtrate was scanned.

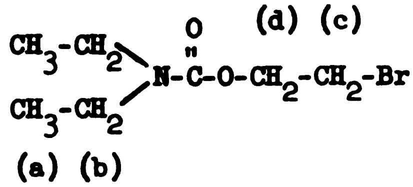
<u>Nmr</u>: Spectrum 71

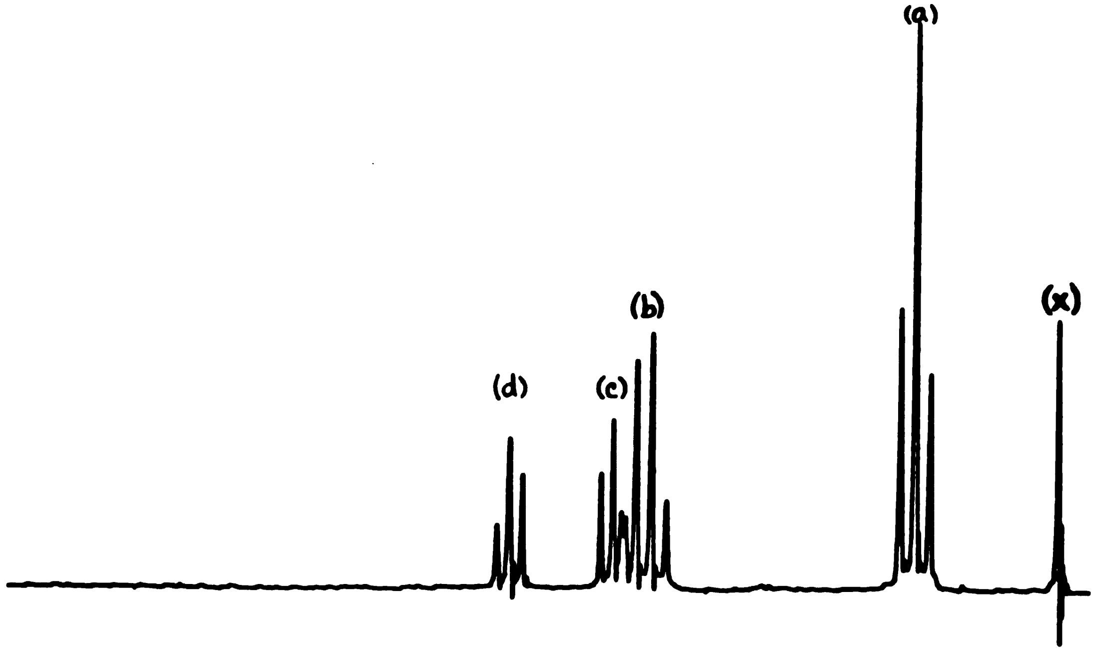
3. <u>Preparation of 2,2',2"-Phenylenetris-1,3-dioxolenium Tetrafluoroborate</u>: Powdered anhydrous silver tetrafluoroborate (1.93 g, 0.01 mole) was added in one portion to a stirred solution of tris(2-bromoethyl) trimesate (1.77 g, 0.0033 mole) in 20 ml of dry methylene chloride under anhydrous conditions. The reaction mixture was allowed to stir for 16 hours at 25-30°, during which time a substantial amount of gray precipitate was formed. This insoluble material was filtered, washed with two 10-ml portions of dry methylene chloride and found to weigh 3.29 g (89%, assuming it consists of silver bromide and trication salt). This material was then slurried in 10 ml of liquid sulfur dioxide, filtered and washed with two 5-ml portions of the same solvent. The trication salt was virtually insoluble in this solvent. An nmr spectrum of this trication was obtained by slurrying approximately 800 mg of the above filter cake in 3 ml of FSO_3H. The slurry was filtered through a sintered glass funnel and the filtrate was scanned.

<u>Nmr</u>: Spectrum 72

VI. NUCLEAR MAGNETIC RESONANCE SPECTRA

Spectrum 1. Nuclear Magnetic Resonance Spectrum of 2-Bromoethyl-N,N-Diethylcarbamic Acid Ester (CCl_4)



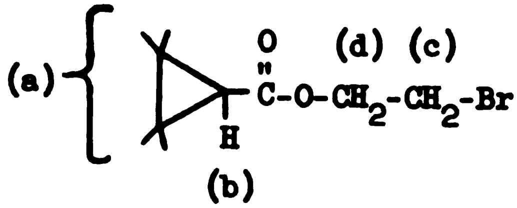


Assignments (δ)

x	0.00 (TMS)
a	1.13 (t); J_{ab} = 7.0 cps
b	3.27 (q)
c	3.53 (t); J_{cd} = 6.0 cps
d	4.33 (t)

a:(b+c):d = 3:3:1

Spectrum 2. Nuclear Magnetic Resonance Spectrum of 2-Bromoethyl Cyclopropane Carboxylate (CCl_4)

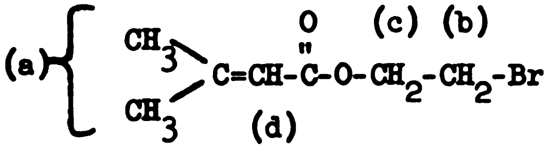


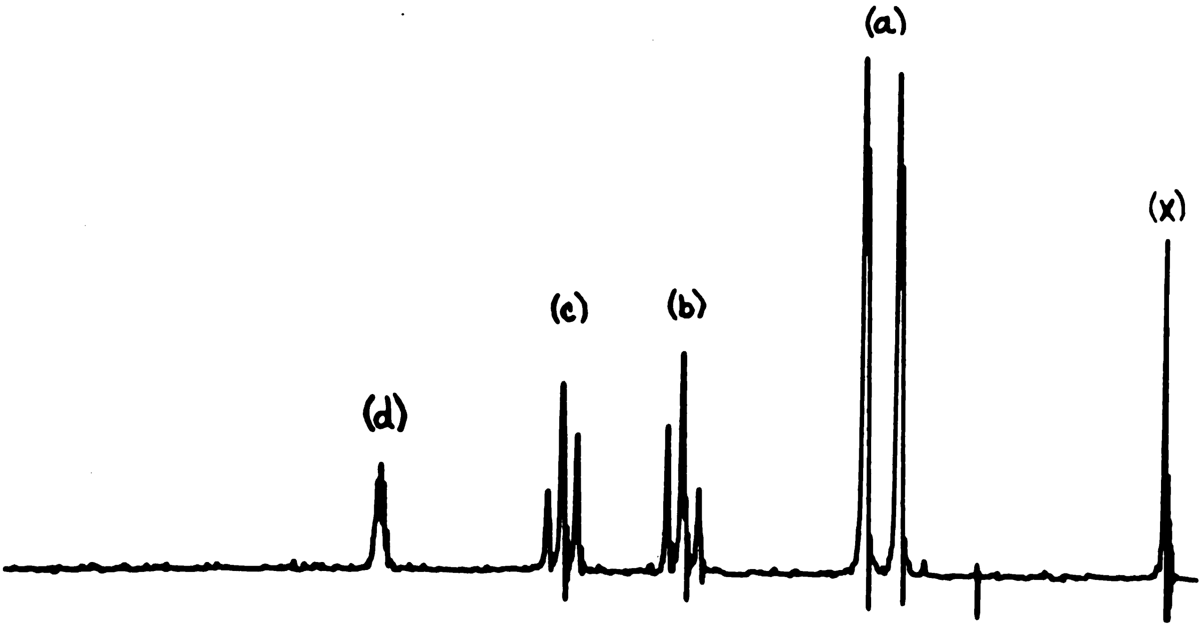
<u>Assignments (δ)</u>

x	0.00 (TMS)
a	0.73-1.20 (m)
b	1.40-1.89 (m)
c	3.50 (t); J_{cd} = 6.5 cps
d	4.35 (t)

a:b:c:d = 4:1:2:2

Spectrum 3. Nuclear Magnetic Resonance Spectrum of 2-Bromoethyl-3,3-Dimethylacrylate (CCl_4)



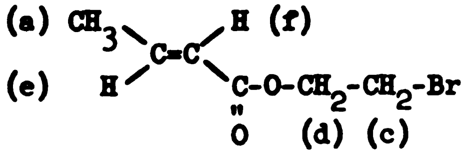


Assignments (δ)

x	0.00 (TMS)
a	2.03 (d); J_{ad} = 15.0 cps
b	3.48 (t); J_{bc} = 6.0 cps
c	4.35 (t)
d	5.66 (m)

a:b:c:d = 6:2:2:1

Spectrum 4. Nuclear Magnetic Resonance Spectrum of <u>trans</u>-2-Bromoethyl Crotonate (CCl_4)

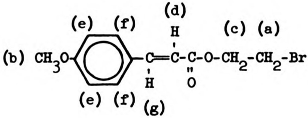


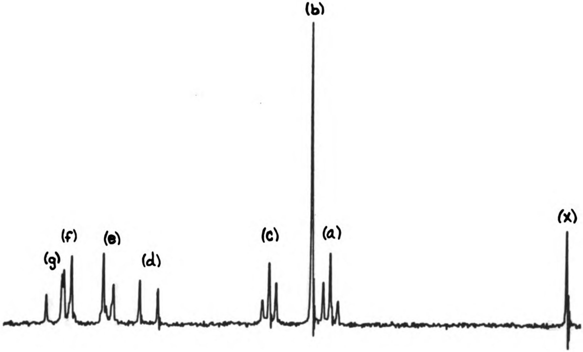
<u>Assignments (δ)</u>

x	0.00 (TMS)
a	1.86, 1.98 (d); j = 1.5 cps
b	2.15 (d) 14.9% <u>cis</u> isomer
c	3.52 (t); J_{cd} = 6.0 cps
d	4.40 (t)
e	5.70, 5.95 (d)
f	6.68-7.34 (m)

a:c:d:e:f = 3:2:2:1:1

Spectrum 5. Nuclear Magnetic Resonance Spectrum of 2-Bromoethyl-p-methoxycinnamate (CCl_4)



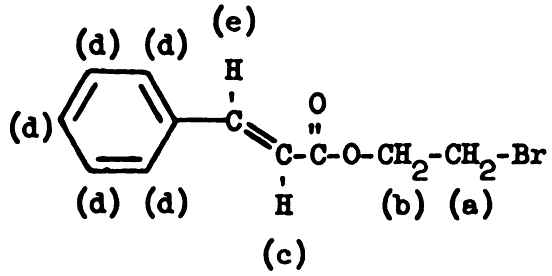


Assignments (δ)

x	0.00 (TMS)
a	3.52 (t); J_{ac} 6.5
b	3.80 (s)
c	4.44 (t); J_{ca} 6.5
d	6.23 (d); J_{dg} 16.2
e	6.83 (d); J_{ef} 8.9
f	7.43 (d); J_{fe} 8.9
g	7.60 (d); J_{gd} 16.2

a:b:c:d:e:(f+g) = 2:3:2:1:2:3

Spectrum 6. Nuclear Magnetic Resonance Spectrum of 2-Bromoethyl Cinnamate (CCl_4)

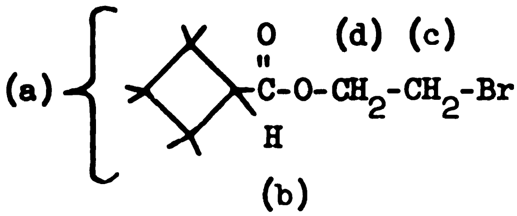


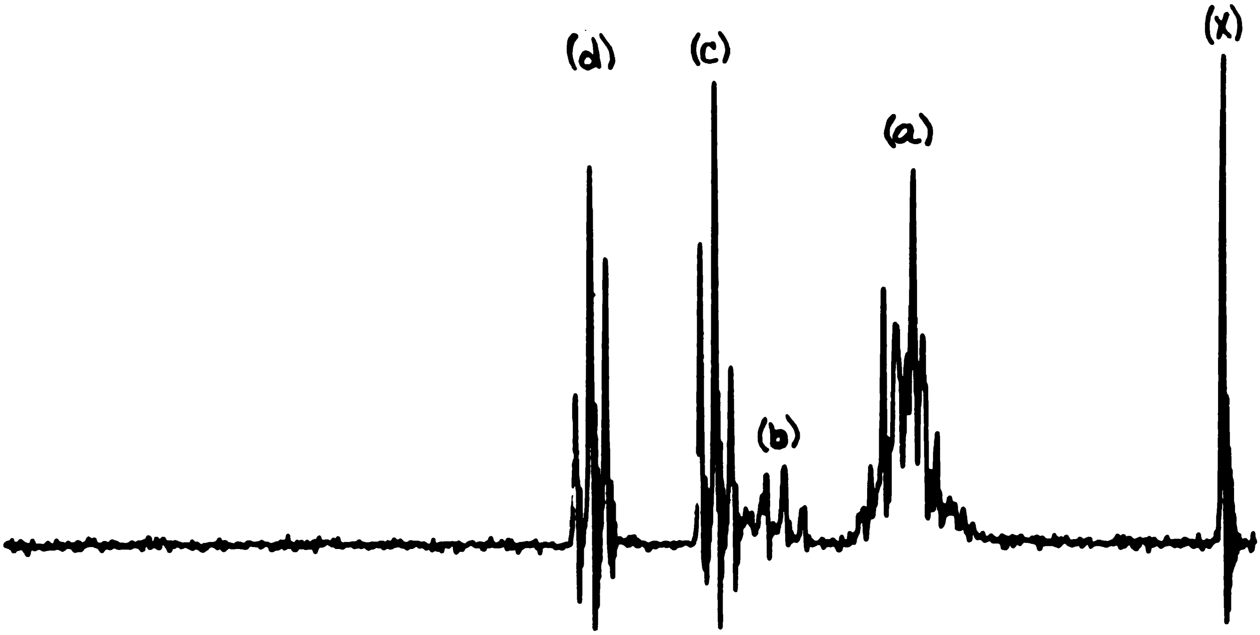
<u>Assignments (δ)</u>

x	0.00 (TMS)
a	3.53 (t); J_{ab} = 6.0 cps
b	4.46 (t).
c	6.37 (d); J_{ce} = 16.2 cps
d	7.42 (m)
e	7.66 (d)

a:b:c:(d+e) = 2:2:1:6

Spectrum 7. Nuclear Magnetic Resonance Spectrum of 2-Bromoethyl Cyclobutylcarboxylate (CCl_4)



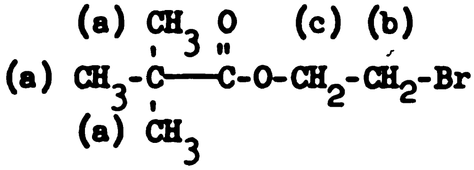


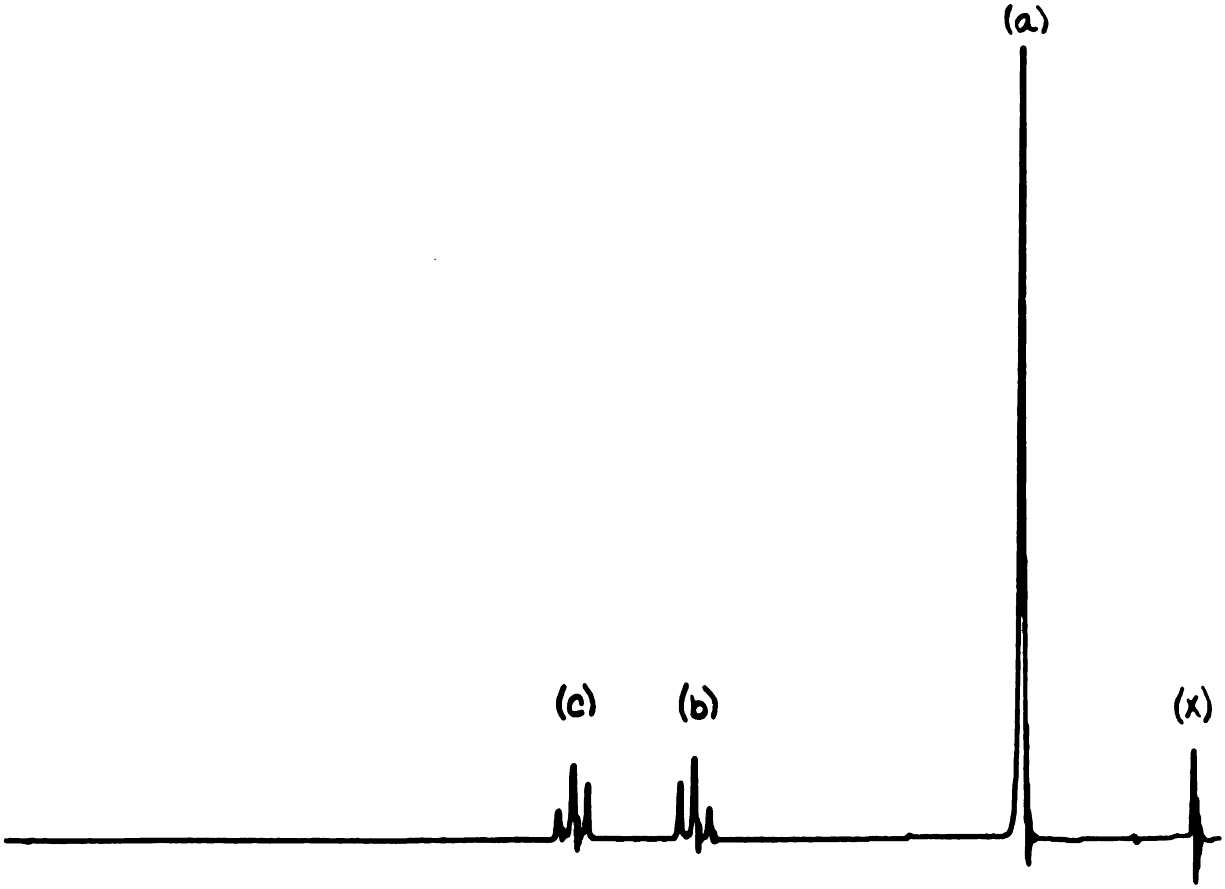
<u>Assignments (δ)</u>

x	0.00 (TMS)
a	2.14 (m)
b	3.12 (m)
c	3.49 (t); J_{cd} = 6.0 cps
d	4.36 (t)

a:b:c:d = 3:1:2:2

Spectrum 8. Nuclear Magnetic Resonance Spectrum of 2-Bromoethyl Pivalate (CCl_4)





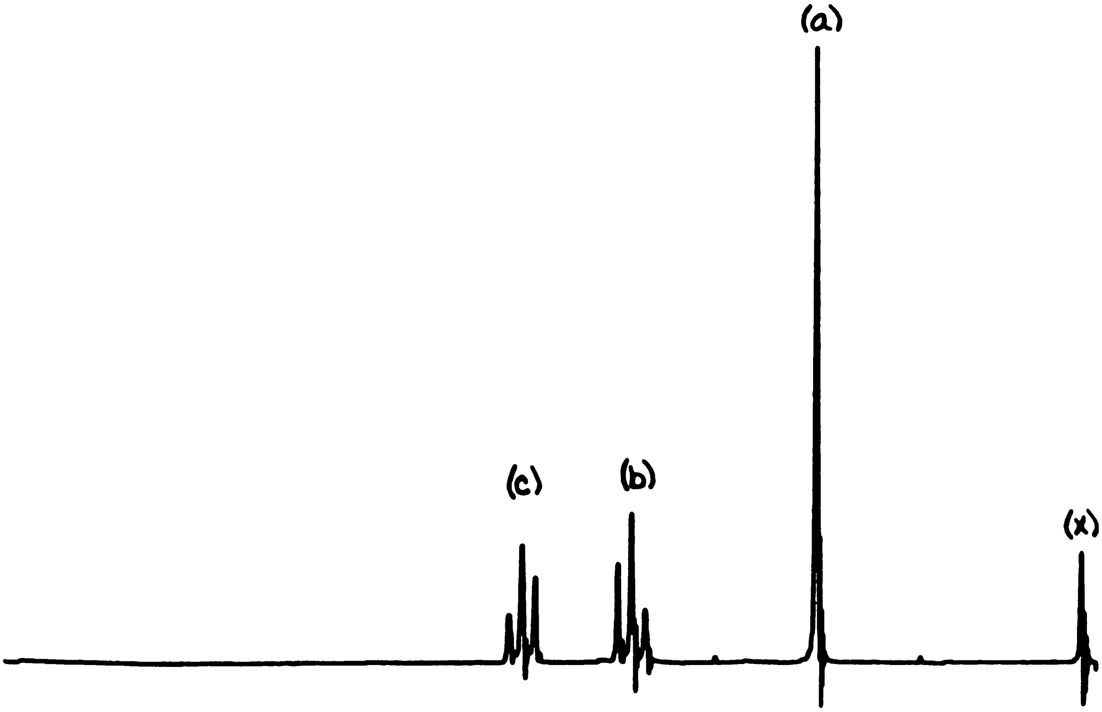
<u>Assignments (δ)</u>

x	0.00 (TMS)
a	1.20 (s)
b	3.50 (t); J_{bc} = 6.0 cps
c	4.35 (t)

a:b:c = 9:2:2

Spectrum 9. Nuclear Magnetic Resonance Spectrum of 2-Bromoethyl Acetate (CCl_4)

$$\overset{(a)}{CH_3}-\overset{O}{\overset{\|}{C}}-O-\overset{(c)}{CH_2}-\overset{(b)}{CH_2}-Br$$

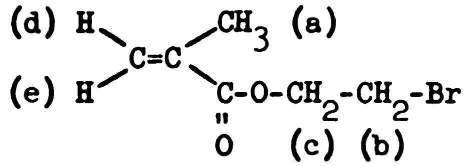


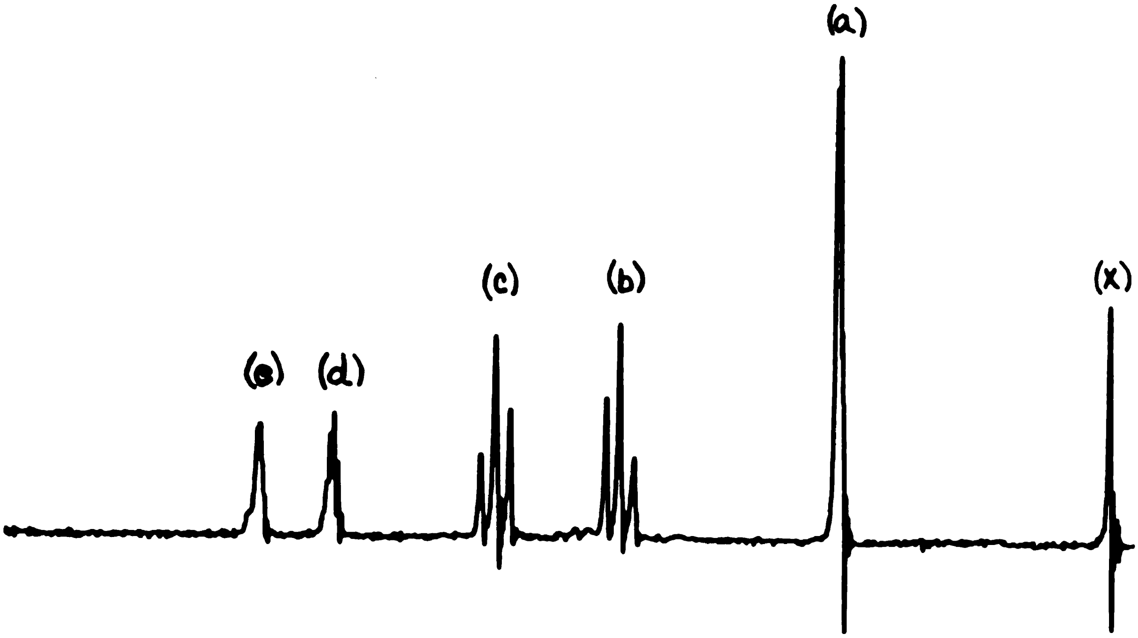
<u>Assignments (δ)</u>

x	0.00 (TMS)
a	2.06 (s)
b	3.50 (t); J_{bc} = 6.0 cps
c	4.35 (t)

a:b:c = 3:2:2

Spectrum 10. Nuclear Magnetic Resonance Spectrum of 2-Bromoethyl Methacrylate (CCl_4)



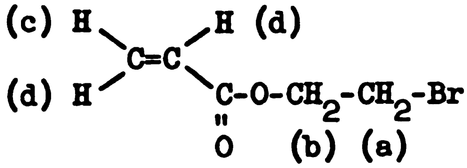


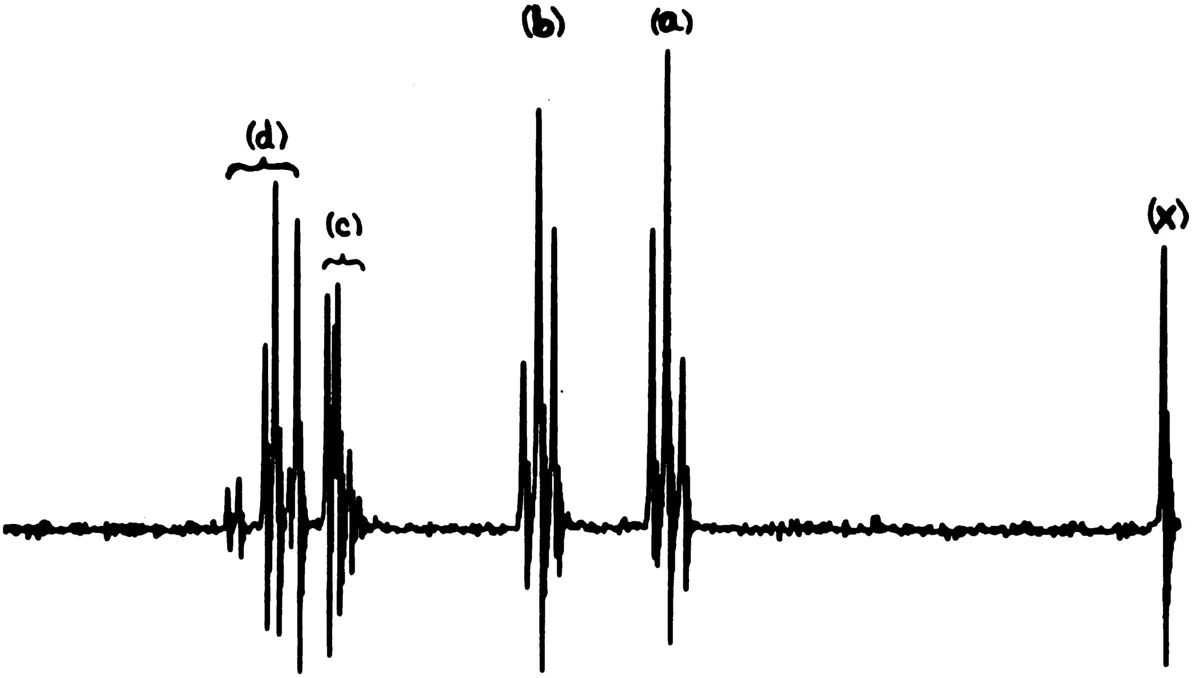
Assignments (δ)

x	0.00 (TMS)
a	1.96 (s)
b	3.54 (t); J_{bc} = 6.0 cps
c	4.43 (t)
d	5.61 (m)
e	6.13 (s)

a:b:c:e:d = 3:2:2:1:1

Spectrum 11. Nuclear Magnetic Resonance Spectrum of 2-Bromoethyl Acrylate (CCl_4)





<u>Assignments (δ)</u>

x	0.00 (TMS)
a	3.52 (t); J_{ab} = 6.0 cps
b	4.44 (t)
c	5.68-5.99 (m)
d	6.12-6.65 (m)

a:b:c:d = 2:2:1:2

Spectrum 12. Nuclear Magnetic Resonance Spectrum of Bis-2-bromoethyl Oxalate (CCl_4)

(a) (b) (b) (a)

$Br-\underset{(a)}{CH_2}-\underset{(b)}{CH_2}-O-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-O-\underset{(b)}{CH_2}-\underset{(a)}{CH_2}-Br$

<u>**Assignments (δ)**</u>

x	0.00 (TMS)
a	3.59 (t); J_{ab} = 6.2 cps
b	4.59 (t)

a:b = 1:1

Spectrum 13. Nuclear Magnetic Resonance Spectrum of Bis(2-bromoethyl) Malonate (CCl_4)

$$\underset{(b)}{Br\text{-}CH_2}\text{-}\underset{(c)}{CH_2}\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}\underset{(a)}{CH_2}\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}\underset{(c)}{CH_2}\text{-}\underset{(b)}{CH_2\text{-}Br}$$

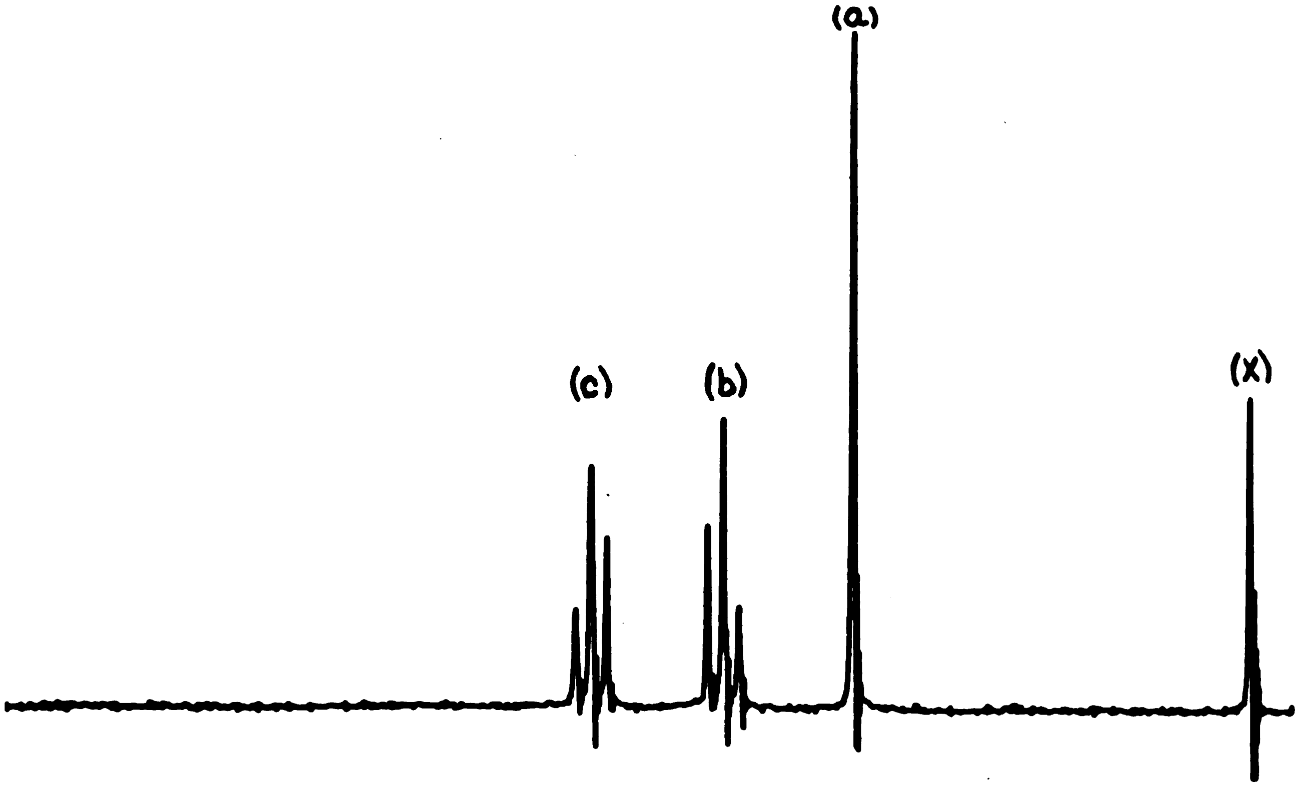
Assignments (δ)

x	0.00 (TMS)
a	3.45 (s)
b	3.54 (t); J_{bc} = 6.0 cps
c	4.45 (t)

(a+b):c = 3:2

Spectrum 14. Nuclear Magnetic Resonance Spectrum of Bis(2-bromoethyl) Succinate (CCl_4)

$$\underset{(b)}{Br\text{-}CH_2}\text{-}\underset{(c)}{CH_2}\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}\underset{(a)}{CH_2}\text{-}\underset{(a)}{CH_2}\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}\underset{(c)}{CH_2}\text{-}\underset{(b)}{CH_2\text{-}Br}$$



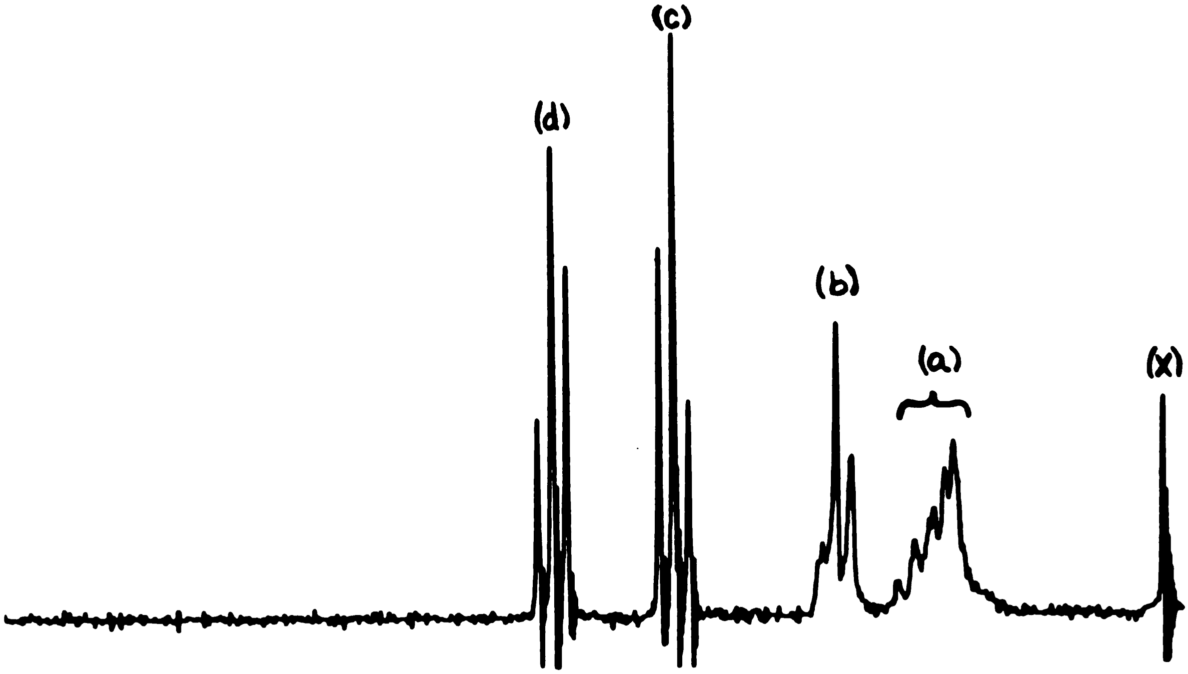
<u>Assignments (δ)</u>

x	0.00 (TMS)
a	2.65 (s)
b	3.52 (t); J_{bc} = 6.0 cps
c	4.40 (t)

a:b:c = 1:1:1

Spectrum 17. Nuclear Magnetic Resonance Spectrum of Bis(2-bromoethyl) Pimelate (CCl_4)

$$\underset{(c)}{Br\text{-}CH_2}\text{-}\underset{(d)}{CH_2}\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}\underset{(b)}{CH_2}\text{-}\underbrace{CH_2\text{-}CH_2\text{-}CH_2}_{(a)}\text{-}\underset{(b)}{CH_2}\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}\underset{(d)}{CH_2}\text{-}\underset{(c)}{CH_2}\text{-}Br$$



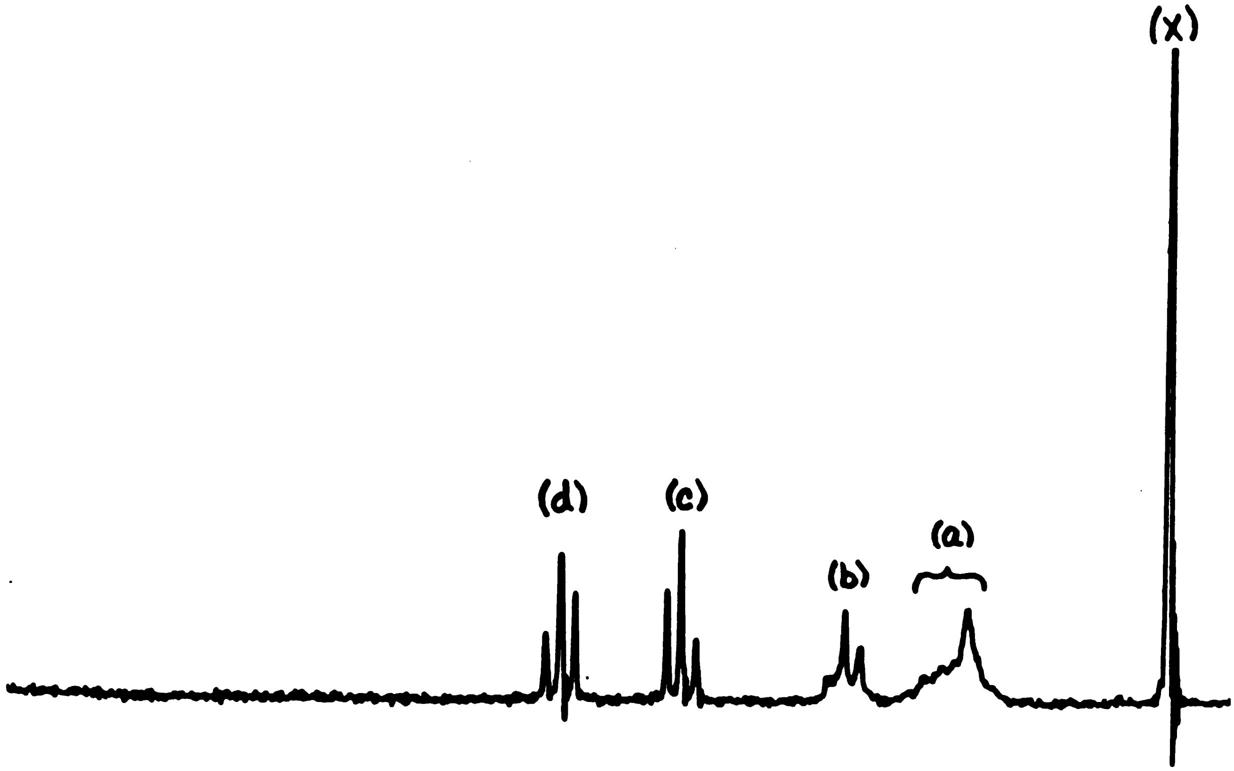
<u>Assignments (δ)</u>

x	0.00 (TMS)
a	1.09-2.00 (m)
b	2.06-2.54 (m)
c	3.49 (t); J_{cd} = 6.0 cps
d	4.35 (t)

a:b:c:d = 3:2:2:2

Spectrum 18. Nuclear Magnetic Resonance Spectrum of Bis(2-bromoethyl) Suberate

$$\underset{(c)}{Br\text{-}CH_2}\text{-}\underset{(d)}{CH_2}\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}\underset{(b)}{CH_2}\text{-}\underbrace{CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2}_{(a)}\text{-}\underset{(b)}{CH_2}\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}\underset{(d)}{CH_2}\text{-}\underset{(c)}{CH_2}\text{-}Br$$

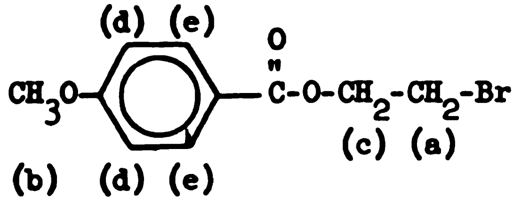


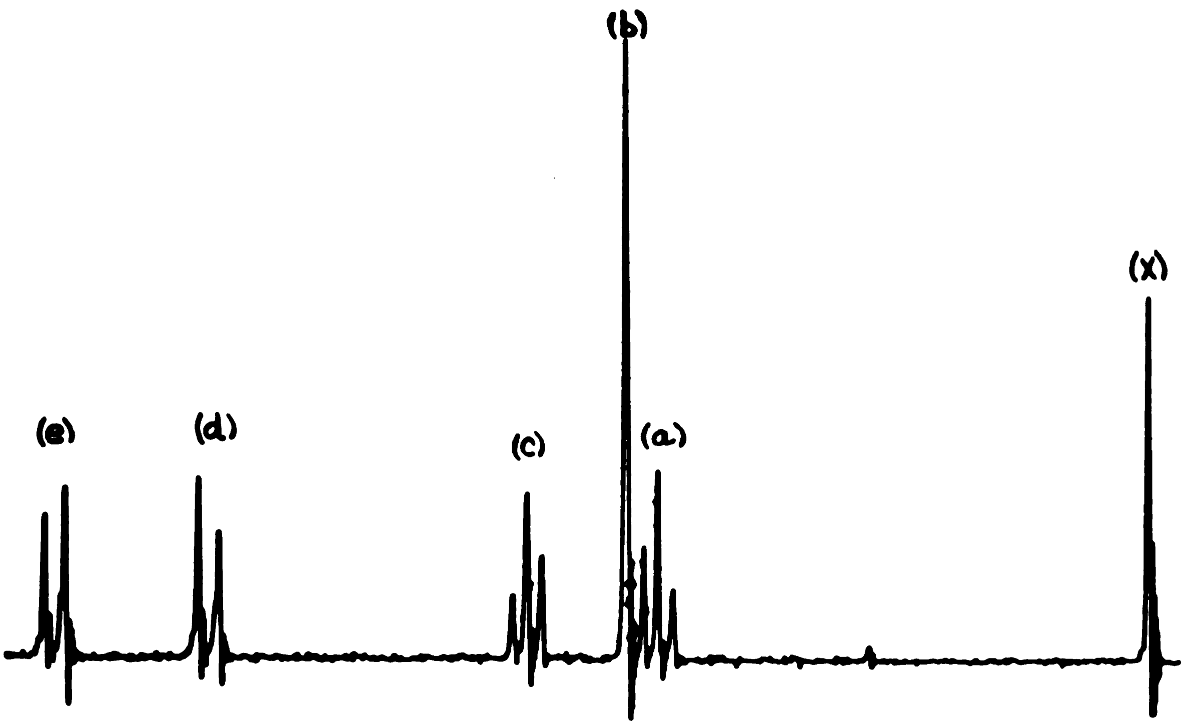
<u>Assignments (δ)</u>

x	0.00 (TMS)
a	1.45 (m)
b	2.32 (t); J_{ba} = 6.5 cps
c	3.49 (t); J_{cd} = 6.0 cps
d	4.35 (t)

a:b:c:d = 2:1:1:1

Spectrum 19. Nuclear Magnetic Resonance Spectrum of 2-Bromoethyl-p-methoxybenzoate (CCl_4)



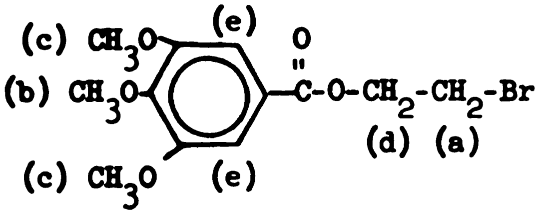


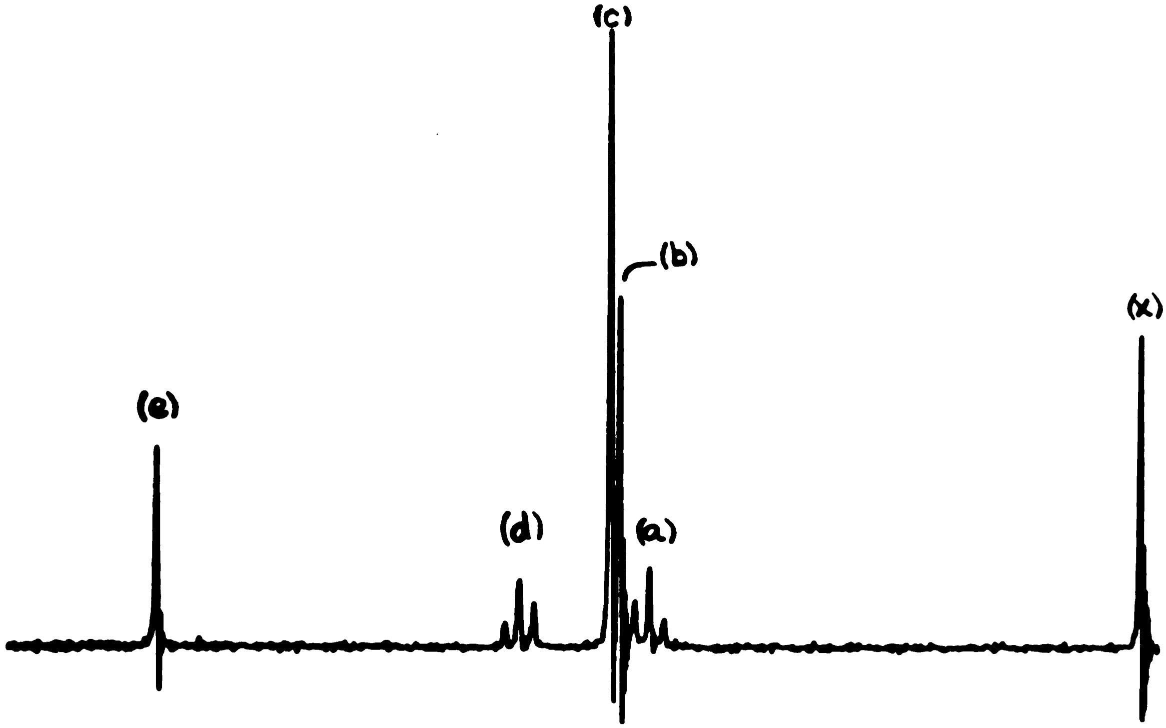
<u>Assignments (δ)</u>

x	0.00 (TMS)
a	3.56 (t); J_{ac} = 6.0 cps
b	3.79 (s)
c	4.52 (t)
d	6.84 (d); J_{de} = 8.7 cps
e	7.93 (e)

a:b:c:d:e = 2:3:2:2:2

Spectrum 20. Nuclear Magnetic Resonance Spectrum of 2-Bromoethyl-3,4,5-trimethoxybenzoate (CCl_4)



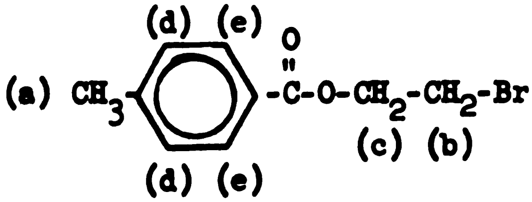


<u>Assignments (δ)</u>

x	0.00 (TMS)
a	3.60 (t); J_{ad} = 6.0 cps
b	3.81 (s)
c	3.87 (s)
d	4.55 (t)
e	7.19 (s)

a:b:c:d:e = 2:3:6:2:2

Spectrum 21. Nuclear Magnetic Resonance Spectrum of 2-Bromoethyl-p-methylbenzoate (CCl_4)

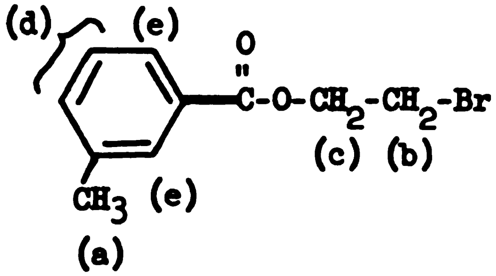


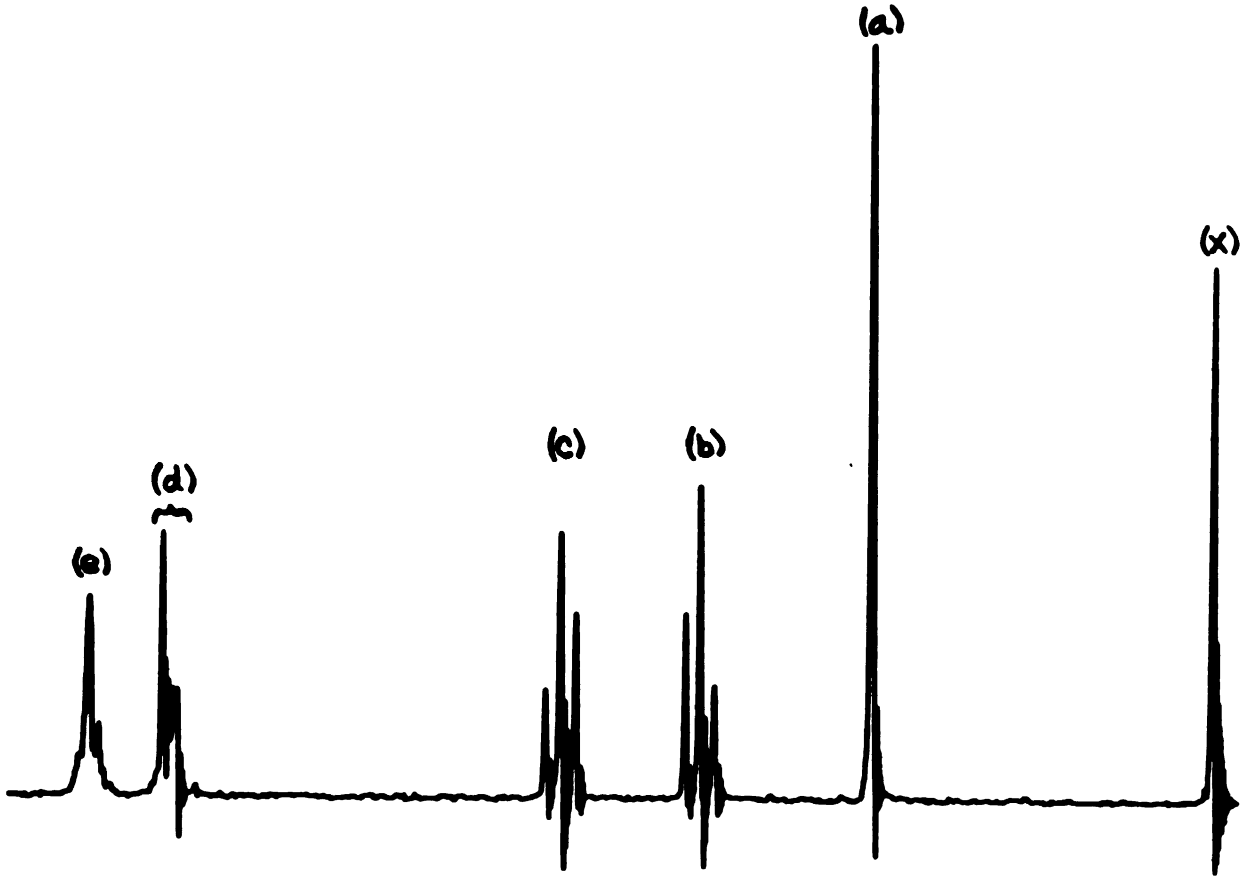
Assignments (δ)

x	0.00 (TMS)
a	2.39 (s)
b	3.57 (t); J_{bc} = 6.0 cps
c	4.53 (t)
d	7.17 (d); J_{de} = 8.0 cps
e	7.89 (d)

a:b:c:d:e: = 3:2:2:2:2

Spectrum 22. Nuclear Magnetic Resonance Spectrum of 2-Bromoethyl-m-methylbenzoate (CCl_4)



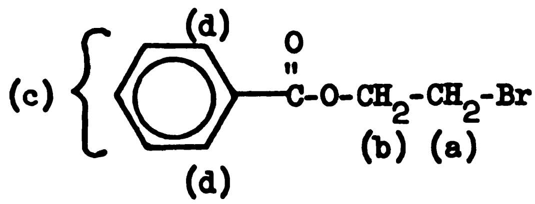


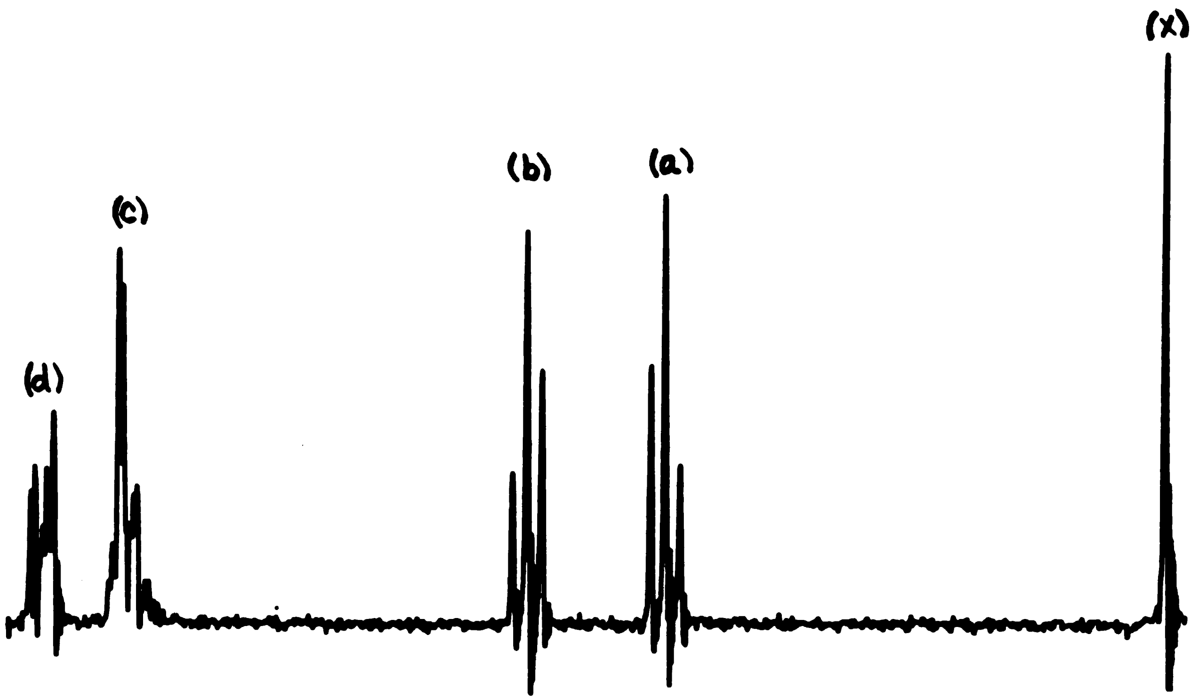
<u>Assignments (δ)</u>

x	0.00 (TMS)
a	2.37 (s)
b	3.57 (t); J_{bc} = 6.0 cps
c	4.54 (t)
d	7.20-7.44 (m)
e	7.82 (s)

a:b:c:d:e = 3:2:2:2:2

Spectrum 23. Nuclear Magnetic Resonance Spectrum of 2-Bromoethyl Benzoate (CCl_4)



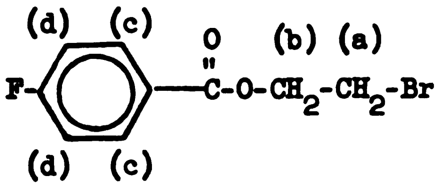


<u>Assignments (δ)</u>

x	0.00 (TMS)
a	3.58 (t); J_{ab} = 6.0 cps
b	4.57 (t)
c	7.40 (m)
d	8.02 (m)

a:b:c:d = 2:2:3:2

Spectrum 24. Nuclear Magnetic Resonance Spectrum of 2-Bromoethyl-p-fluorobenzoate (CCl_4)

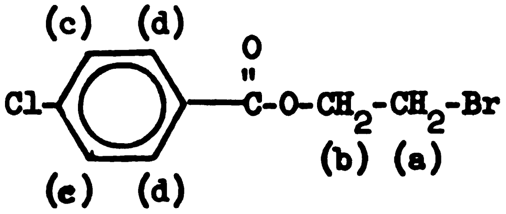


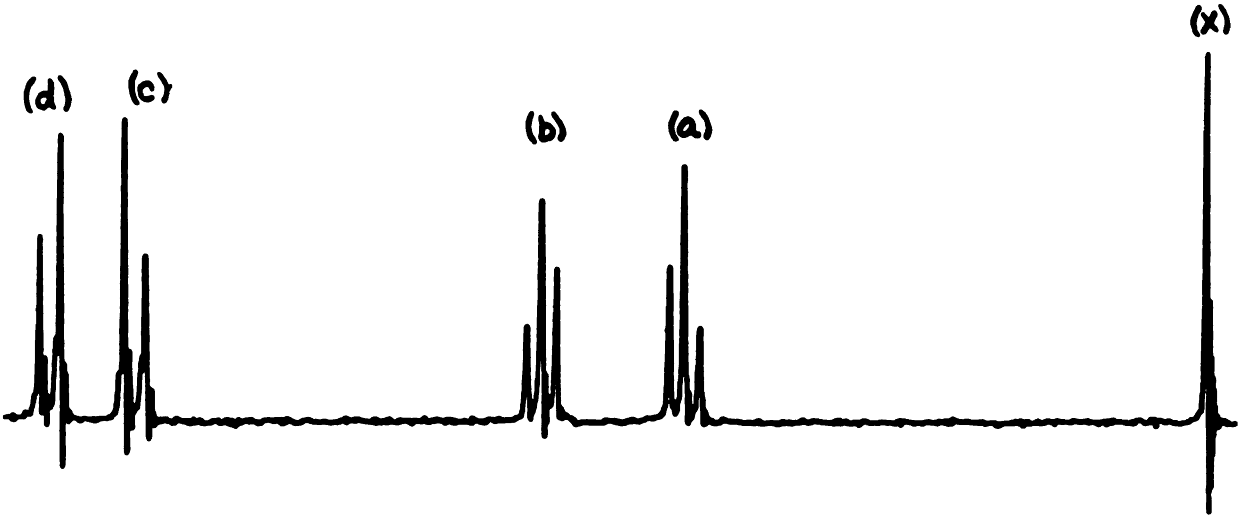
Assignments (δ)

x	0.00 (TMS)
a	3.61 (t); J_{ab} = 6.0 cps
b	4.60 (t)
c	7.12 (m)
d	8.08 (m)

a:b:c:d = 1:1:1:1

Spectrum 25. Nuclear Magnetic Resonance Spectrum of 2-Bromoethyl-p-chlorobenzoate (CCl_4)



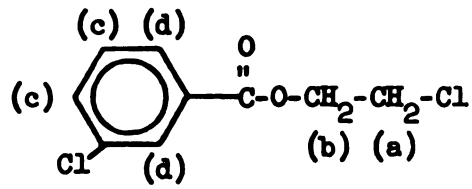


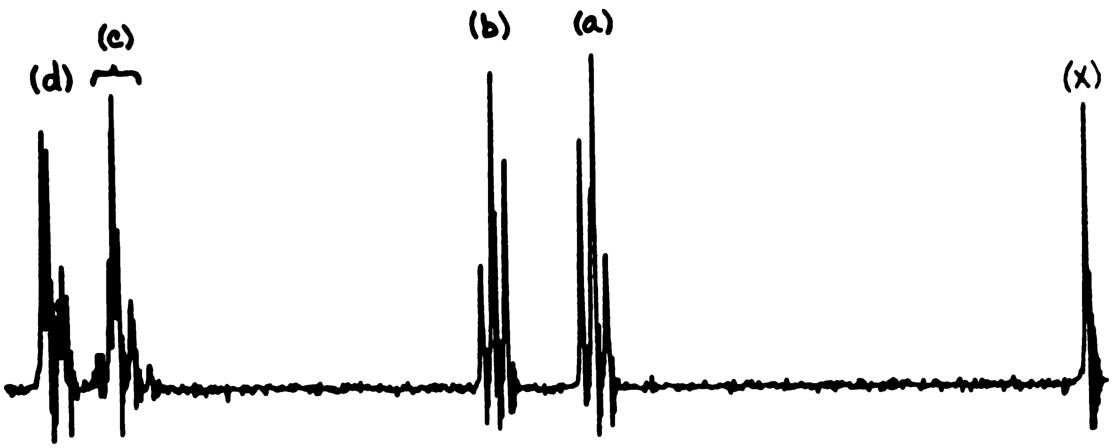
Assignments (δ)

x	0.00 (TMS)
a	3.60 (t); J_{ab} = 6.0 cps
b	4.57 (t)
c	7.36 (d); J_{cd} = 8.5 cps
d	7.94 (d)

a:b:c:d = 1:1:1:1

Spectrum 26. **Nuclear Magnetic Resonance Spectrum of 2-Chloroethyl-m-chlorobenzoate (CCl_4)**



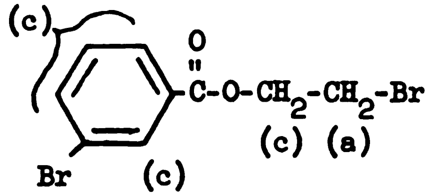


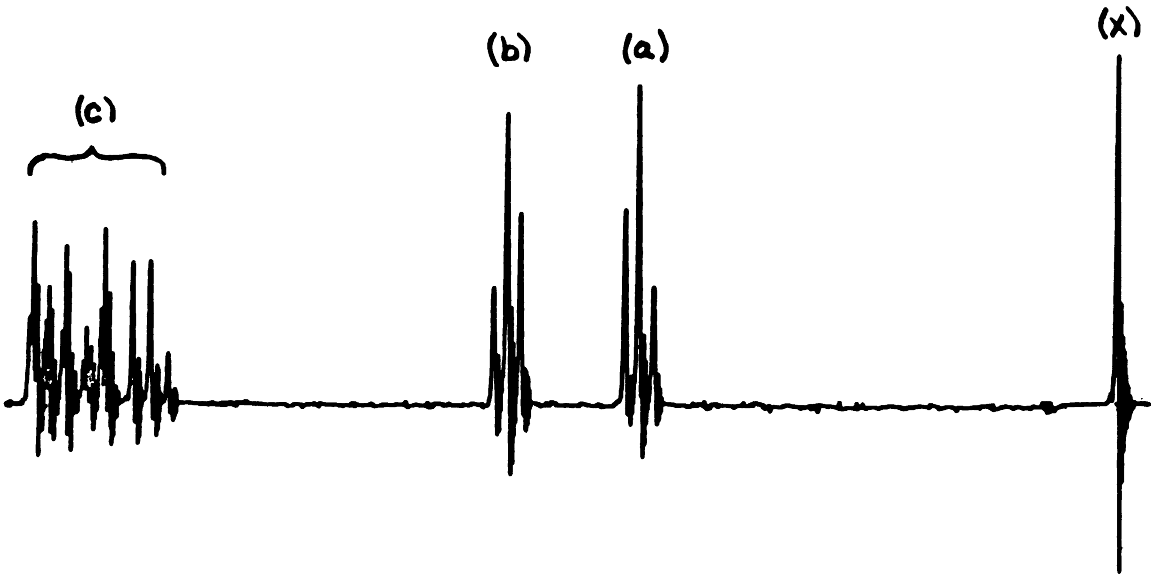
Assignments (δ)

x	0.00 (TMS)
a	3.78 (t); J_{ab} = 5.5 cps
b	4.54 (t)
c	7.40 (m)
d	7.88 (m)

a:b:c:d = 1:1:1:1

Spectrum 27. **Nuclear Magnetic Resonance Spectrum of 2-Bromoethyl-m-bromobenzoate (CCl_4)**



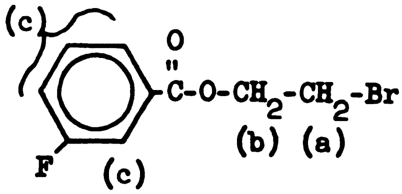


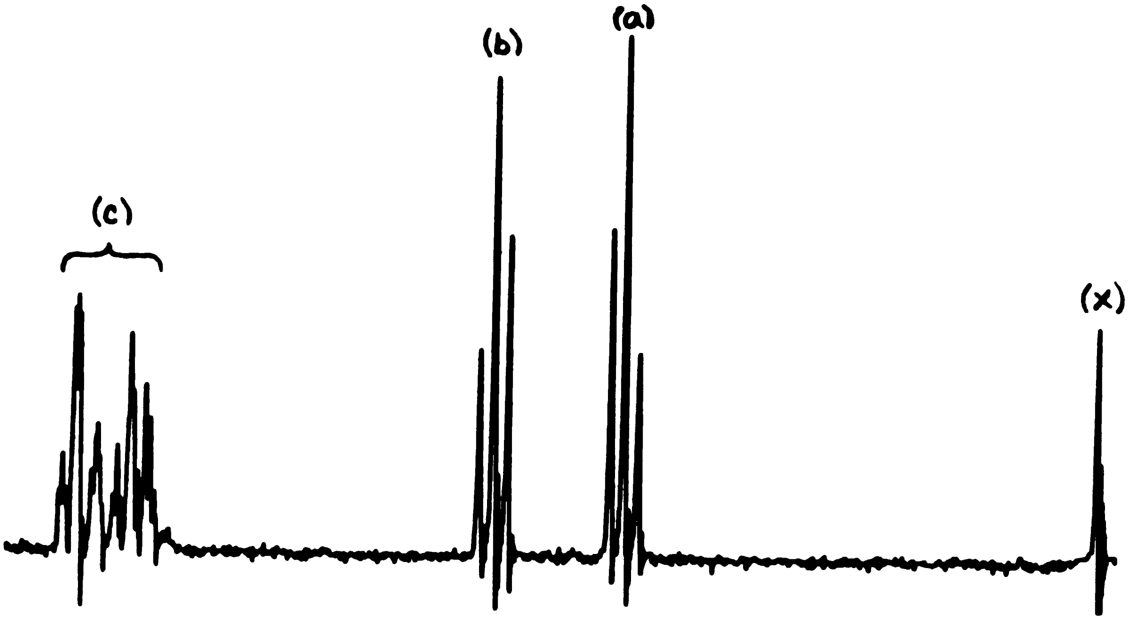
<u>Assignments (δ)</u>

x	0.00 (TMS)
a	3.61 (t); J_{ab} = 6.0 cps
b	4.59 (t)
c	7.12-8.19 (m)

a:b:c = 1:1:2

Spectrum 28. Nuclear Magnetic Resonance Spectrum of 2-Bromoethyl-m-fluorobenzoate (CCl_4)



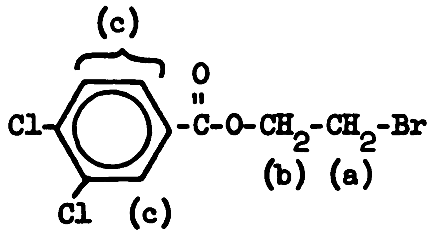


Assignments (δ)

x	0.00 (TMS)
a	3.52 (t); J_{ab} = 6.0 cps
b	4.61 (t)
c	7.03-7.95 (m)

a:b:c = 1:1:2

Spectrum 29. Nuclear Magnetic Resonance Spectrum of 2-Bromoethyl-3,4-Dichlorobenzoate (CCl_4)

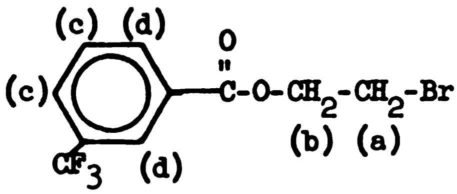


Assignments (δ)

x	0.00 (TMS)
a	3.60 (t); J_{ab} = 6.0 cps
b	4.61 (t)
c	7.40-8.17 (m)

a:b:c = 2:2:3

Spectrum 30. Nuclear Magnetic Resonance Spectrum of 2-Bromoethyl-m-trifluoromethylbenzoate (CCl_4)

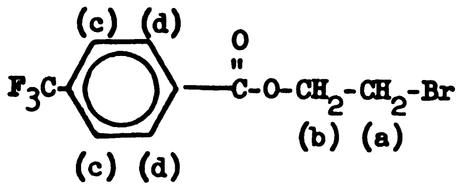


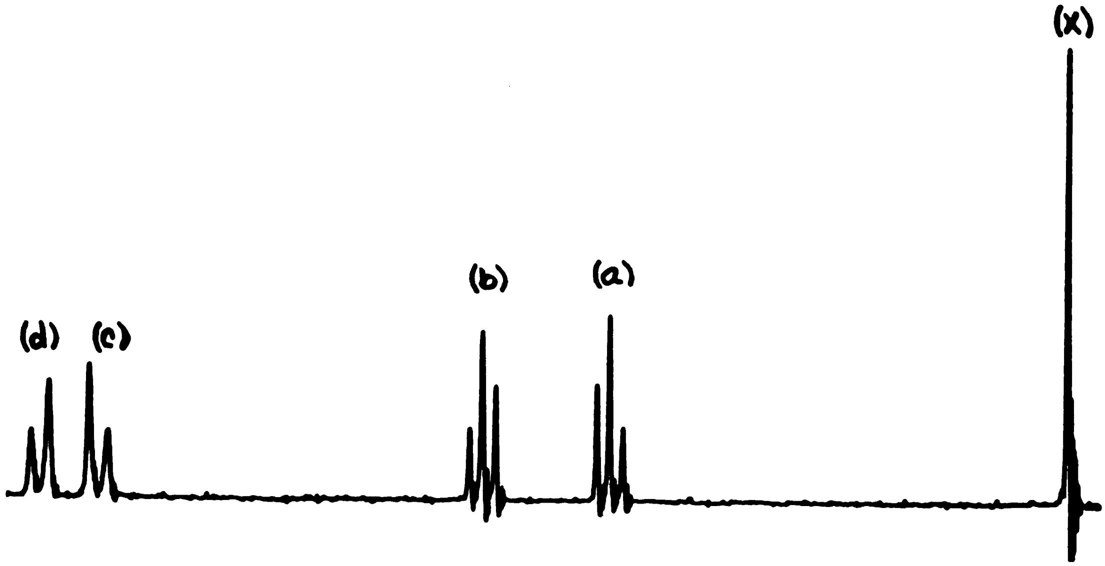
Assignments (δ)

x	0.00 (TMS)
a	3.63 (t); J_{ab} = 6.0 cps
b	4.64 (t)
c	7.84-8.03 (m)
d	8.11-8.36 (m)

a:b:c:d = 1:1:1:1

Spectrum 31. **Nuclear Magnetic Spectrum of 2-Bromoethyl-p-trifluoromethylbenzoate (CCl_4)**



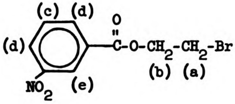


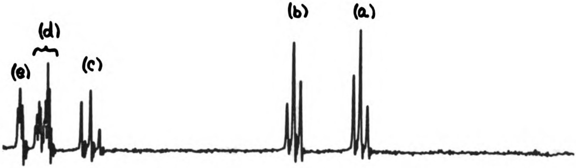
<u>Assignments (δ)</u>

x	0.00 (TMS)
a	3.64 (t); J_{ab} = 6.0 cps
b	4.65 (t)
c	7.66 (d); J = 8.6 cps
d	8.14 (d)

a:b:c:d = 1:1:1:1

Spectrum 32. Nuclear Magnetic Resonance Spectrum of 2-Bromoethyl-m-nitrobenzoate (CCl_4) (TMA·BF_4 internal standard)



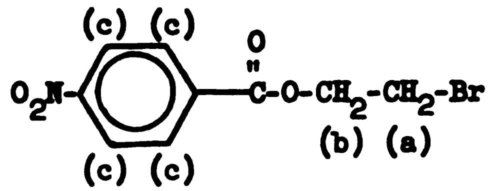


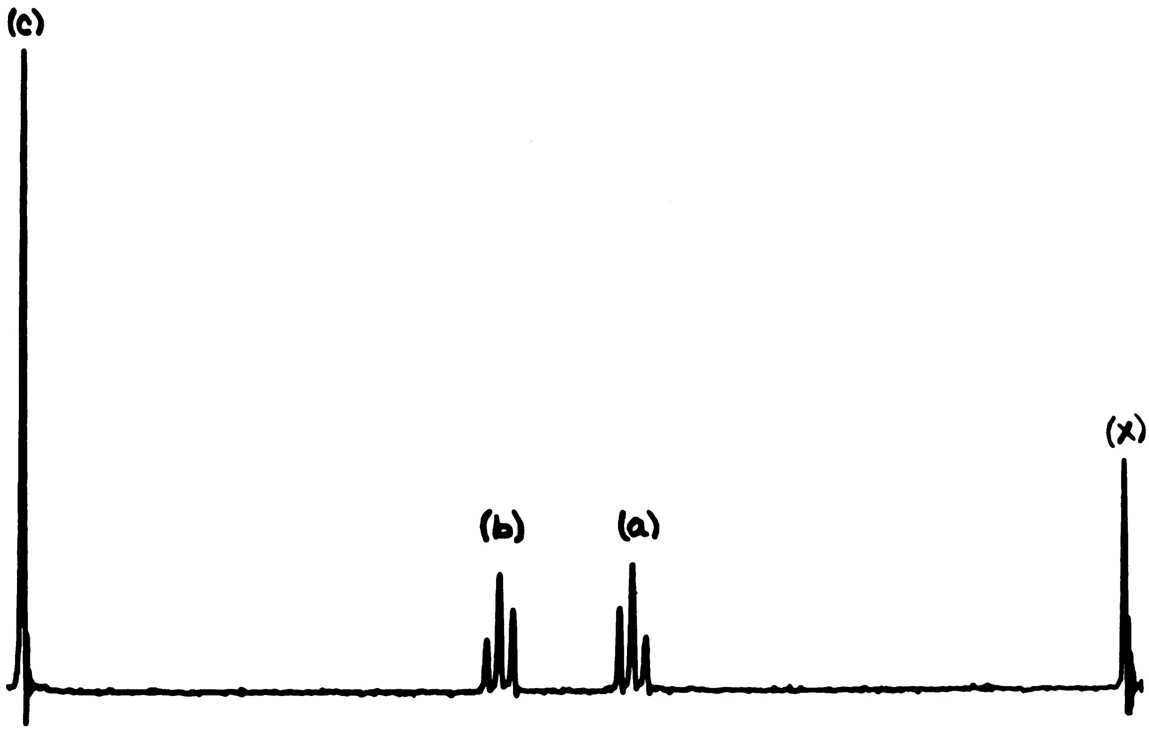
<u>Assignments (δ)</u>

a	3.72 (t); J_{ab} = 6.0 cps
b	4.70 (t)
c	7.68 (t); J = 7.5 cps
d	8.36 (m)
e	8.70 (m)

a:b:c:d:e = 2:2:1:2:1

Spectrum 33. Nuclear Magnetic Resonance Spectrum of 2-Bromoethyl-p-nitrobenzoate (CCl_4)



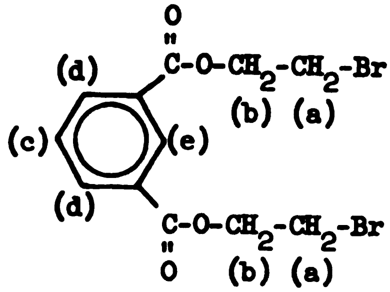


Assignments (δ)

x	0.00 (TMS)
a	3.68 (t); J_{ab} = 6.0 cps
b	4.67 (t)
c	8.23 (s)

a:b:c = 1:1:2

Spectrum 34. Nuclear Magnetic Resonance Spectrum of 2-Bromoethyl Isophthalate (CCl_4)

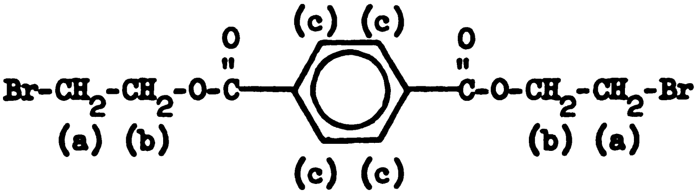


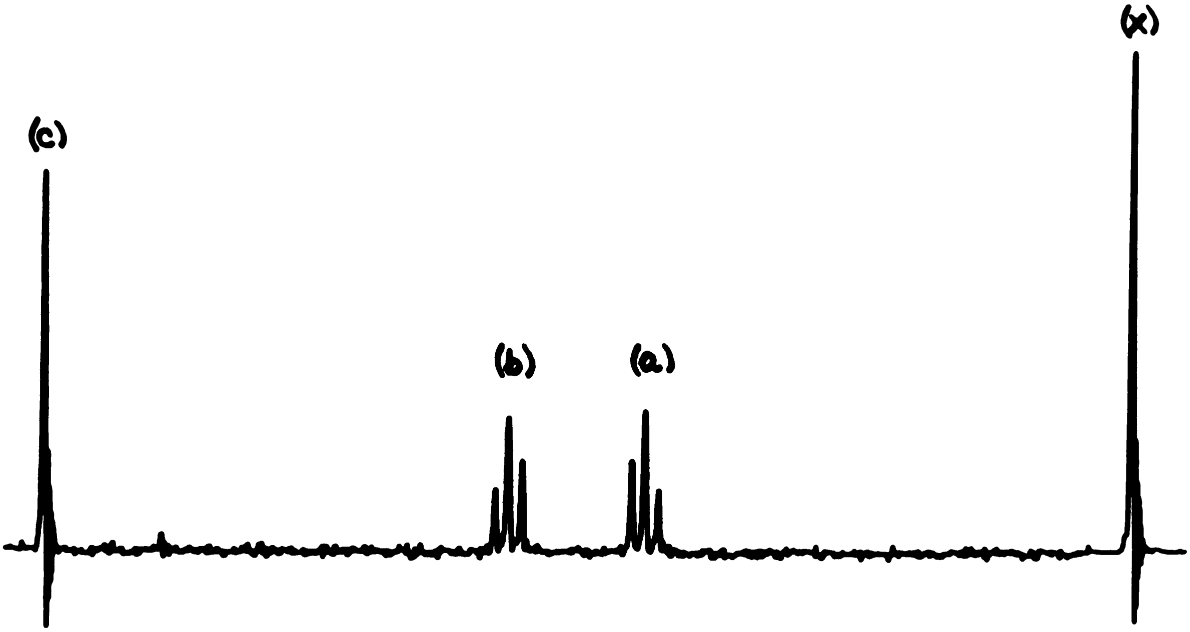
<u>Assignments (δ)</u>

x	0.00 (TMS)
a	3.64 (t); J_{ab} = 6.0 cps
b	4.63 (t)
c	7.52 (m)
d	8.24 (m)
e	8.66 (m)

a:b:c:d:e = 4:4:2:1:1

Spectrum 35. Nuclear Magnetic Resonance Spectrum of 2-Bromoethyl Terephthalate (CCl_4)



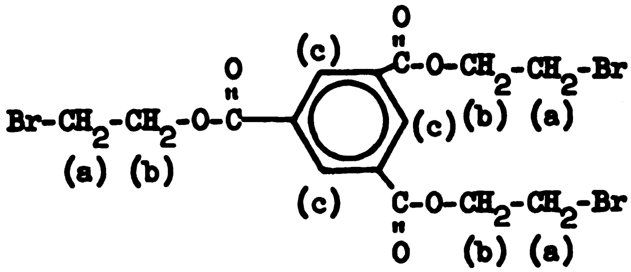


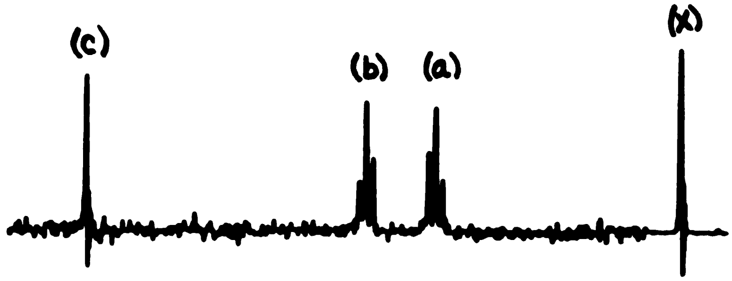
Assignments (δ)

x	0.00 (TMS)
a	3.67 (t); J_{ab} = 6.0 cps
b	4.68 (t)
c	8.15 (s)

a:b:c = 1:1:1

Spectrum 36. Nuclear Magnetic Resonance Spectrum of 2-Bromoethyl Trimesate (CCl_4)



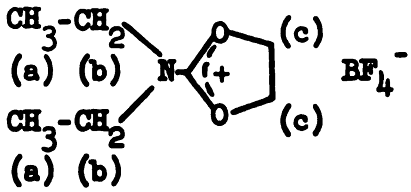


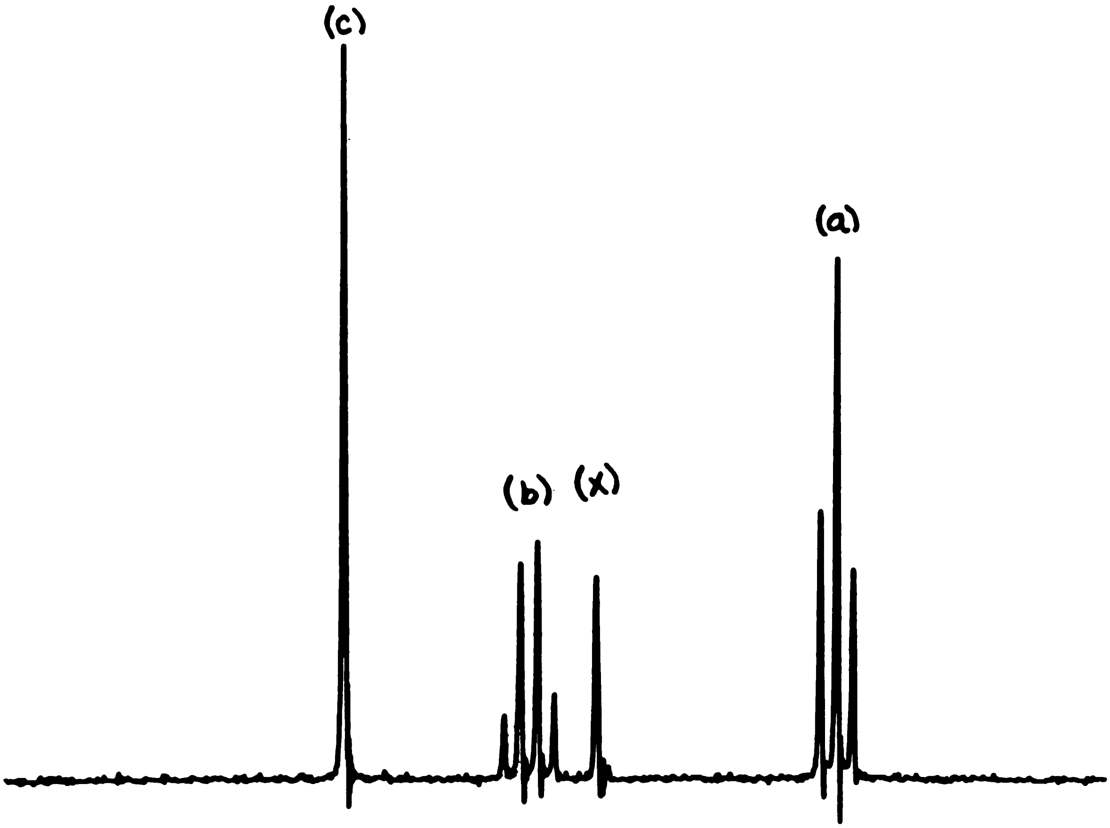
<u>Assignments (δ)</u>

x	0.00 (TMS)
a	3.70 (t); J_{ab} = 6.0 cps
b	4.73 (t)
c	8.91 (s)

a:b:c = 2:2:1

Spectrum 37. Nuclear Magnetic Resonance Spectrum of 2-(N,N-Diethylamino)-1,3-dioxolenium Tetrafluoroborate (FSO_3H)



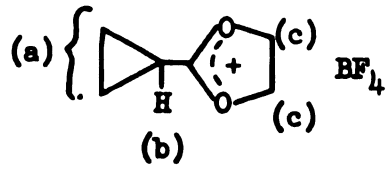


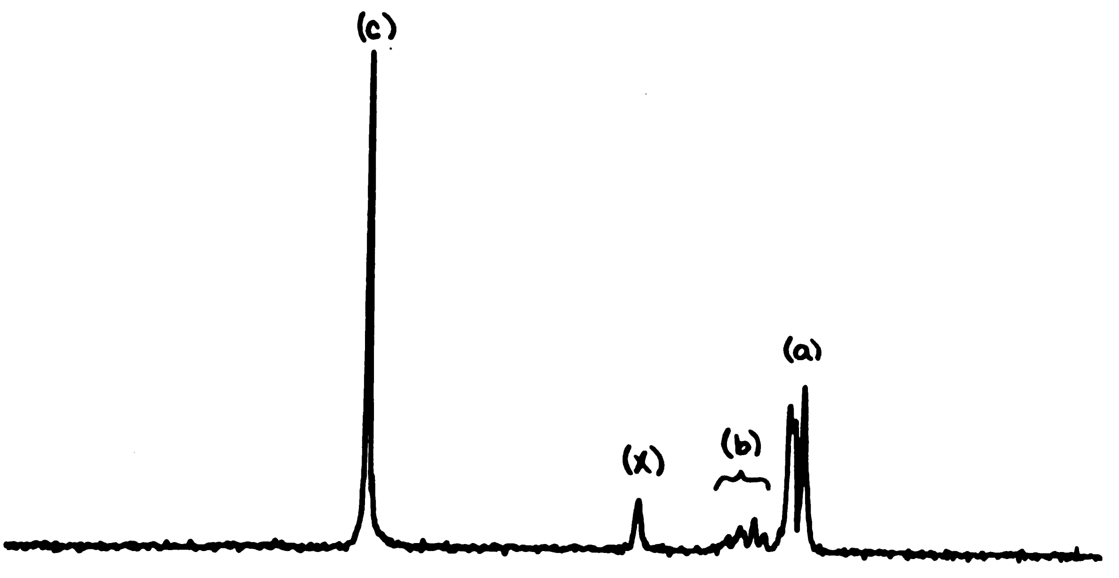
Assignments (δ)

x	3.10 (TMA·BF_4)
a	1.32 (t); J_{ab} = 7.5 cps
b	3.59 (q)
c	4.98 (s)

a:b:c = 3:2:2

Spectrum 38. Nuclear Magnetic Resonance Spectrum of 2-(Cyclopropyl)-1,3-dioxolenium Tetrafluoroborate (FSO_3H)



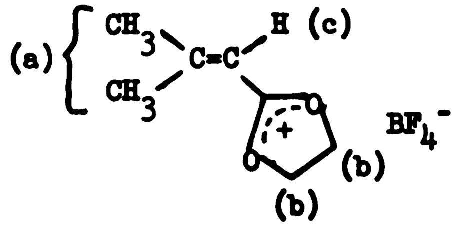


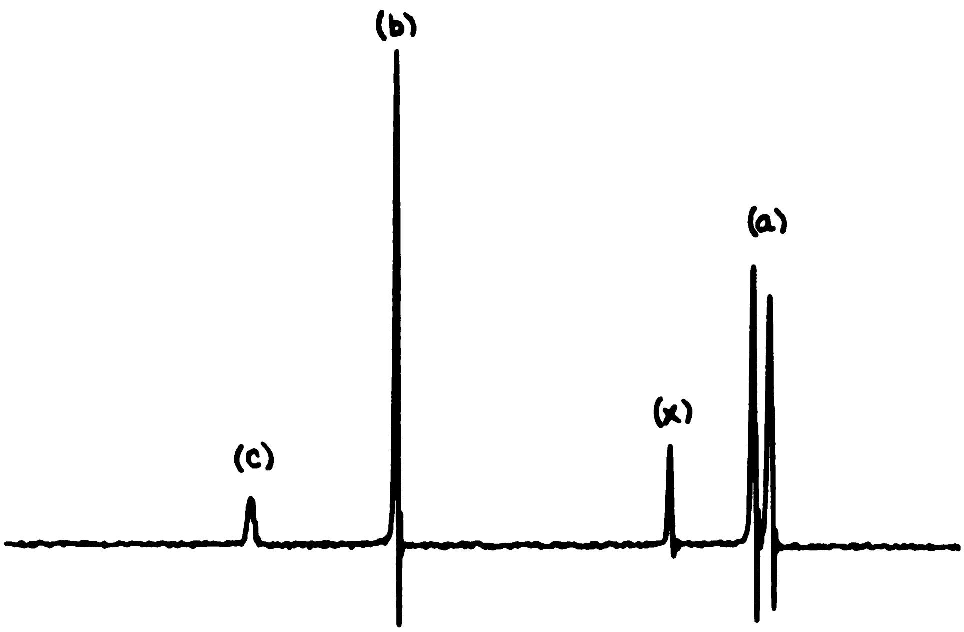
Assignments (δ)

x	3.10 (TMA·BF_4)
a	1.75-2.07 (m)
b	2.10-2.53 (m)
c	5.17 (s)

a:b:c = 4:1:4

Spectrum 39. Nuclear Magnetic Resonance Spectrum of 2-(2-Methylpropenyl)-1,3-dioxolenium Tetrafluoroborate (FSO_3H)



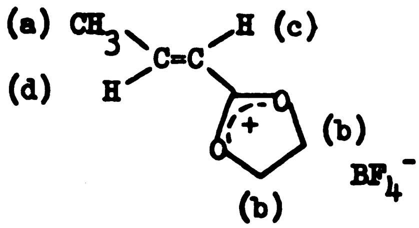


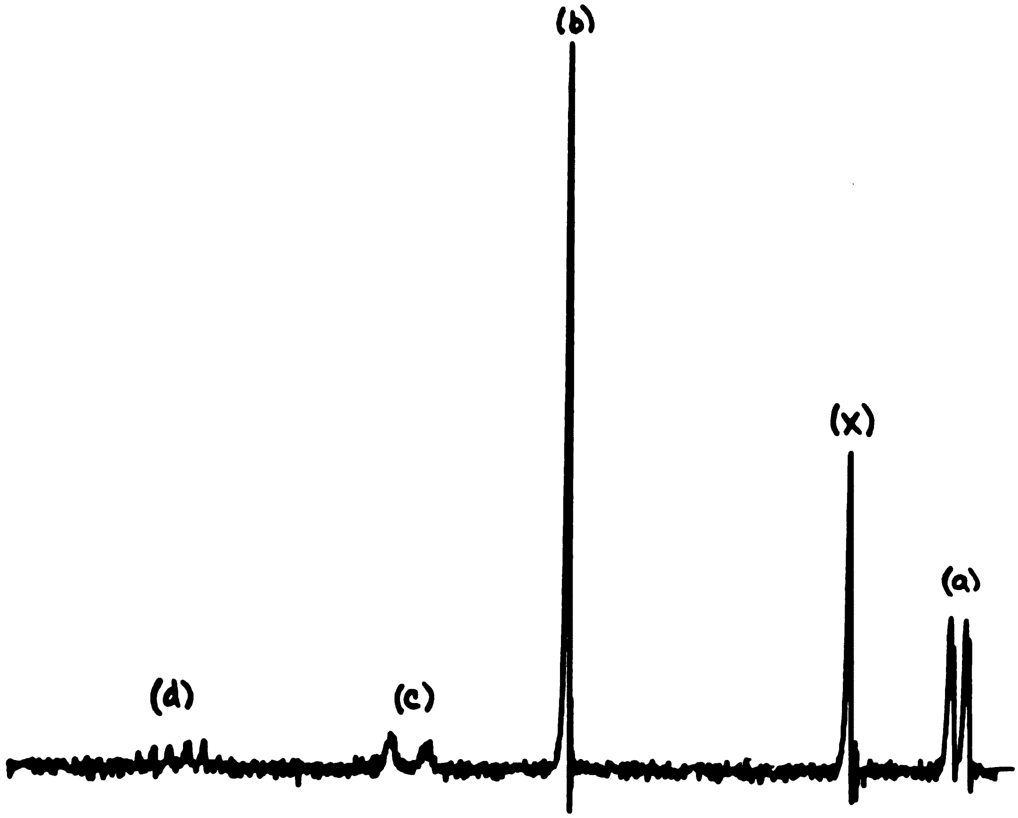
Assignments (δ)

x	3.10 (TMA·BF_4)
a	2.37 (d); J_{ac} = 7.5 cps
b	5.19 (s)
c	6.27 (m)

a:b:c = 6:4:1

Spectrum 40. **Nuclear Magnetic Resonance Spectrum of trans-2-(Propenyl)-1,3-dioxolenium Tetrafluoroborate (FSO_3H)**



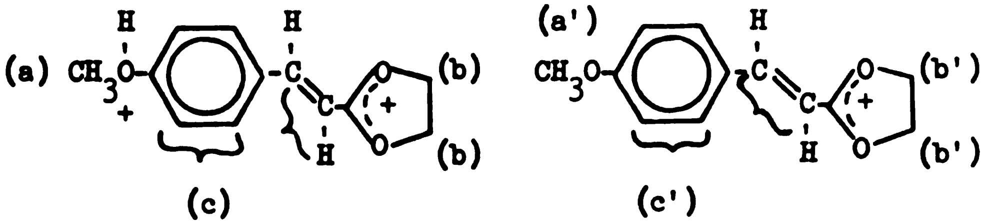


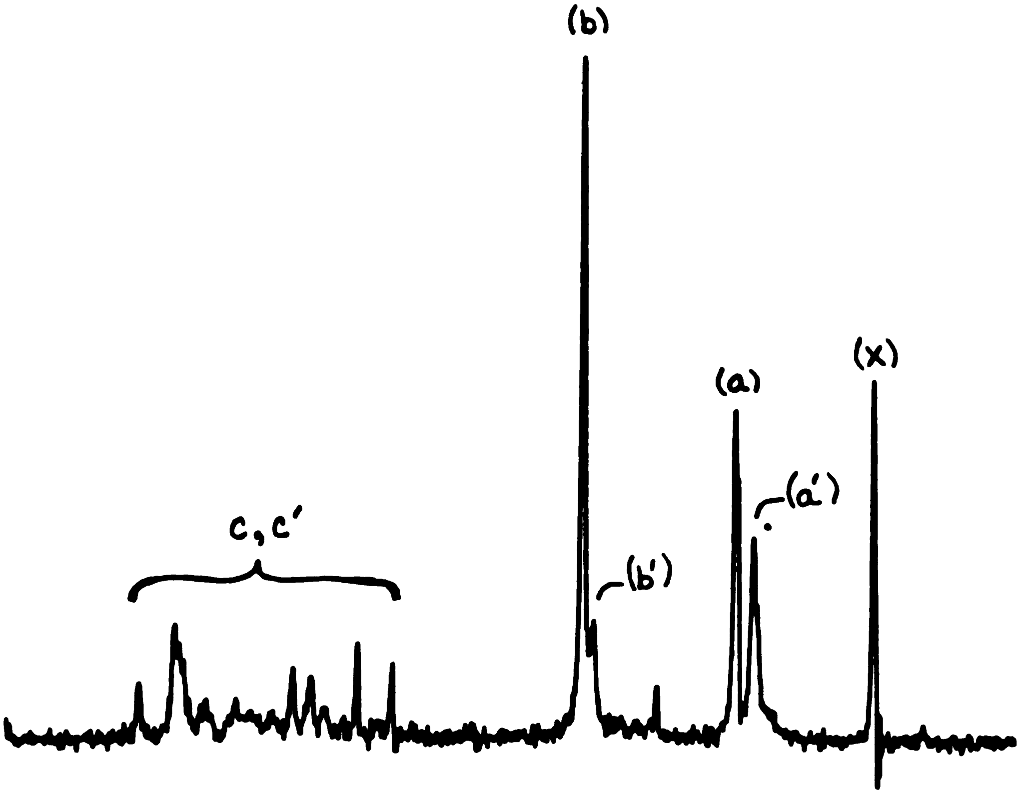
Assignments (δ)

x	3.10 (TMA·BF_4)
a	2.27 (d); J = 7.0 cps; J = 1.5 cps
b	5.23 (s)
c	6.44 (m)
d	8.22 (m)

a:b:c:d = 3:4:1:1

Spectrum 41. Nuclear Magnetic Resonance Spectrum of 2-(p-Methoxystyrl)-1,3-dioxolenium Tetrafluoroborate (~20% in FSO_3H)

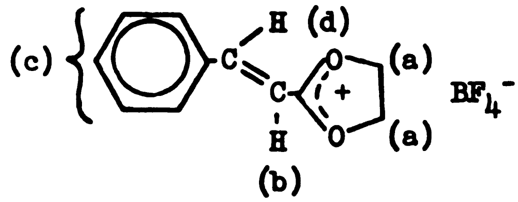


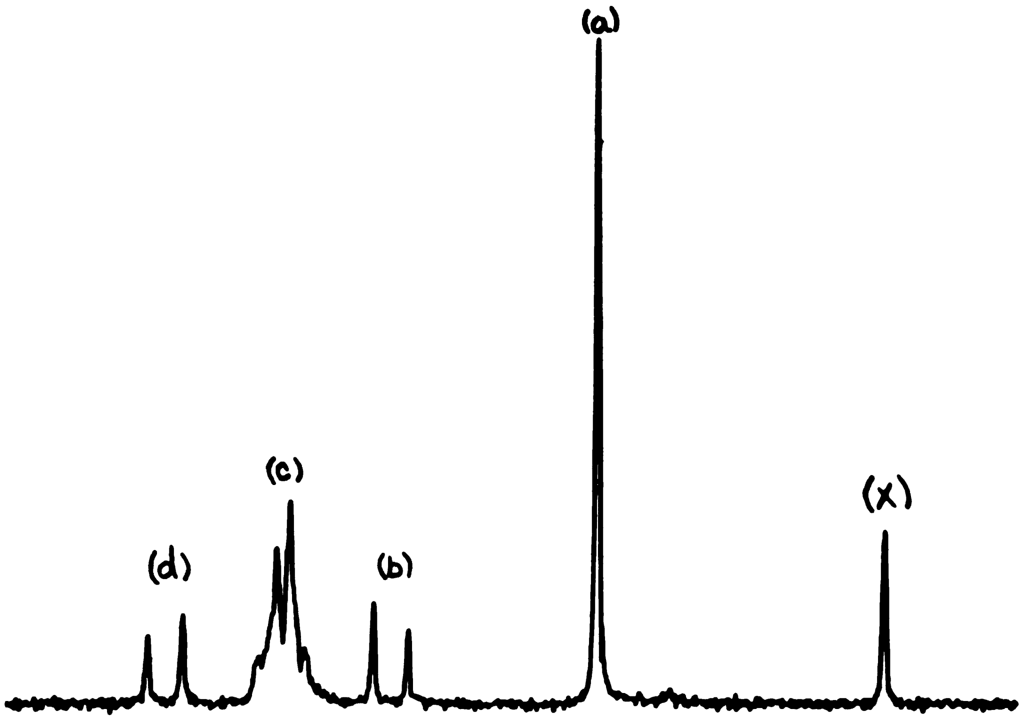


Assignments (δ)

	I		II
x	0.00 ($TMA \cdot BF_4$)	x	0.00 ($TMA \cdot BF_4$)
a	4.15 (s)	a'	4.02 (s)
b	5.29 (s)	b'	5.22 (s)
c, c'	6.74-8.67 (m)	c, c'	6.74-8.67 (m)

Spectrum 42. Nuclear Magnetic Resonance Spectrum of 2-(Styrl)-1,3-dioxolenium Tetrafluoroborate (FSO_3H)



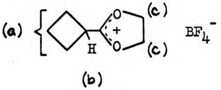


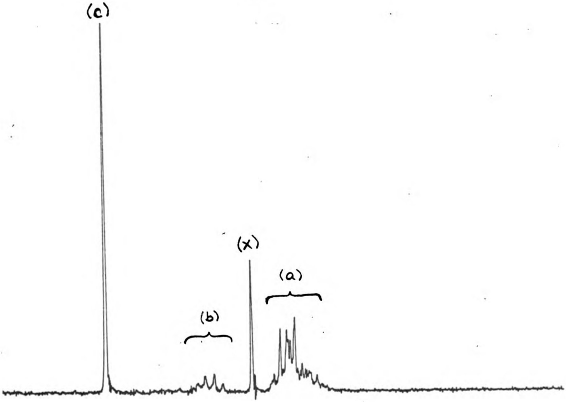
Assignments (δ)

x	3.10 ($TMA \cdot BF_4$)
a	5.25 (s)
b	6.86 (d); J_{bd} = 16.0 cps
c	7.35-7.93 (m)
d	8.59 (d)

a:b:c:d = 4:1:5:1

Spectrum 43. Nuclear Magnetic Resonance Spectrum of 2-(Cyclobutyl)-1,3-dioxolenium Tetrafluoroborate (FSO_3H)



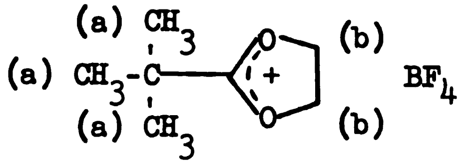


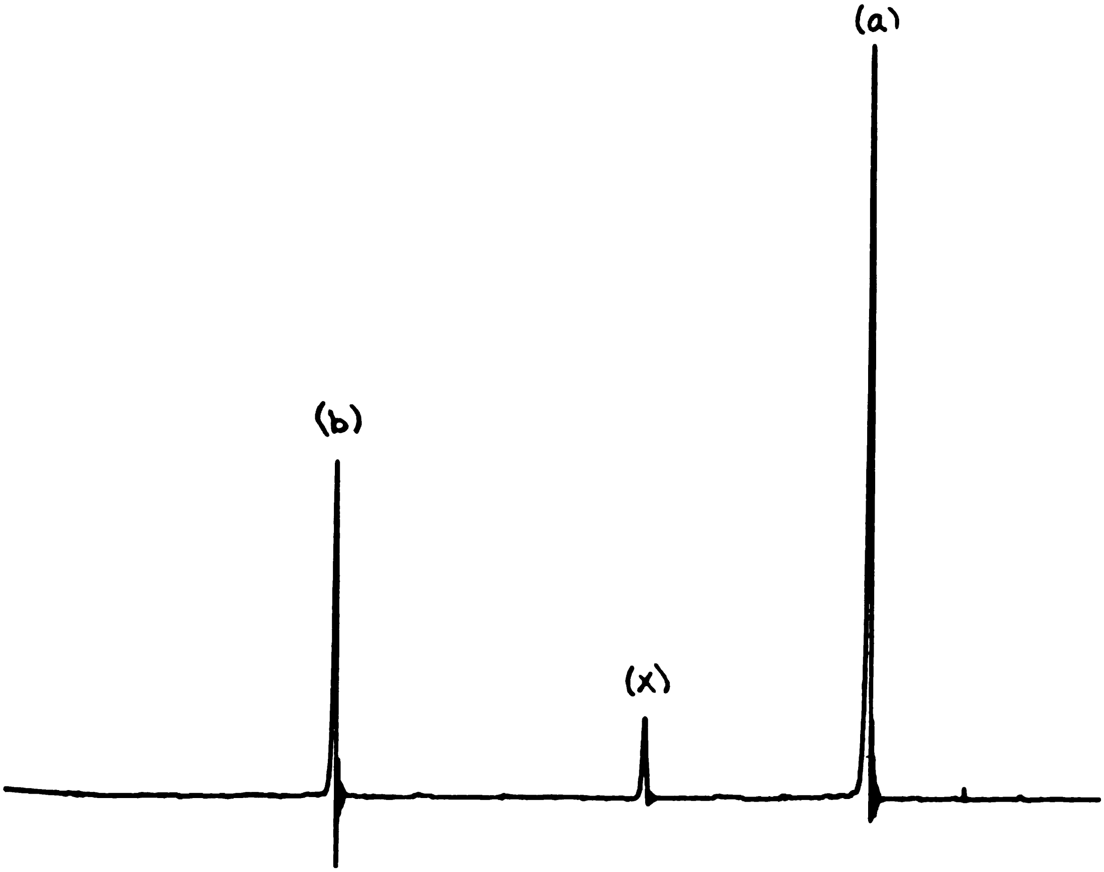
Assignments (δ)

x	3.10 ($TMA \cdot BF_4$)
a	1.86-2.83 (m)
b	3.42-3.89 (q)
c	5.29 (s)

a:b:c = 6:1:4

Spectrum 44. Nuclear Magnetic Resonance Spectrum of 2-(t-Butyl)-1,3-dioxolenium Tetrafluoroborate (FSO_3H)



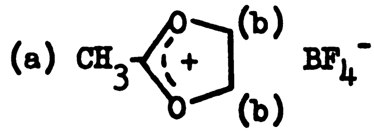


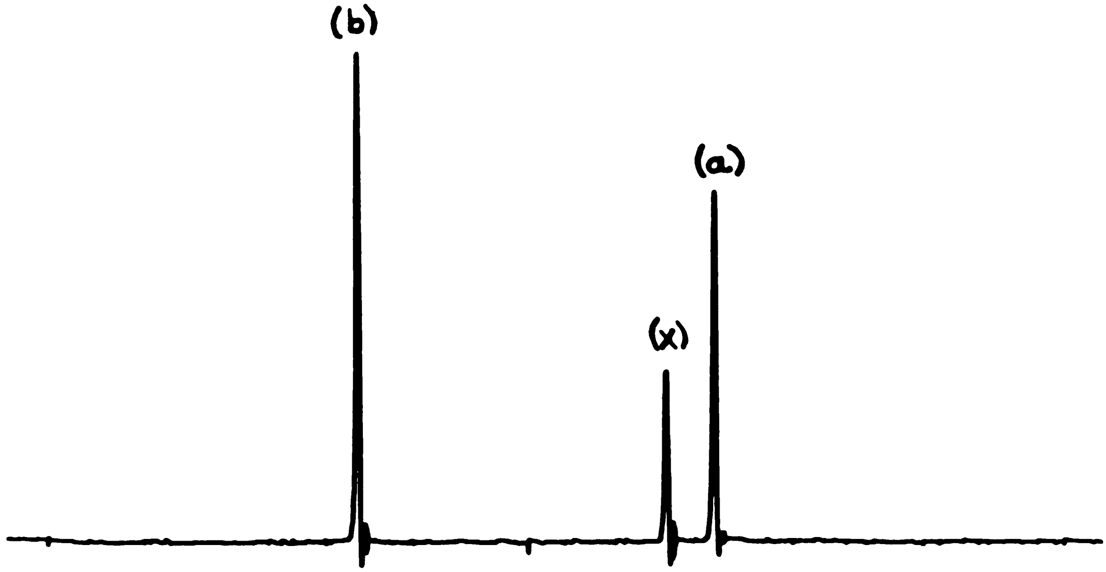
Assignments (δ)

x	3.10 ($TMA\cdot BF_4$)
a	1.50 (s)
b	5.30 (s)

a:b = 9:4

Spectrum 45. Nuclear Magnetic Resonance Spectrum of 2-(Methyl)-1,3-dioxolenium Tetrafluoroborate (FSO_3H)



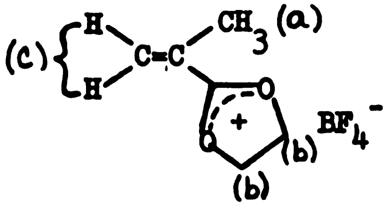


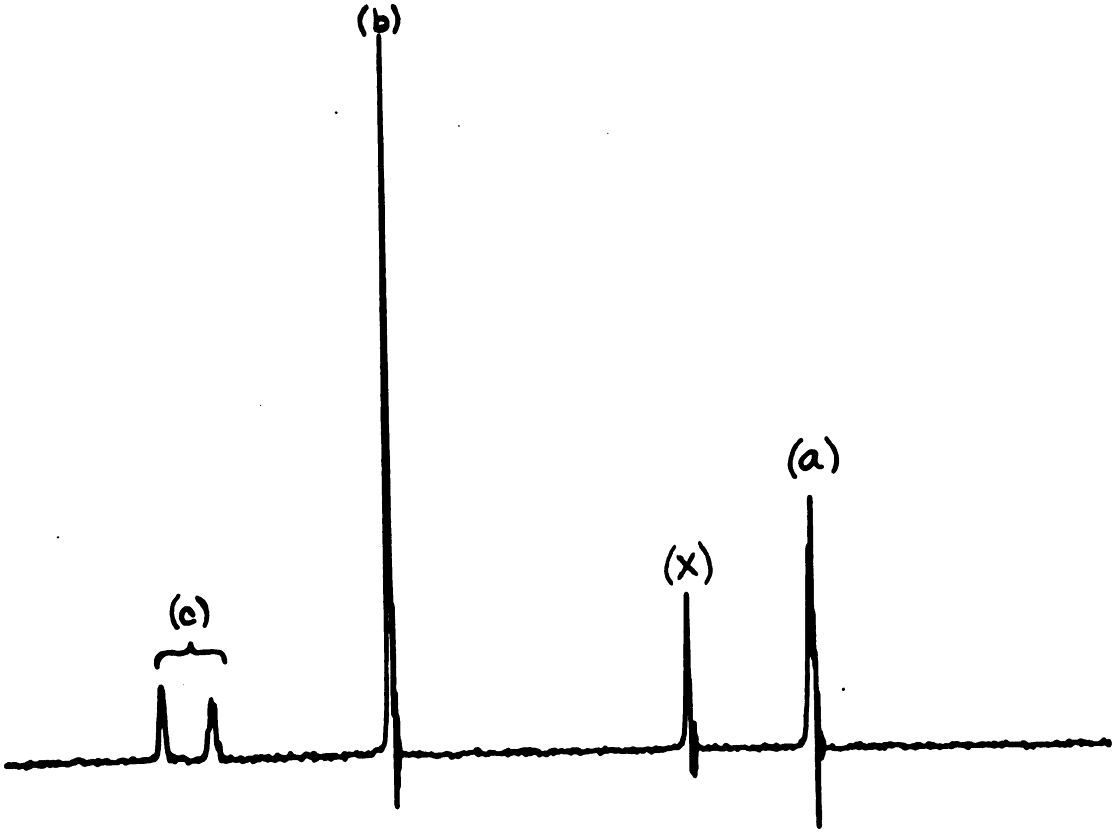
<u>Assignments (δ)</u>

x	3.10 (TMA·BF_4)
a	2.75 (s)
b	5.30 (s)

a:b = 3:4

Spectrum 46. Nuclear Magnetic Resonance Spectrum of 2-Isopropenyl-1,3-dioxolenium Tetrafluoroborate (FSO_3H)



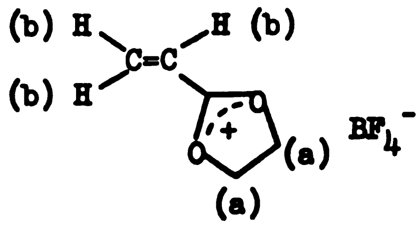


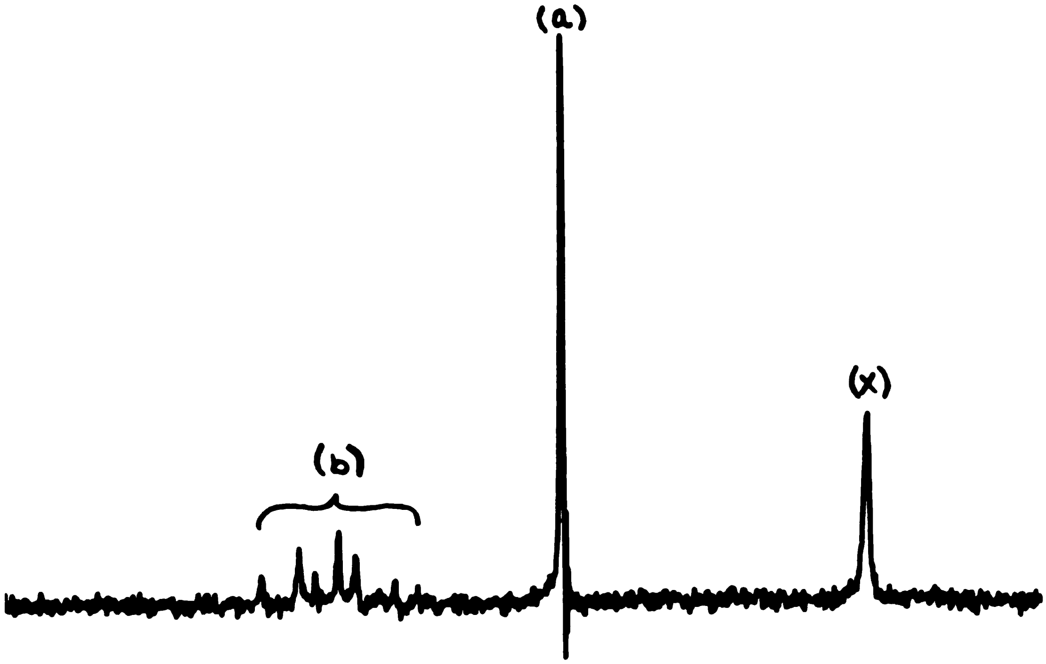
<u>Assignments (δ)</u>

x	3.10 (TMA·BF_4)
a	2.15 (s)
b	5.34 (s)
c	6.85 (d)

a:b:c = 3:4:2

Spectrum 47. Nuclear Magnetic Resonance Spectrum of 2-(Vinyl)-1,3-dioxolenium Tetrafluoroborate (FSO_3H)



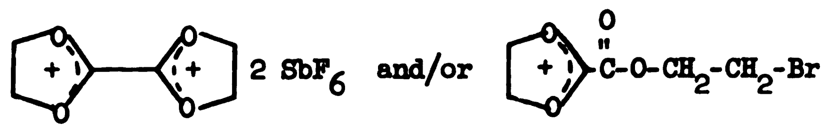


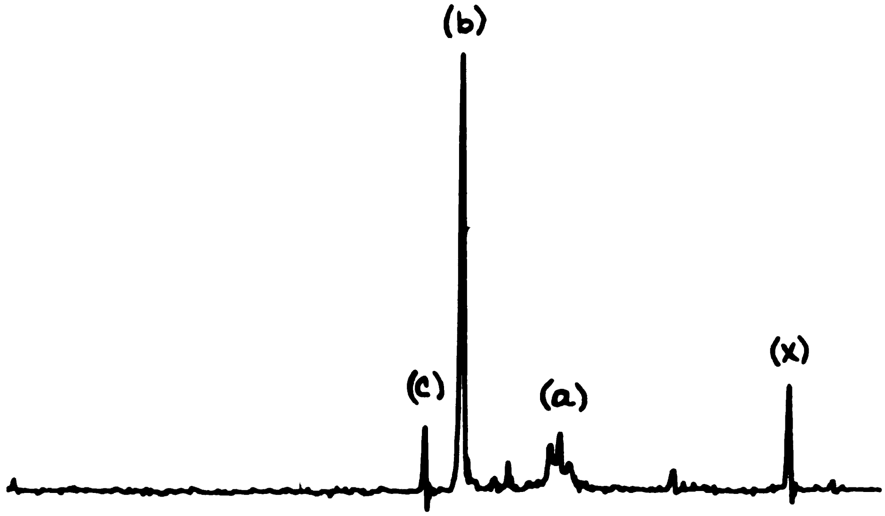
<u>Assignments (δ)</u>

x	3.10 (TMA·BF_4)
a	5.35 (s)
b	6.28-7.57 (m)

a:b = 2:1

Spectrum 48. Nuclear Magnetic Spectrum of Product From Bis(2-bromoethyl) Oxalate and Two Equivalents of $AgSbF_6$ (FSO_3H)





<u>Assignments (δ)</u>

x 3.10 (TMA·BF_4)

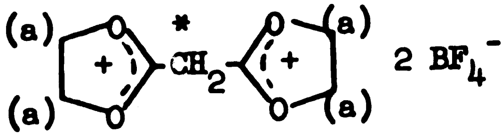
a 4.79-5.07 (m)

b 5.70 (s)

c 6.00 (s)

a:b:c = 5:12:1

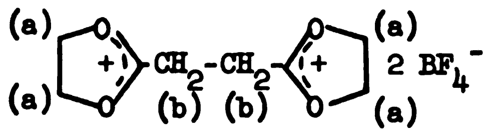
Spectrum 49. Nuclear Magnetic Resonance Spectrum of 2,2'-Methylenebis-1,3-dioxolenium Tetrafluoroborate (FSO_3H)

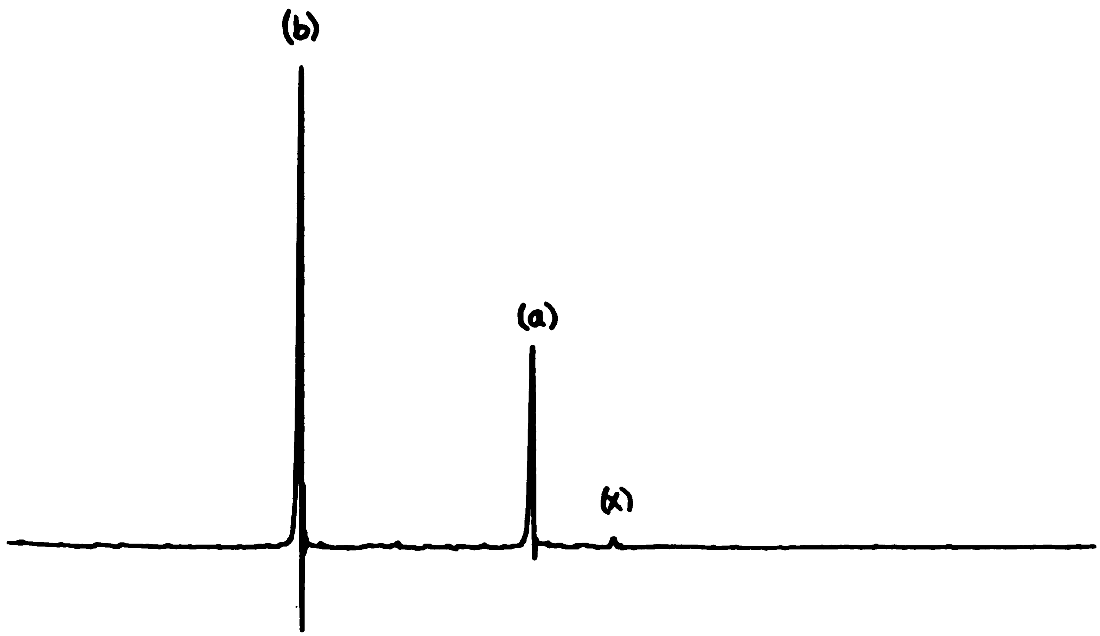


<u>Assignments (δ)</u>

x	3.10 ($TMA \cdot BF_4$)
a	5.61 (s)
*	Exchanges with FSO_3H

Spectrum 50. Nuclear Magnetic Resonance Spectrum of 2,2'-Ethylenebis-1,3-dioxolenium Tetrafluoroborate (FSO_3H)



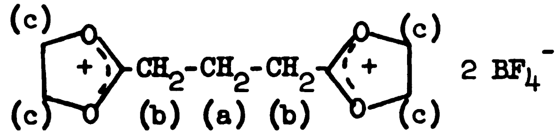


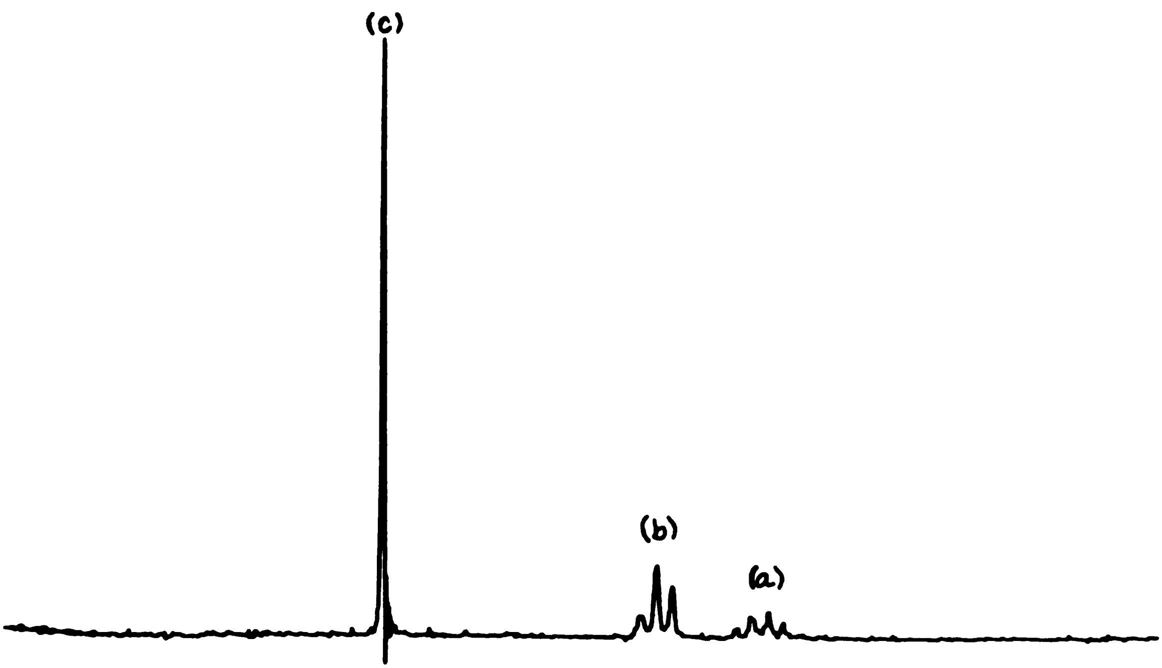
<u>Assignments (δ)</u>

x	3.10 ($TMA \cdot BF_4$)
a	3.70 (s)
b	5.48 (s)

a:b = 1:2

Spectrum 51. Nuclear Magnetic Resonance Spectrum of 2,2'-Trimethylenebis-1,3-dioxolenium Tetrafluoroborate (FSO_3H)



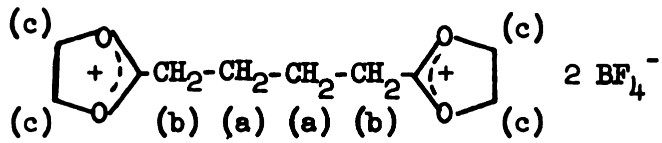


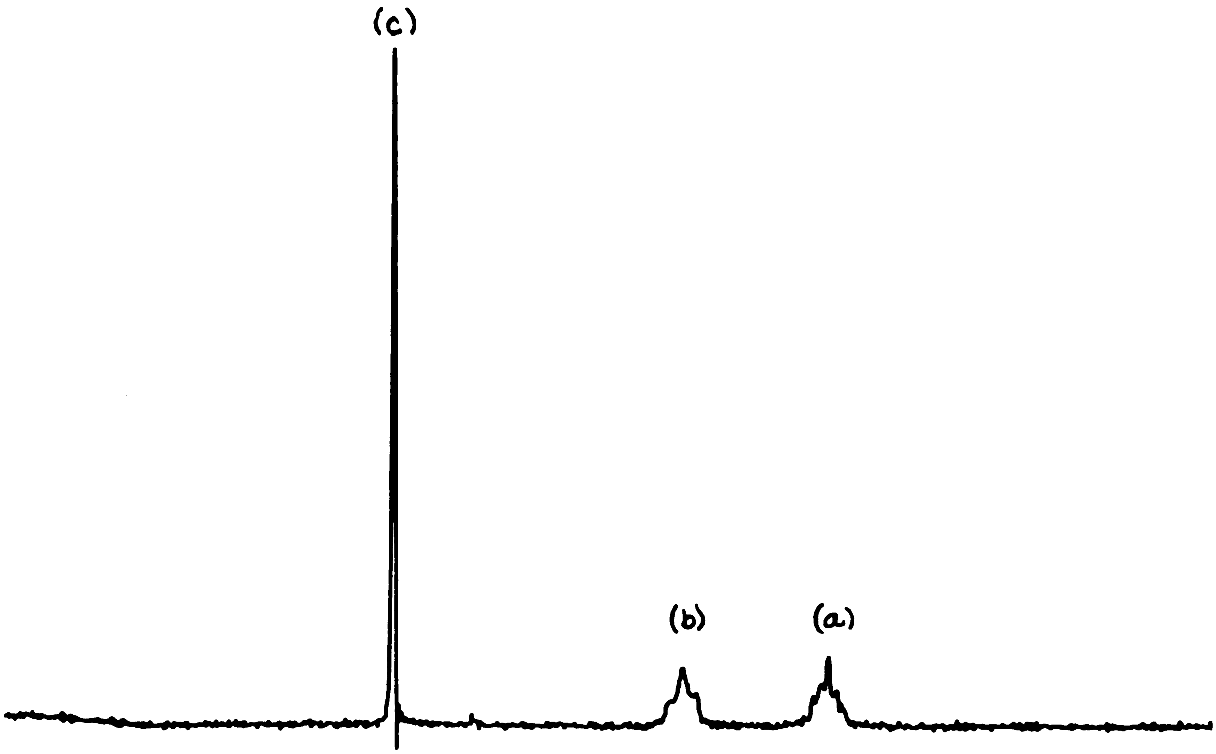
<u>Assignments (δ)</u>

a	2.46 (q)
b	3.26 (t)
c	5.40 (s)

a:b:c = 1:2:4

Spectrum 52. Nuclear Magnetic Resonance Spectrum of 2,2'-Tetramethylbis-1,3-dioxolenium Tetrafluoroborate (FSO_3H)



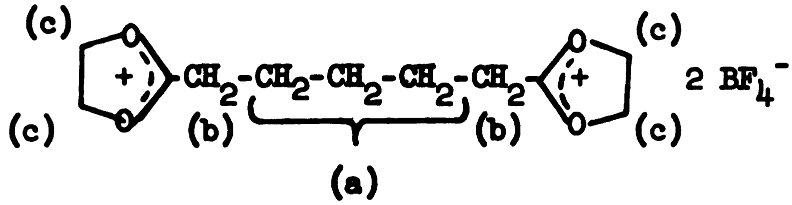


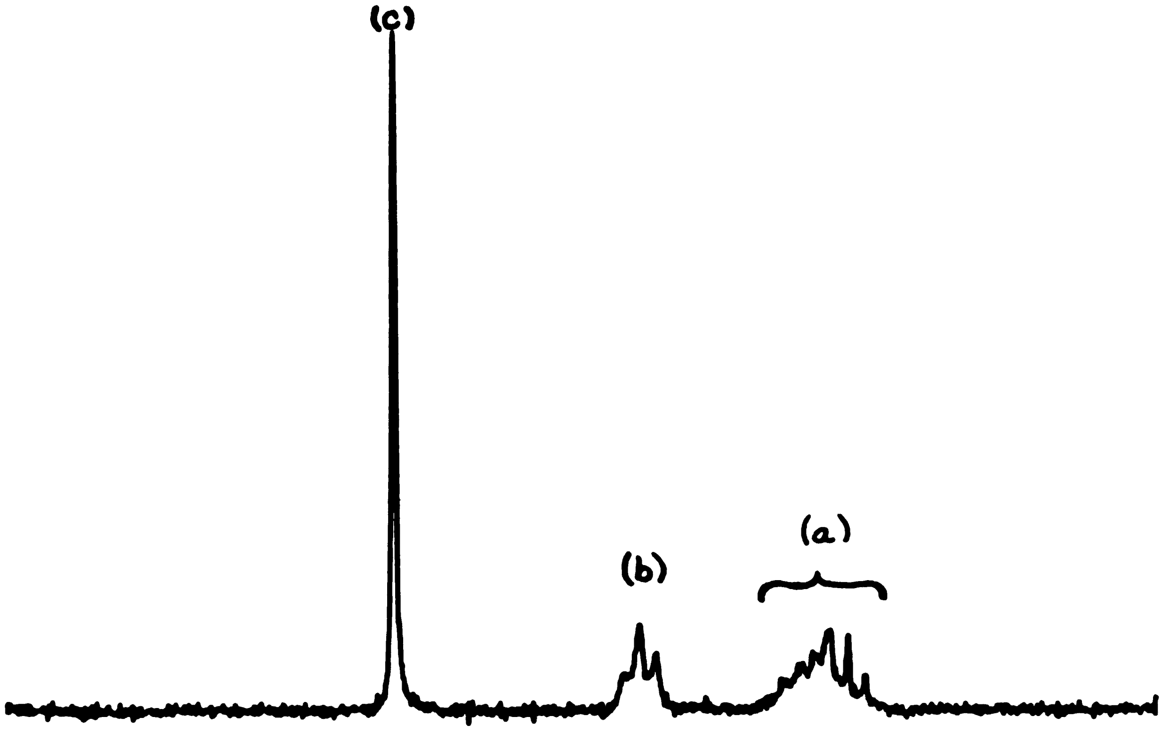
<u>Assignments (δ)</u>

a	2.02 (m)
b	3.10 (m)
c	5.36 (s)

a:b:c = 1:1:2

Spectrum 53. **Nuclear Magnetic Resonance Spectrum of 2,2'-Pentamethylenebis-1,3-dioxolenium Tetrafluoroborate (FSO_3H), (TMA·BF_4 Internal Standard)**



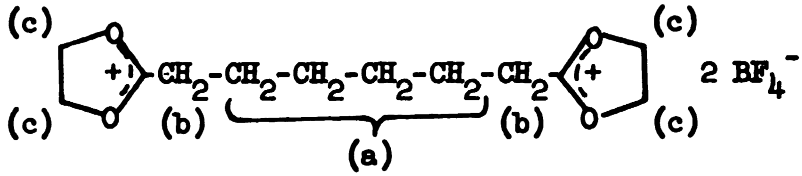


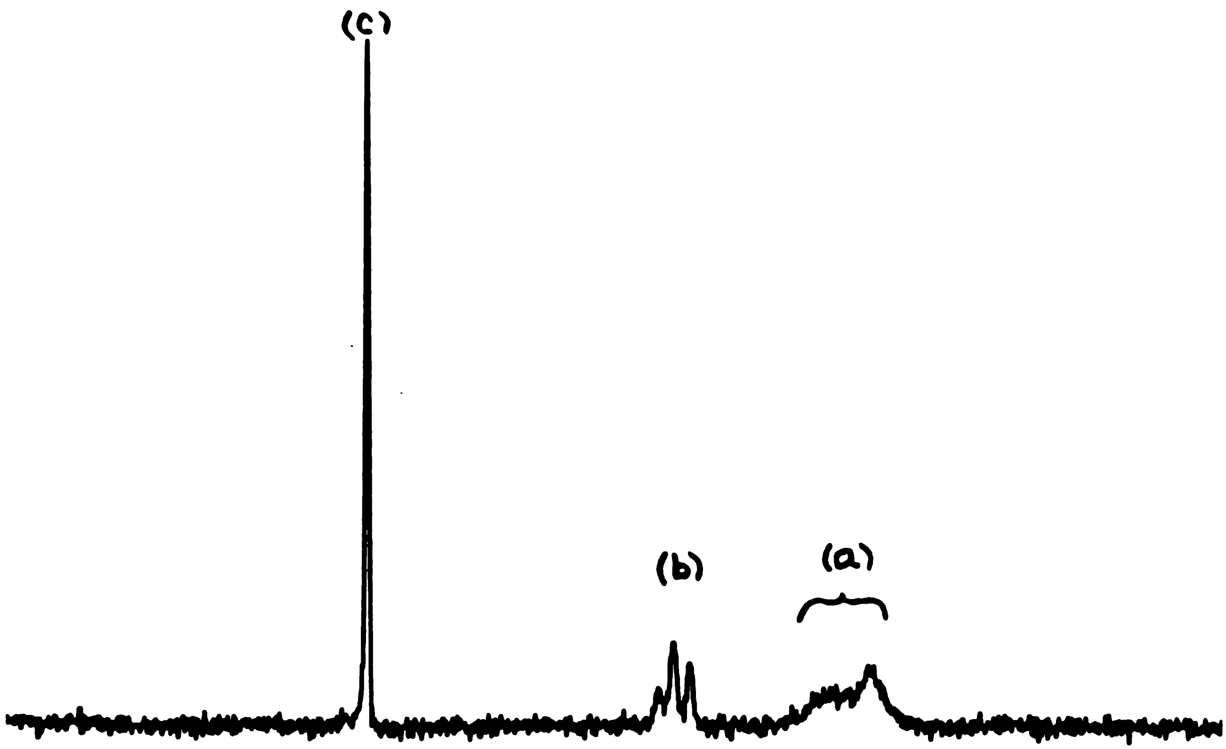
<u>Assignments (δ)</u>

a	1.36-2.36 (m)
b	3.06 (m)
c	5.34 (s)

a:b:c = 3:2:4

Spectrum 54. Nuclear Magnetic Resonance Spectrum of 2,2'-Hexamethylenebis-1,3-dioxolenium Tetrafluoroborate (FSO_3H), ($TMA\cdot BF_4$ Internal Standard)



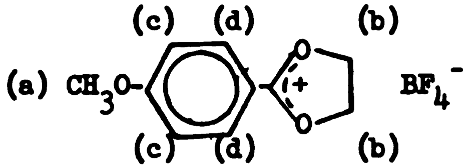


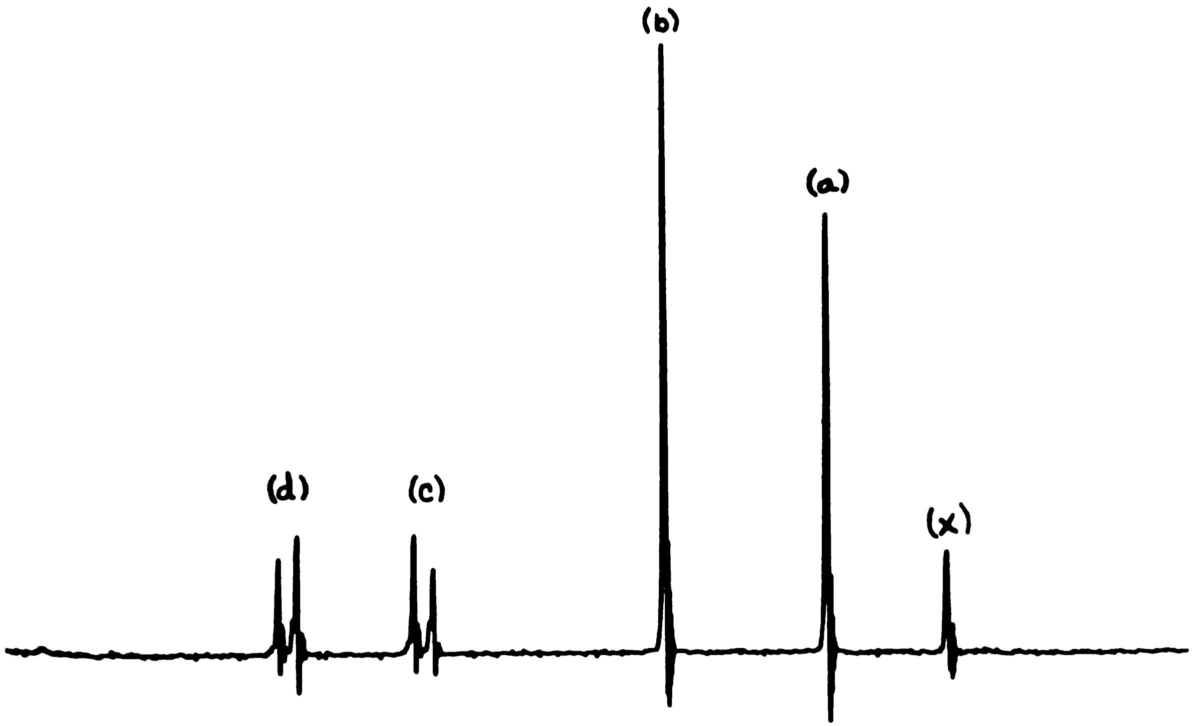
<u>Assignments (δ)</u>

a	1.35-2.20 (m)
b	3.05 (m)
c	5.32 (s)

a:b:c = 2:1:2

Spectrum 55. Nuclear Magnetic Resonance Spectrum of 2-(p-Methoxyphenyl)-1,3-dioxolenium Tetrafluoroborate (FSO_3H)



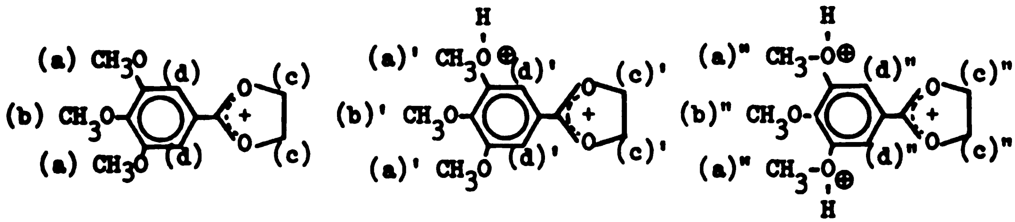


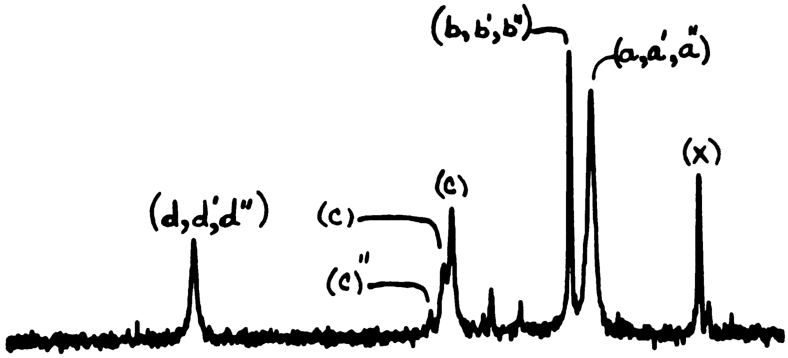
<u>Assignments (δ)</u>

x	3.10 ($TMA \cdot BF_4$)
a	4.08 (s)
b	5.33 (s)
c	7.26 (d); J_{cd} = 9.2 cps
d	8.31 (d)

a:b:c:d = 3:4:2:2

Spectrum 56. Nuclear Magnetic Resonance Spectrum of 2-(3,4,5-Trimethoxyphenyl)-1,3-dioxolenium Tetrafluoroborate (FSO_3H)



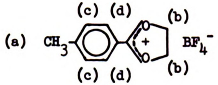


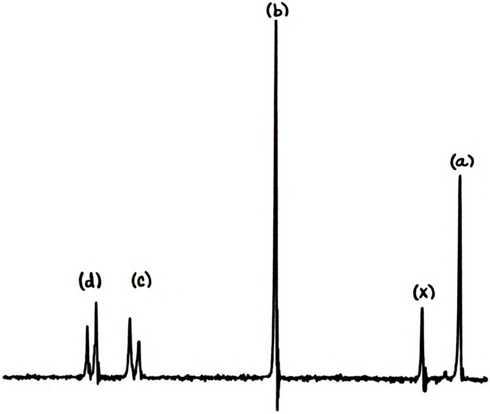
<u>Assignments (δ)</u>

x	3.10	($TMA \cdot BF_4$)
a,a',a"	4.09	(s)
b,b',b"	4.29	(s)
c	5.37	(s)
c'	5.46	(s)
c"	5.59	(s)
d,d',d"	7.72	(s)

(a,a',a" + b,b',b"):(c+c'+c"):(d,d',d") = ~9:4:2

Spectrum 57. Nuclear Magnetic Resonance Spectrum of 2-(p-Methylphenyl)-1,3-dioxolenium Tetrafluoroborate (FSO_3H)



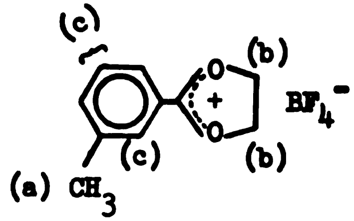


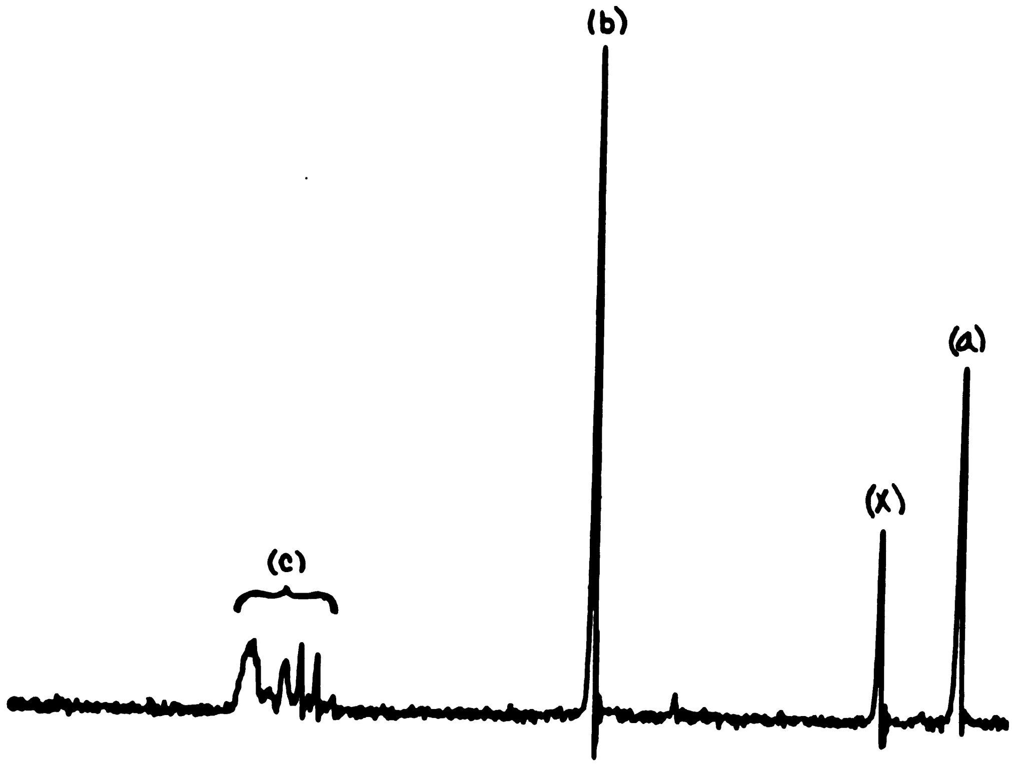
<u>Assignments (δ)</u>

x	3.10 (TMA·BF_4)
a	2.55 (s)
b	5.37 (s)
c	7.55 (d); J_{cd} = 8.5 cps
d	8.20 (d)

a:b:c:d = 3:4:2:2

Spectrum 58. Nuclear Magnetic Resonance Spectrum of 2-(m-Methylphenyl)-1,3-dioxolenium Tetrafluoroborate (FSO_3H)



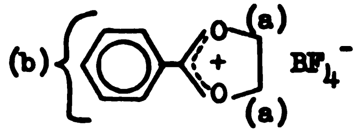


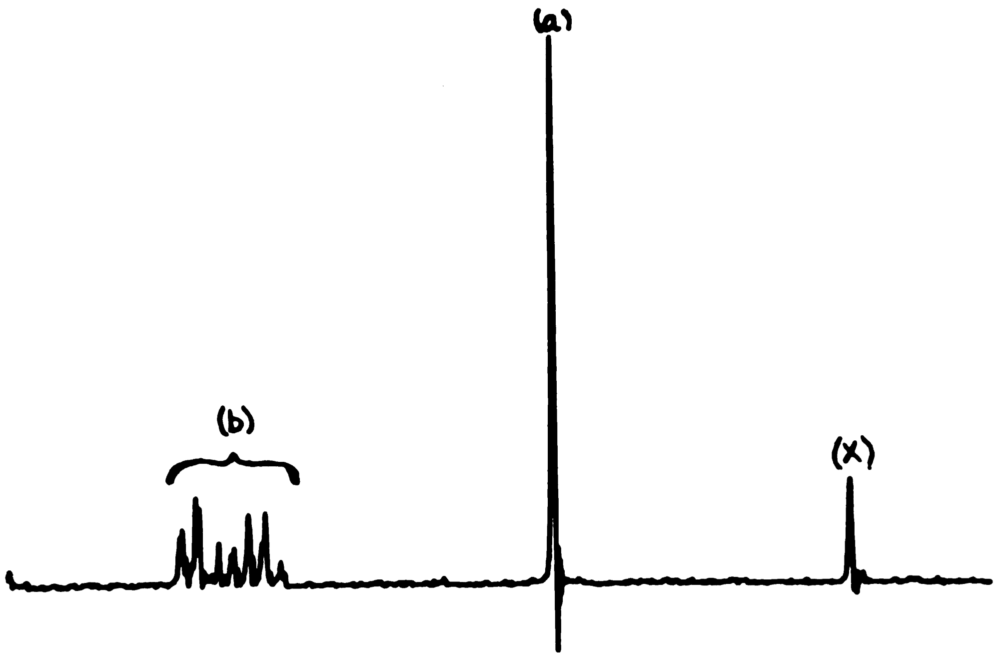
<u>Assignments (δ)</u>

x	3.10 ($TMA \cdot BF_4$)
a	2.47 (s)
b	5.40 (s)
c	7.55 - 8.47 (m)

a:b:c = 3:4:4

Spectrum 59. Nuclear Magnetic Resonance Spectrum of 2-(Phenyl)-1,3-dioxolenium Tetrafluoroborate (FSO_3H)

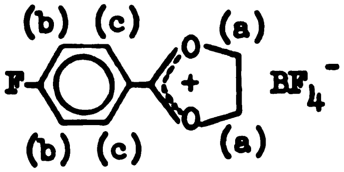


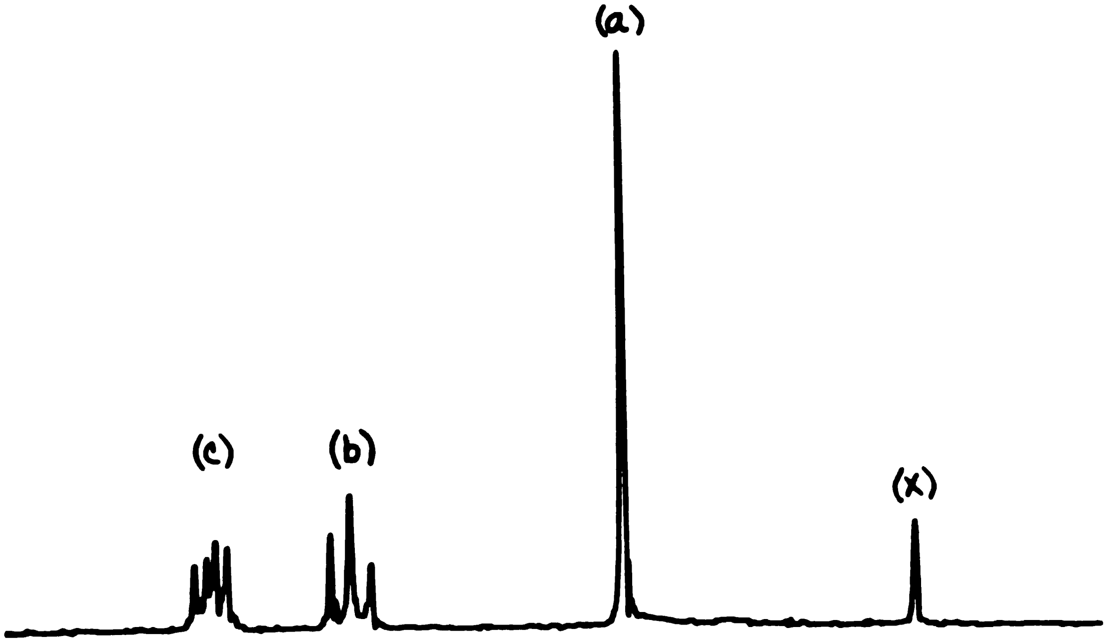


	Assignments (δ)
x	3.10 (TMA·BF_4)
a	5.42 (s)
b	7.55 - 8.47 (m)

a:b = 4:5

Spectrum 60. Nuclear Magnetic Resonance Spectrum of 2-(p-Fluorophenyl)-1,3-dioxolenium Tetrafluoroborate (FSO_3H)

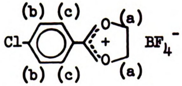


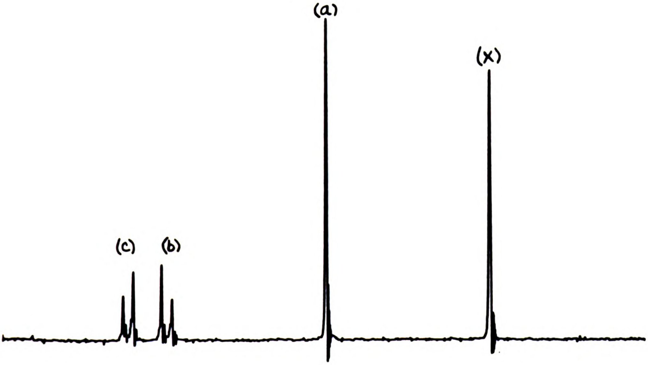


	<u>Assignments (δ)</u>
x	3.10 (TMA·BF_4)
a	5.42 (s)
b	7.42 (t)
c	8.41 (q)

a:b:c = 2:1:1

Spectrum 61. Nuclear Magnetic Resonance Spectrum of 2-(p-Chlorophenyl)-1,3-dioxolenium Tetrafluoroborate (FSO_3H)



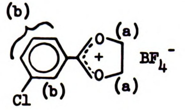


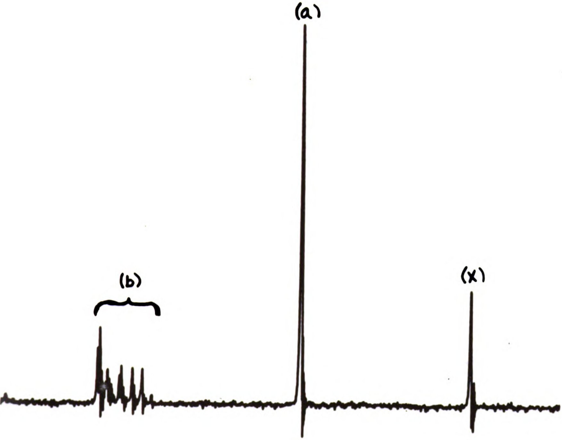
<u>Assignments (δ)</u>

x	3.10 ($TMA \cdot BF_4$)
a	5.43 (s)
b	7.71 (d)
c	8.25 (d)

a:b:c = 2:1:1

Spectrum 62. Nuclear Magnetic Resonance Spectrum of 2-(m-Chlorophenyl)-1,3-dioxolenium Tetrafluoroborate (FSO_3H)



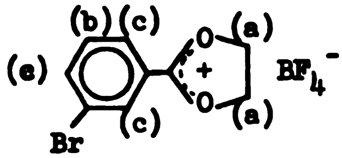


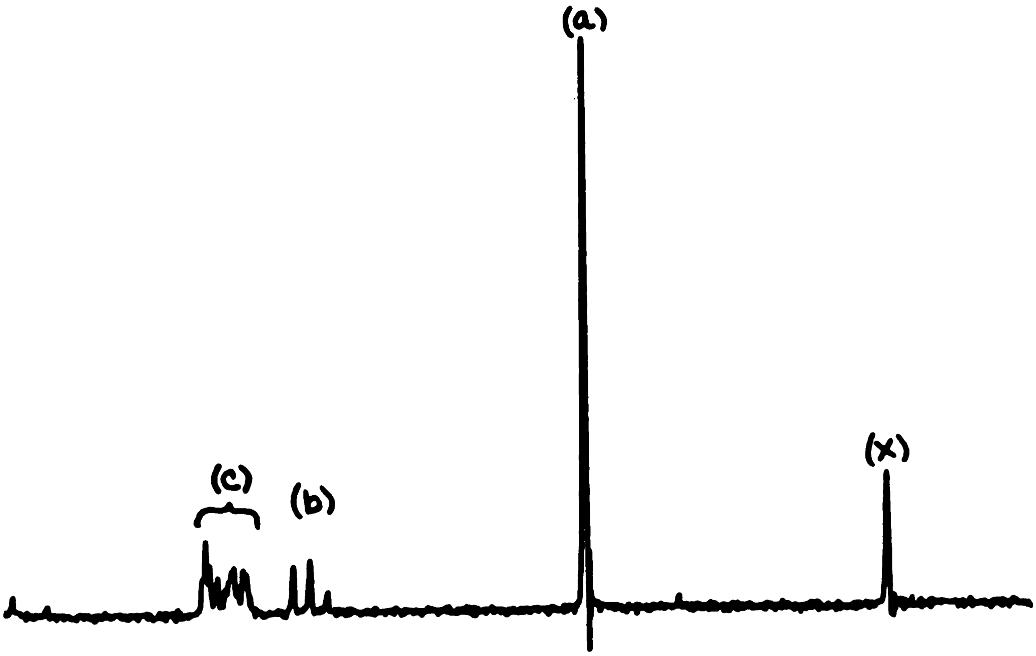
Assignments (δ)

x	3.10 ($TMA \cdot BF_4$)
a	5.44 (s)
b	7.52 - 8.32 (m)

a:b = 1:1

Spectrum 63. Nuclear Magnetic Resonance Spectrum of 2-(m-Bromophenyl)-1,3-dioxolenium Tetrafluoroborate (FSO_3H)



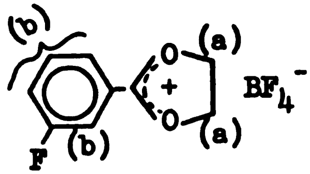


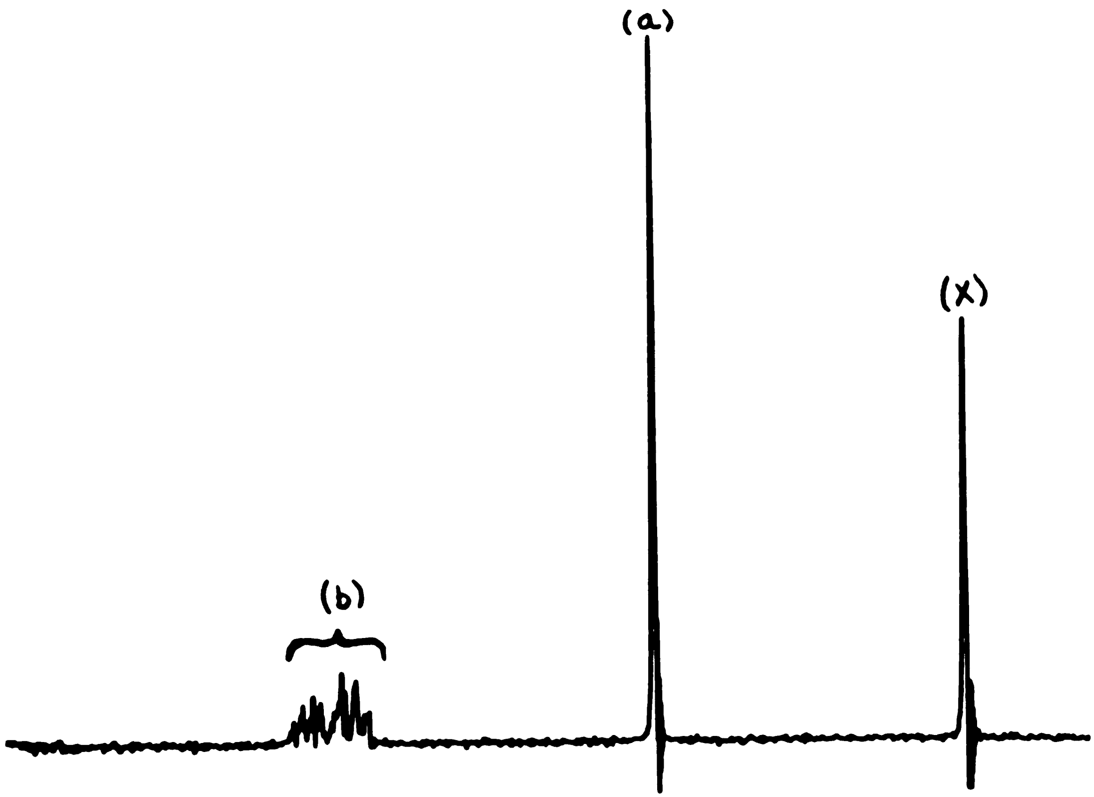
<u>Assignments (δ)</u>

x	3.10 ($TMA\cdot BF_4$)
a	5.47 (s)
b	7.62 (t)
c	8.04-8.49 (m)

a:b:c = 4:1:3

Spectrum 64. Nuclear Magnetic Resonance Spectrum of 2-(m-Fluorophenyl)-1,3-dioxolenium Tetrafluoroborate (FSO_3H)



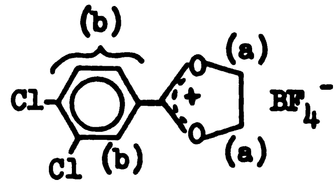


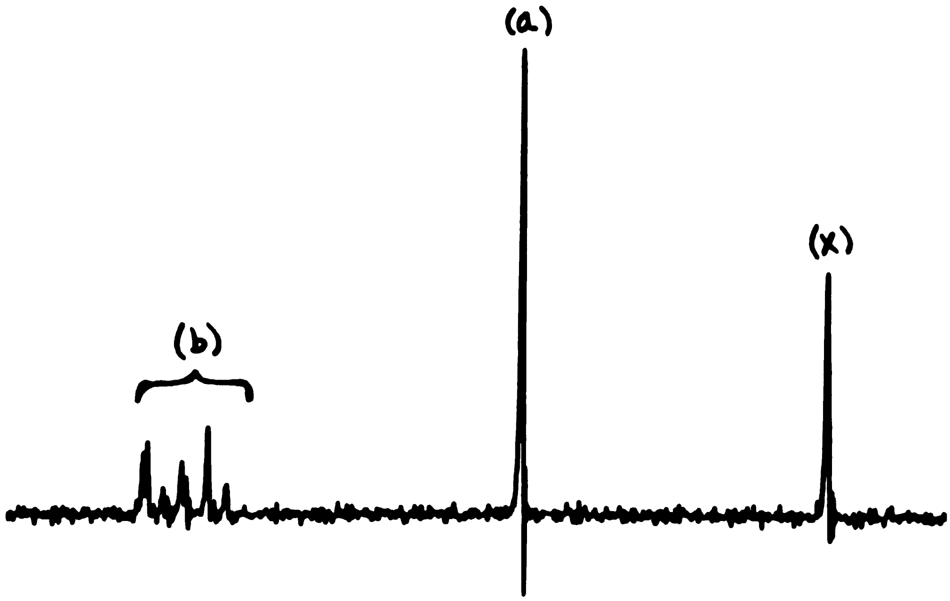
<u>Assignments (δ)</u>

x	3.10 (TMA·BF_4)
a	5.47 (s)
b	7.63—8.27 (m)

a:b = 1:1

Spectrum 65. Nuclear Magnetic Resonance Spectrum of 2-(3,4-Dichlorophenyl)-1,3-dioxolenium Tetrafluoroborate (FSO_3H)



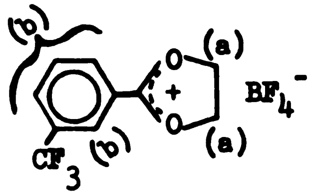


<u>Assignments (δ)</u>

x	3.10 (TMA·BF_4)
a	5.47 (s)
b	7.73 - 8.43 (m)

a:b = 4:3

Spectrum 66. Nuclear Magnetic Resonance Spectrum of 2-(m-Trifluoromethylphenyl)-1,3-dioxolenium Tetrafluoroborate (FSO_3H)

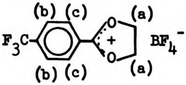


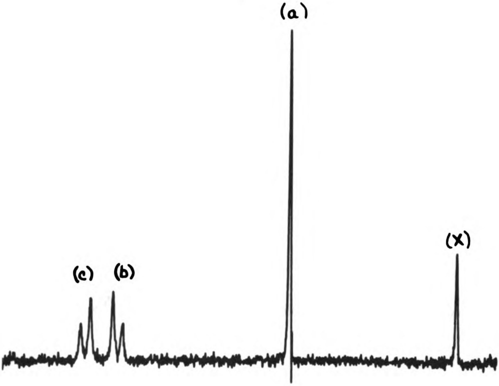
Assignments (δ)

x	3.10 (TMA·BF_4)
a	5.52 (s)
b	7.68 - 8.64 (m)

a:b = 1:1

Spectrum 67. Nuclear Magnetic Resonance Spectrum of 2-(p-Trifluoromethylphenyl)-1,3-dioxolenium Tetrafluoroborate (FSO_3H)



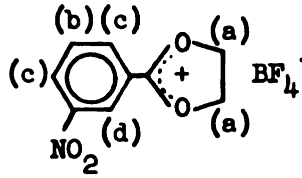


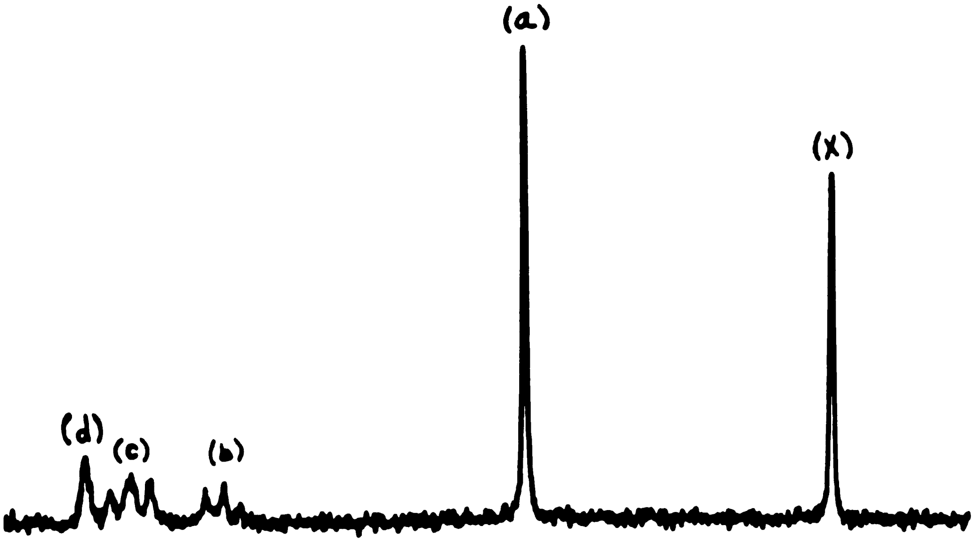
Assignments (δ)

x	3.10 ($TMA \cdot BF_4$)
a	5.52 (s)
b	8.01 (d); J_{bc} = 8.2 cps
c	8.47 (d)

a:b:c = 2:1:1

Spectrum 68. Nuclear Magnetic Resonance Spectrum of 2-(m-Nitrophenyl)-1,3-dioxolenium Tetrafluoroborate (FSO_3H)

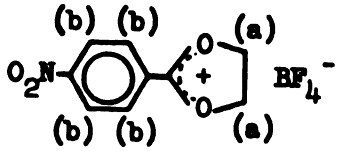


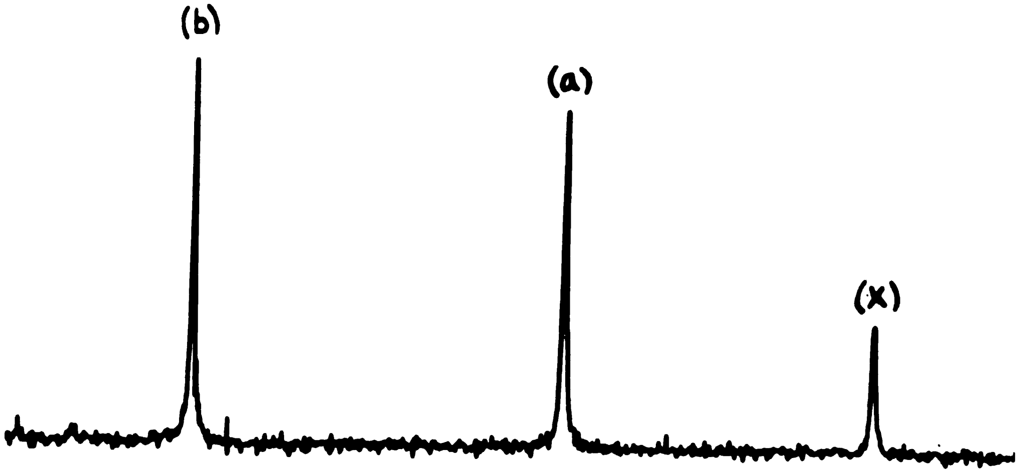


Assignments (δ)	
x	3.10 (TMA·BF_4)
a	5.58 (s)
b	8.07 (t)
c	8.80 (t)
d	9.17 (s)

a:b:c:d = 4:1:2:1

Spectrum 69. Nuclear Magnetic Resonance Spectrum of 2-(p-Nitrophenyl)-1,3-dioxolenium Tetrafluoroborate (FSO_3H)





<u>Assignments (δ)</u>

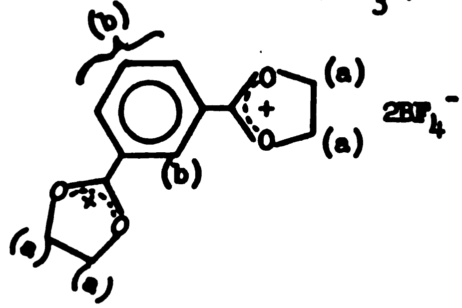
x 3.10 ($TMA \cdot BF_4$)

a 5.59 (s)

b 8.58 (s)

a:b = 1:1

Spectrum 70. **Nuclear Magnetic Resonance Spectrum of 2,2'-m-Phenylenebis-1,3-dioxolenium Tetrafluoroborate (FSO_3H)**



Assignments (δ)

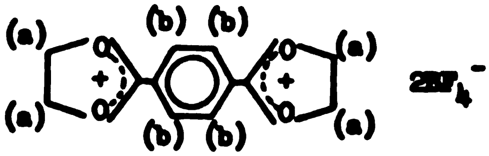
x   3.10 (TMA·BF_4)

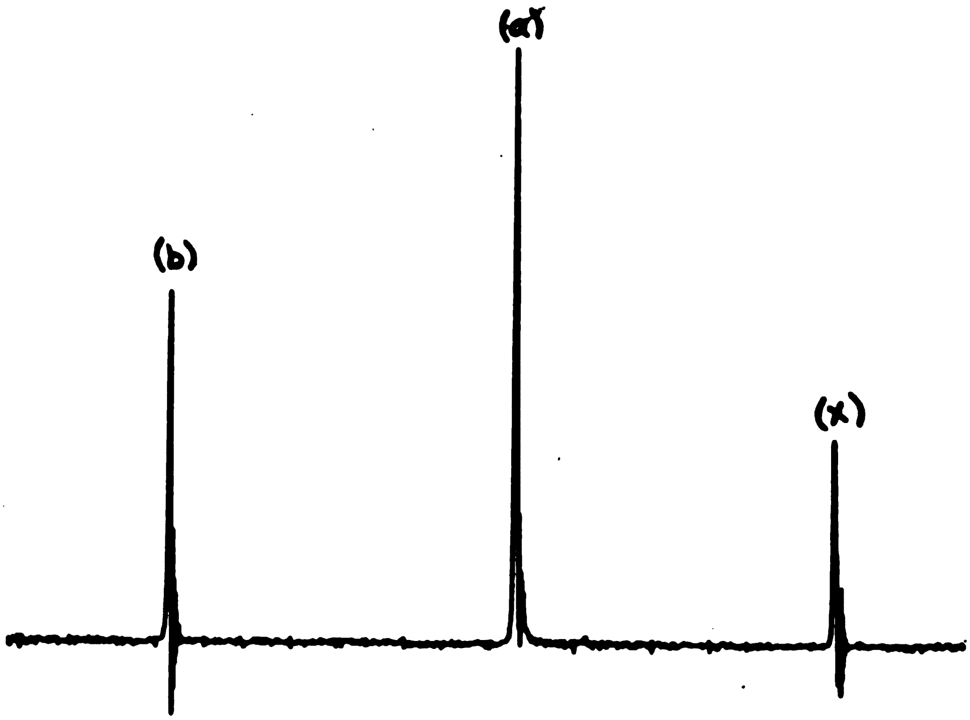
a   5.60 (s)

b   8.03 - 9.26 (m)

a:b = 2:1

Spectrum 71. Nuclear Magnetic Resonance Spectrum of 2,2'-p-Phenylenebis-1,3-dioxolenium Tetrafluoroborate (FSO_3H)

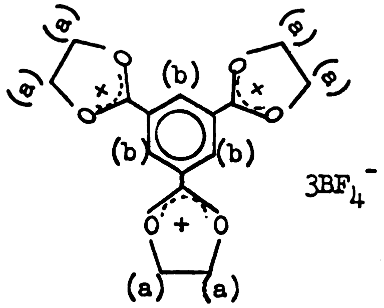


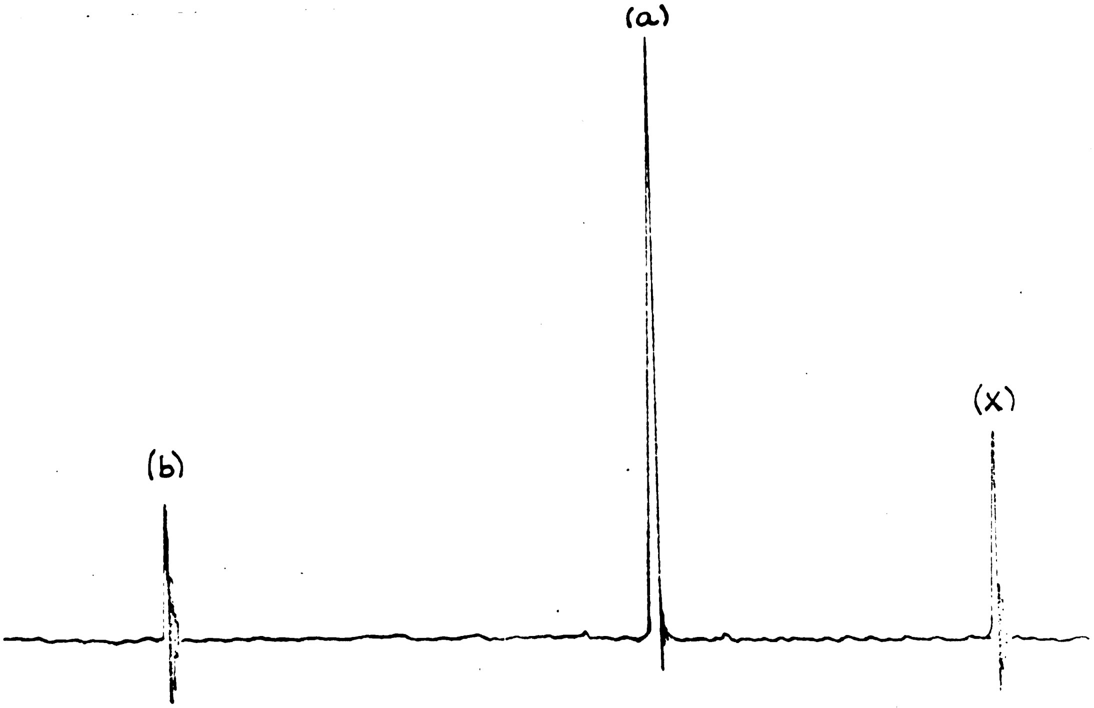


<u>**Assignments (δ)**</u>

x	3.10 ($TMA \cdot BF_4$)
a	5.63 (s)
b	8.62 (s)
	a:b = 2:1

Spectrum 72. Nuclear Magnetic Resonance Spectrum of 2,2',2"-Phenylenetris-1,3-dioxolenium Tetrafluoroborate (FSO_3H)





<u>Assignments (δ)</u>

x	3.10 ($TMA \cdot BF_4$)
a	5.77 (s)
b	9.58 (s)
	a:b = 4:1

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