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CONDENSATION AND CYCLIZATION

OF 1,3-DIKETONES

USING ORGANOHALOSILANES

Thomas F. Ignacz

A THESIS

in

The Department

of

Chemistry

Presented in Partial Fulfillment of the Requirements
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. Concordia University
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ABSTRACT

CONDENSATION AND CYCLIZATION

OF 1,3-DIKETONES

USING ORGANOHALOSILANES

Thomas F. Ignacz

The reaction of a β-diketone, or salt of a β-diketone, and an organohalosilane yields a substituted pyrylium salt. Reaction between 2,4-pentanedione, or the Tl or Na salts of 2,4-pentanedione, and $(CH_3)_2SiCl_2$ yield a water soluble, bright yellow compound, analyzing as the 2,4-dimethyl-6-(2'-hydroxy-1'-propenyl)pyrylium chloride. This compound has also been prepared using various other Lewis acids $(CH_3SiCl_3, (C_6H_5)_2SiCl_2,$ and $BCl_3)$. Reaction between $(CH_3)_2SiCl_2$ and 2,4-hexanedione, or 4,6-nonanedione, produces 2-ethyl-4,5-dimethyl-6-(2'-hydroxy-1'-propenyl)pyrylium chloride, or 2,4-di-n-propyl-5-ethyl-6-(2'-hydroxy-1'-pentenyl)pyrylium chloride, respectively. The pyrylium salts were characterized by standard nuclear magnetic resonance, infrared, ultraviolet-visible and mass spectral techniques.

The reaction of a fluorinated β-diketone and silicon tetrachloride yields a substituted 2H-pyran. Reaction between 1,1,1-trifluoro-2,4-pentanedione, 1,1,1-trifluoro-2,4-hexanedione, or 1,1,1-trifluoro-7-methyl-2,4-octanedione, and silicon tetrachloride produces 6-trifluoromethyl-4-methyl-2-trifluoroacetyl-pyranylidene (I), 6-trifluoromethyl-4-ethyl-3-methyl-2-trifluoroacetyl-pyranylidene, or 6-trifluoromethyl-4-isopentyl-3-isobutyl-2-trifluoroacetyl-pyranylidene, respectively. The structure of compound (I) was ascertained by nuclear magnetic resonance experiments, such as, double- and triple-resonance techniques, and ^{19}F and ^{13}C nmr spectroscopy. All of the pyrans were characterized by standard nuclear magnetic resonance, infrared, ultra-violet-visible and mass spectral techniques.

TO SIMONE

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ACKNOWLEDGEMENTS

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I.A.1. GENERAL —— SILICON

Carbon and silicon belong to Group IV B of the Periodic Table and, therefore, have similar electronic configurations, namely C $1s^2 2s^2 2p^2$, and Si $1s^2 2s^2 2p^6 3s^2 3p^2$. The valency shell contains the same number of electrons in each case, and as expected the normal covalency of silicon is four, the same as that of carbon. The normal orbital hybridization is sp^3. Based on this close resemblance to carbon, the chemistry of silicon is expected to be vast, and this is attested to by the numerous books published on the subject.[1-7] In addition, several reviews have appeared on many different aspects of silicon chemistry: cyclic organosilicon compounds,[8] silicon-nitrogen polymers,[9] the direct synthesis of alkylhalosilanes,[10] keto derivatives of Group IV elements,[11] the infrared spectra of trimethylsilyl compounds,[12] organosilicon-phosphorous compounds,[13] pi-bonding in Group IV B elements,[14] organo-element(Si, Ge, Sn, Pb) derivatives of keto-enols,[15] molecular rearrangements of organosilicon compounds,[16] silicon analogs of unsaturated compounds,[17] silylureas,[18] and silylurethanes.[19]

I.A.2. BONDING IN SILICON COMPOUNDS

The position of silicon in the second row of the Periodic Table should lead to great differences between the chemistry of carbon and silicon. The main difference is the availability of low lying d-orbitals to silicon and their possible involvement in bond formation. The existence of double-bond character in certain bonds and the ease of formation of five- and six-coordinated silicon complexes has generally been rationalized in terms of the d-orbital participation in the bonding[1]. These two important aspects will now be discussed in detail.

There are three types of pi-bonding in silicon chemistry: (p-p)π-bonding, (p-d)π-bonding, and (d-d)π-bonding[7]. Carbon is capable of forming stable compounds containing double and triple bonds. However, the isolation of stable silicon analogs of the olefins, ketones, etc., has not been realized (for example, see refs 1,4). Monomeric species, such as SiO[20] and $SiNH$,[21] have been described, but the reaction conditions may be considered to be rather drastic. Alkene-analogous compounds containing $Si=C$ bonds have frequently been postulated to explain reaction mechanisms[22-25] but definite proof of these short-lived intermediates was obtained only recently from pyrolysis reactions[26,27] and from photochemical experiments[28,29]

Several explanations have been advanced for the failure of silicon to form a stable (p-p)π-bond with

carbon, nitrogen, or oxygen. Douglas and McDaniel[30] have proposed that for the larger Si atom the (p-p) π-orbital overlap is less favorable because of the larger and more diffuse nature of the p-orbitals.
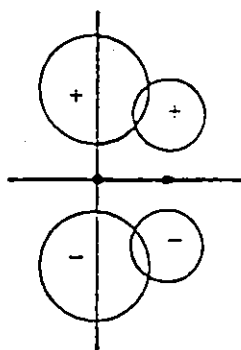
p(Si) p(C)

Pitzer,[31] on the other hand, suggested that repulsions between the inner electron shells prevent the atoms from approaching one another to achieve the multiple bond.

The existence of Si≡C (p-p) π-bonds may depend on bond polarities which can be very great in some cases. These bond polarities arise from the differences in electronegativity[32] between the participating elements, and thus lead to unequal electron distributions, especially in the readily polarizable π-system.[33] Depending on the elements involved, varying contributions of the resonance hybrid (B) to the ground state of the π-bonded molecules must be expected. Theoretical calculations[33] indicate that there is a possibility of the Si≡Si (p-p) π-bonded moiety being isolated.

These explanations have been criticized,[34-38] and new theories have appeared[39-41] in an attempt to explain this

$$Si{=}C \rightleftarrows \overset{+}{Si}{-}\overset{-}{C:}$$
$$(\underline{A}) \qquad\qquad (\underline{B})$$
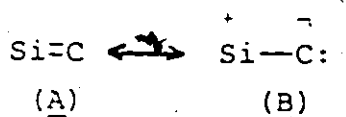
inability of silicon to form stable (p-p)π-bonds. The theory currently accepted for the absence of (p-p)π-bonding in silicon chemistry indicates that formation of two σ-bonds is more favorable than one double bond.[42] In other words, there is a stronger tendency to form polymers rather than unsaturated monomers.

The participation of d-orbitals in bonding for the second row elements has been postulated for many years.[43,44] Several reviews[1,34,35,38,45] of this concept pertaining to silicon chemistry have appeared. There is much evidence for the reality of (p-d)π-bonding in silicon chemistry[1]: (a) the planar structure of $(SiH_3)_3N$;[46] (b) the large Si-O-Si bond angles in siloxanes;[47,48] (c) bond shortening below the covalent radii in Si-O and Si-X (X$\equiv$halogen) bonds;[49-52] and (d) dipole moment measurements.[53,54]

The third type of π-bonding involves the d-orbitals of silicon and, usually, although not always, the d-orbitals of a transition metal. The filled d-orbitals of the transition metal overlap with the vacant d-orbitals of silicon appear to produce the multiple-bond character in the Si-M bond of transition metal derivatives, as evidenced from infrared spectral studies.[55,56] Further indication of a (d-d)π-interaction comes from structural determinations on

a number of these compounds.[57] The shortening of the Si-M bond relative to the sum of the appropriate atomic radii has been taken as indicative of a (d-d)π-interaction. The major difficulty encountered appears to be the problem of obtaining sets of values for the radii of the transition metals; as yet, no one set of values is generally accepted.[57,58]

The stereochemistry usually exhibited by simple molecular silicon compounds is tetrahedral. The penta-coordinate silicon complexes, if they are formed, would presumably exhibit sp^3d hybridization and a trigonal bi-pyramidal configuration.[1]
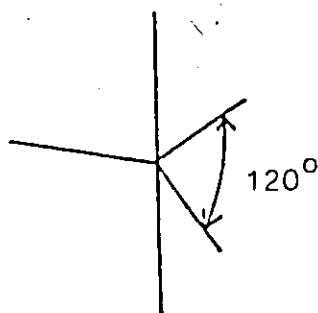
Investigation into the stereochemistry of five-coordinate silicon compounds has led to some considerable advances in recent years.[59-62] A major complication encountered in five-coordinate silicon chemistry is determining whether a true five-coordinate species is present. While the stoichiometry may indicate a five-coordinate species, as for example, $SiH_3I \cdot NMe_3$ or $SiF_4 \cdot NMe_3$, in reality the ionic $(SiH_3NMe_3)^+ I^-$ [63] or the halogen-bridged structure $SiF_4 \cdot NMe_3$[64] is present. Silicon complexes that have been assigned trigonal-bipyramidal

structures have included neutral, as well as cationic and anionic species. Some examples are: $SiCl_4NMe_3$,[65] $SiH_3 \cdot C_5H_5N$,[66] and SiF_5^-.[67] Five-coordinate silicon species have also been postulated as intermediates in numerous reactions.[4,34,59]

The octahedral six-coordinate chemistry of silicon is better established than the five-coordinate chemistry.[65] There are known examples of neutral, anionic, and cationic species. Perhaps the best known example of silicon using its d-orbitals is in the SiF_6^{2-} anion. The X-ray crystallographic analysis of this anion has confirmed that six fluorine atoms are octahedrally coordinated to silicon with sp^3d^2 hybridization.[68]
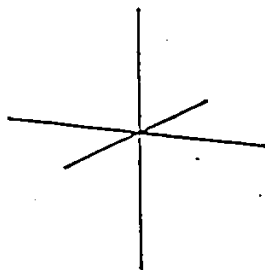
The corresponding heavier halides, SiX_6^{2-} (X=Cl, Br, or I), are unknown, and has been attributed to the small size of the silicon atom,[1] to the lower electronegativities of the heavier halides,[4] or to a combination of both.

There are many six-coordinated silicon complexes containing Si-O bonds, particularly when a tetravalent silicon compound, for example $SiCl_4$, is reacted with a β-diketone or a β-ketoester. A very well known reaction is that between $SiCl_4$ and 2,4-pentanedione ($CH_3COCH_2COCH_3$,

Hacac) to give the hexacoordinated ion pair $Si(acac)_3^+HCl_2^-$.[69]
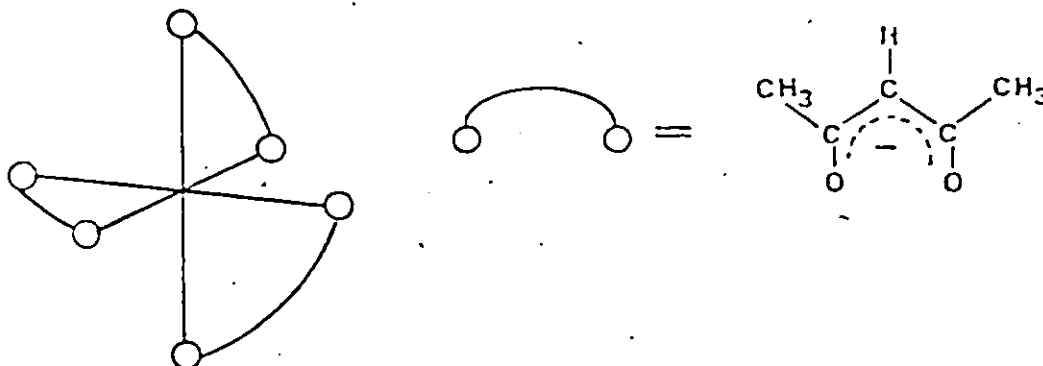
The structure of the cation was confirmed by infrared spectral studies[70] and by resolution into optical enantiomers through the dibenzoyl-d-hydrogen tartrate salt.[71] The organosilicon compounds $PhSiCl_3$ and $MeSiCl_3$ also react with 2,4-pentanedione to give the corresponding six-coordinate silicon chelates, $PhClSi(acac)_2$ and $MeClSi(acac)_2$, respectively.[70] However, when dialkyl- or trialkylhalosilanes (for example, Me_2SiCl_2 or Me_3SiCl) react with 2,4-pentane-dione, only the O-silylated non-chelated enols are obtained.[70]
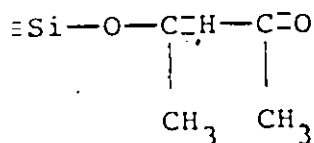
I.A.3. SILICON COMPOUNDS IN SYNTHESIS

The importance of silicon compounds has been demonstrated in their usefulness as precursors in the preparation of organic compounds. Ketones may be formed from vinylsilanes with an epoxide as an intermediate.[72] In reaction Scheme 1, I is converted into the olefin II by a Peterson reaction.[73] Compound III is produced by the addition of alkyl-lithium compounds, R'Li. Epoxidation of IV and hydrolysis of V results in the formation of the required ketone.

$$(\equiv Si)_3 CLi \xrightarrow{CH_2O} (\equiv Si)_2 C = CH_2 \xrightarrow{R'Li}$$
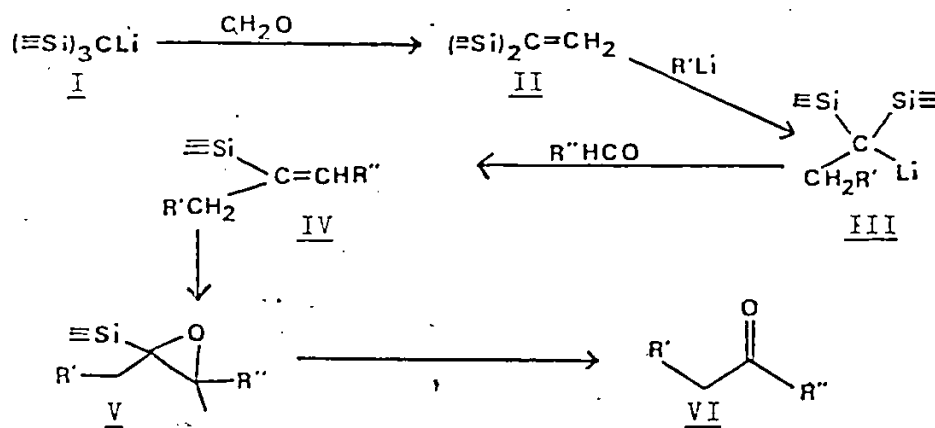
Scheme 1

In a recent article, Conia[74] has discussed the conversion of enones to cyclobutanones and cyclopentanones (Scheme 2). An improved[75] Simmons-Smith reaction[76] was described in which a shorter reaction time and higher yields resulted. The cyclopropanation of VIII was carried out via

a modified Simmons-Smith[75] reaction to give the 1-siloxy-1-vinylcyclopropanes of type IX. An acid-catalyzed ring expansion[77] of IX yields the cyclobutanone X. On heating the vinylcyclopropane IX, the cyclopentanone silyl enol ether XI is formed[78] which on acidification[77] yields the cyclopentanone XII.
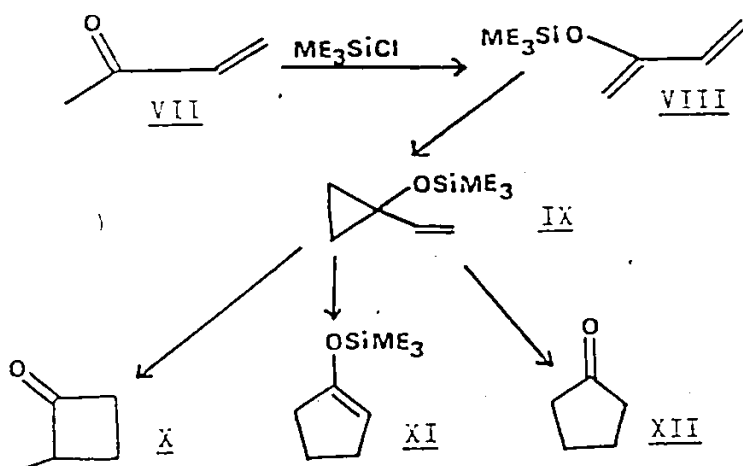
Scheme 2

These are but two examples that demonstrate the potential usefulness of silanes in the synthesis of organic compounds; other uses may be found in the literature (for example, see refs 79,80).

I.B.1. GENERAL — PYRYLIUM SALTS AND PYRANS

As part of the continuing studies[81] in this laboratory
on configurational rearrangement phenomena, investigations
have been carried out on the stereochemistry and lability of
organotin(IV), organogermanium(IV), and organosilicon(IV)
β-diketonate complexes.[82] Studies into the latter complexes
were concentrated on $PhClSi(acac)_2$, $MeClSi(acac)_2$,
$Ph_2Si(acac)_2$, and $Me_2Si(acac)_2$, where acac is the 2,4-
pentanedionate anion. Not surprisingly, such efforts were
successful only for the phenylchloro- and methylchloro-
silicon compounds; the latter white complex apparently
decomposed within 30 min of preparation of the nmr sample,
though great care was taken to maintain anhydrous conditions.
The decomposition was observed as a change in color from a
colorless solution to a deep reddish-brown solution. This
color change was also observed after 5 min from the start
of the synthesis of $Ph_2Si(acac)_2$, and almost immediately
for the corresponding dimethylsilicon complex. Depending on
the β-diketone used in the synthesis, a pyran or a pyrylium
salt may be obtained.[83] Further investigation into these
reactions may result in the synthesis of new, as yet
unattainable, oxygen heterocycles.

I.B.2. ELECTRONIC STRUCTURE

The replacement of a -CH= group in benzene with N, O^+, or S^+ produces six-membered heteroaromatics which are iso-electronic with benzene. The structure of pyridine and benzene are analogous, being related by the substitution of a -CH= by -N=. The principal differences between pyridine and benzene are:[84]

    a) the irregular hexagonal geometry caused by the shorter carbon-nitrogen bonds;[85]

    b) the basicity of pyridine due to the unshared electron pair on the nitrogen atom,[86] and

    c) the strong permanent dipole moment in pyridine.[87]

The principal contributing forms of the resonance hybrid are the Kekulé structures XIII and XIV, but other structures XV-XVII may also be important.[88]

XIII   XIV   XV   XVI   XVII
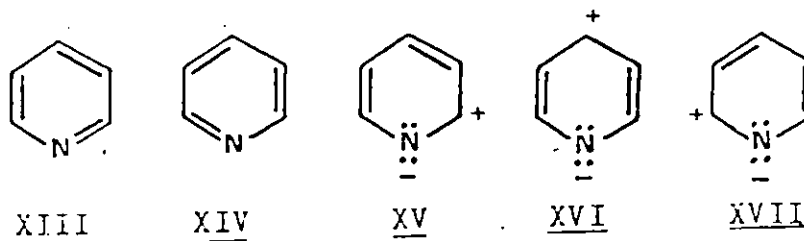
To summarize the electronic properties of pyridine, it has been suggested[84] that in pyridine the dipole is a result of the inductive and mesomeric effects working in the same direction, and that C-2, C-4, and C-6 carry the

positive fractional charges.

$$\longrightarrow \quad 2.2 \text{ D}$$
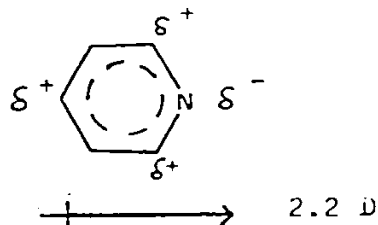
The pyridinium ion is formed by the electrophilic addition to the pyridine nitrogen. The pyridinium cation is isoelectronic with benzene, and still contains very much aromatic character.
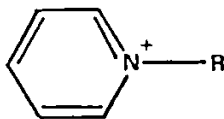
The system is positively charged, a consequence of the higher nuclear charge on nitrogen. The electronic structure of the pyridinium cation is similar to that of pyridine, but the positive fractional charges carried on C-2, C-4, and C-6 are much higher in the pyridinium cation than in pyridine.[84]

Since the covalency of oxygen is usually two, unlike nitrogen, it cannot replace a -CH= group in an aromatic ring. The compounds produced would be the pyrans XVIII

or <u>XIX</u>.[89] However, two series of aromatic derivatives may

be formed from these pyrans ——— the pyrylium salts <u>XX</u>

and the pyrones <u>XXI</u> and <u>XXII</u>.

<u>XVIII</u>   <u>XIX</u>   <u>XX</u>   <u>XXI</u>   <u>XXII</u>
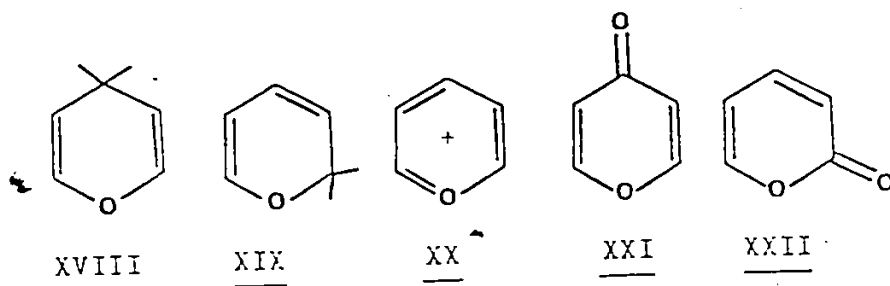
The pyrylium salts may be formed by the dehydrogenation

of a pyran by removal of a hydride anion from the methylene

group. The lone-pair electrons on the oxygen atom would

then replenish this deficiency of the carbon atom from which

the hydride ion was abstracted, and would result in an

aromatic ring with six π-electrons. Again, the Kekulé

structures <u>XXIII</u> and <u>XXIV</u> are the major contributors to

the pyrylium cation hybrid.[90]

<u>XXIII</u>   <u>XXIV</u>   <u>XXV</u>   <u>XXVI</u>   <u>XXVII</u>
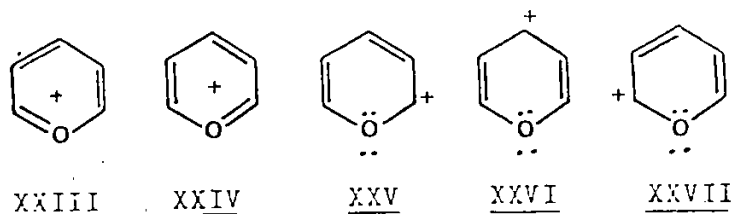
In the pyrylium cation, the formal positive charge is more strongly delocalized on the carbon (C-2, C-6) than it is in the pyridinium cation.[84] Oxygen tolerates less of a positive charge than the nitrogen atom because of the more electronegative nature of the oxygen atom.[32] Thus, in the pyrylium cation the 2- and 4-ring carbons are much more electrophilic than the corresponding ring carbons of the pyridinium cation.[84]

The fact that pyrylium ions are cyclic conjugated carboxonium ions with a π-electron sextet, makes them particularly stable when substituents occupy the reactive positions (C-2, C-4, C-6). Thus, most of the known pyrylium salts synthesized have substituents in the 2, 4, and 6 positions.

I.B.3. GENERAL SYNTHESIS OF PYRYLIUM SALTS

Most pyrylium salts are produced by the dehydration of the conjugate acids of cis-2-ene-1,5-diones.[91] Balaban and co-workers[91] have classified the synthesis of pyrylium salts according to the number of building blocks needed to form the ring in a one-step process. A one-component synthesis, B, has a pyran B1 or a 1,5-enedione B2 ready for reaction to produce the pyrylium cation. In a two-component synthesis, C, the five-membered carbon chain can be formed in two ways: a 4+1, C1, or a 3+2, C2. The three-component synthesis

involves the reaction of a 1+2+2, D1 and D2, or a 1+1+3, D3, type to produce a five-membered carbon chain.
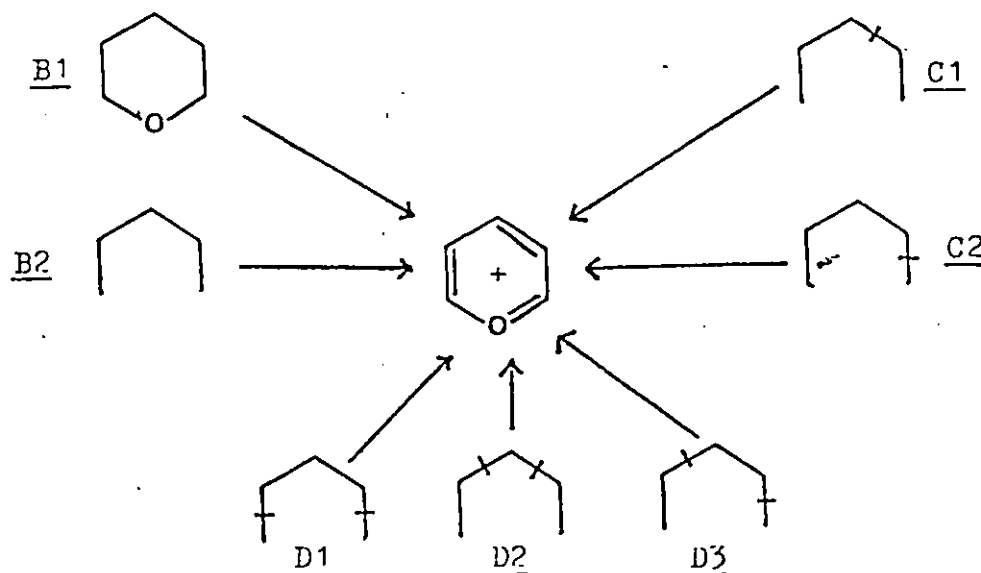
The general methods just described for preparing oxygen heterocycles are the 'usual' syntheses. However, recently, other more exotic syntheses have been described. These will be discussed chronologically.

The acid catalysis of 1,2- and 1,3-diketones has yielded a novel 2,4,6,8-tetraoxatricyclo 3.3.1.0^{3,7} nonane.[92] The reaction between 2,3-butanedione and 2,4-pentanedione in the presence of 10% sulfuric acid for 1-3 days at 0-25° resulted in the formation of 1,3,5,7-tetramethyl-2,4,6,8-tetraoxatricyclo 3.3.1.0^{3,7} nonane (Scheme 3, XXVIII) ($R^I = R^{II} = R^V = R^{VII} = CH_3$). Several other substituted products

were obtained with different starting diketones and
reaction times. The generality of this reaction may be
seen from Table 1.
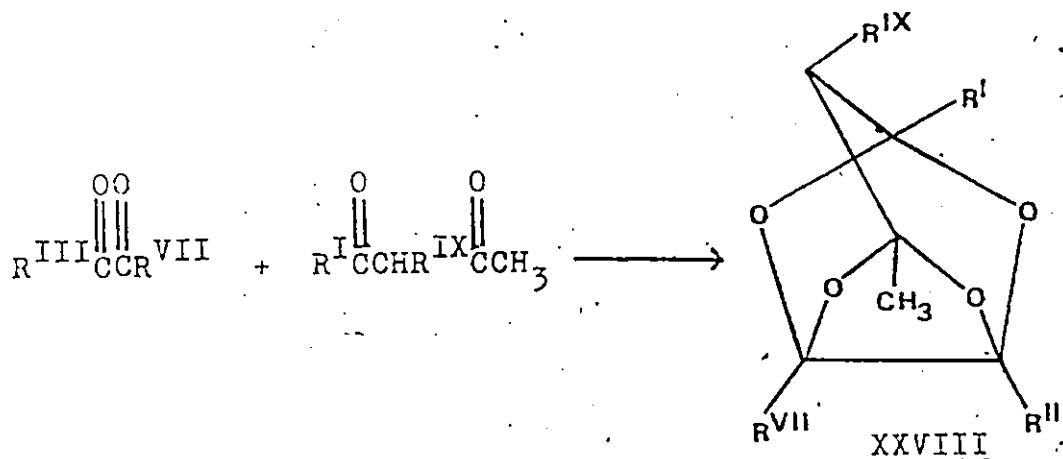
Scheme 3

By way of a solvolysis reaction, dilute solutions
of 2,4-pentanedione and tungsten(VI)oxytetrachloride yield
$WOCl_3(CH_3CO)_2CH$;[92] similarly, $MoOCl_4$ is reduced to yield
$MoOCl_3(CH_3CO)_2CH_2$.[94] However, when undiluted 2,4-pentanedione
is reacted with the same compounds, namely $WOCl_4$ and $MoOCl_4$,
new products are formed.[95] Reaction of undiluted 2,4-
pentanedione with $MoOCl_4$ results in the dimerization of
two molecules of the β-diketone to form XXIX.
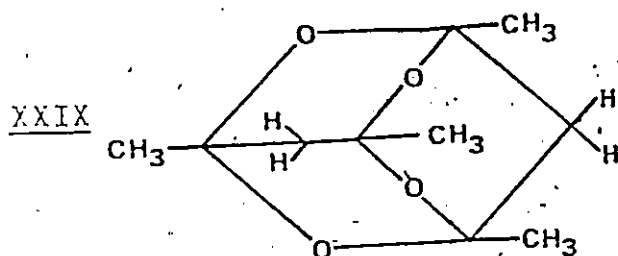
1,3,5,7-tetramethyl-
2,4,6,8-tetraoxa-
adamantane

Table 1. Generality of the reaction between 1,2-diketones and 1,3-diketones in the presence of acid.[92]

R^I	R^{III}	R^{VII}	R^{IX}	% Yield
CH_3	H	H	H	3
CH_3	H	CH_3	H	40
CH_3	CH_3	CH_3	H	80
CH_3	CH_3	CH_3	CH_3	70
CH_3	CH_2Cl	CH_3	H	75
CH_3	CH_2Br	CH_2Br	H	50
CH_3	CH_3	CH_3	$CH_2CH=CH_2$	23
CH_3	CH_3	CH_3	$CH_2C\equiv CH$	31
$i-C_4H_9$	CH_2Br	CH_3	H	12
CH_3	CH_3	CH_3	$CH_2CO_2CH_3$	10
CH_3	CH_3	CH_3	$CH_2CH_2CO_2CH_3$	60

In a similar manner, $WOCl_4$ has been reported to react with undiluted 2,4-pentanedione to yield the 2,4,6-trimethyl-3-acetylpyrylium cation XXX (Scheme 4) and the dichloro-dioxo-2,4-pentanedionatotungsten(VI) XXXI. In a recent publication Fowles and co-workers[96] gave no information as to the purpose of the Lewis acid in the production of the pyrylium cation XXX. The authors have proposed that the hydrogen chloride liberated in the reaction between $WOCl_4$

and Hacac resulted in the formation of the pyrylium cation. Isolation of the pyrylium salt was accomplished by addition of metal halides (Lewis acids) with the purpose of forming large anions.

$$WOCl_4 \; + \; 3Hacac \longrightarrow \left[WO_2Cl_2(acac)\right]^- + \; 2HCl \; + \; H_2O$$

XXXI

+

XXX
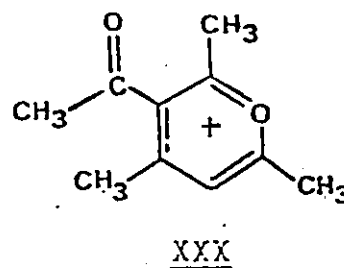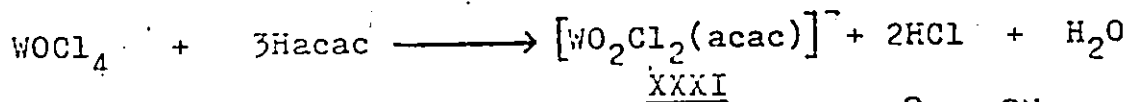
Scheme 4

The reaction of fresh platinum tetrachloride and freshly distilled, undiluted 2,4-pentanedione results in a pyrylium cation[97] identical to XXX (Scheme 4). The counterion in this case was the $PtCl_6^{2-}$ species.

The last reaction concerning the synthesis of pyrylium salts is based on platinum. By reacting 1,1-dimethylcyclopropane with chloroplatinic acid in anhydride solvents (for example, acetic anhydride) for 3 hr results in the formation of a pyrylium salt[98] (Scheme 5). The reaction was shown to proceed via diacylation of the cyclopropane ring to produce the 1,5-diketone. Dehydration and ring closure produce the pyrylium cation.

$$H_2PtCl_6 \; + \; (RCO)_2O \longrightarrow \overset{+}{RCO}$$
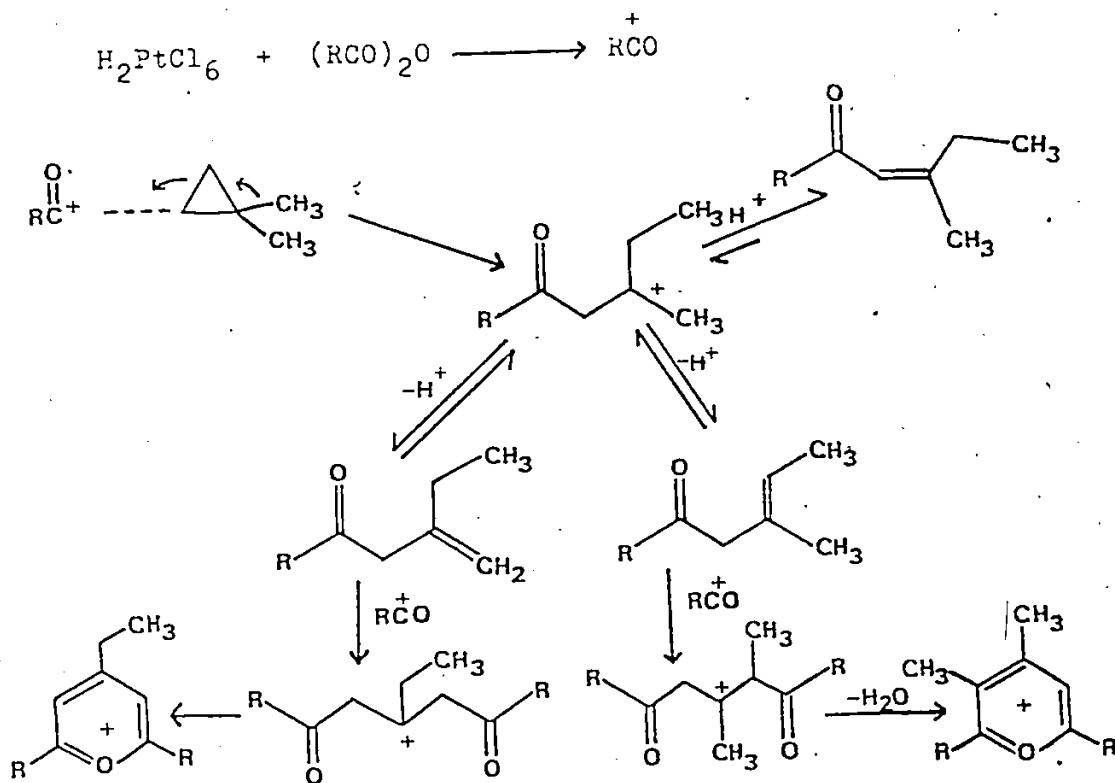
Scheme 5

In a subsequent paper, Earnest and Brown[99] prepared several alkyl substituted pyrylium salts, in a manner analogous to the synthesis described above. They have expanded on their mechanism and demonstrated the role of platinum in the reaction (Scheme 6). Thus, the reaction sequence is: (a) initial activation by insertion of platinum to the least-substituted cyclopropane ring bond; (b) the acylation of the platinum-bonded carbon by the anhydride solvent; (c) proton loss to yield a β,γ-unsaturated carbonyl;

(d) a second acylation to give a 1,5-diketone; and finally

(e) ring closure.
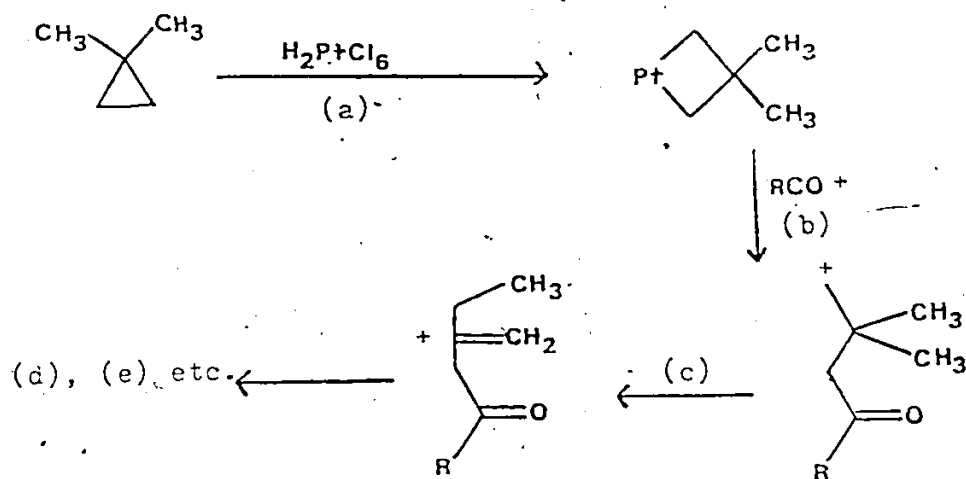
Scheme 6

II. EXPERIMENTAL

II.A. REAGENTS AND SOLVENTS

The chemicals used in the reactions are listed in Table 2. Generally, the chemicals were used as received from the supplier without further purification. The β-diketones were freshly distilled prior to use. Dichloromethane and practical hexanes were dried by refluxing over calcium hydride chips for at least 12 hr.

II.B. GENERAL TECHNIQUES

The initial mixing of the reagents in all syntheses was carried out in a glovebag under an atmosphere of dry nitrogen gas. In most cases, refluxing was carried out with an oil-bubbler attached to the reflux condenser. Reaction was considered complete when the evolution of gas ceased. Glassware was oven-dried and cooled by passing nitrogen gas through the apparatus. Addition of a liquid reagent was accomplished <u>via</u> 1.00 or a 10.0 ml syringe.

The solvent was removed by passing a stream of nitrogen gas over the surface of the solution and applying gentle heat <u>via</u> a heat-gun.

Table 2. Chemicals and suppliers.

i) Chemical	Supplier
Thallium carbonate (99.95%)	a
Chlorotrimethylsilane (98%)	b
Dichlorodimethylsilane (99%)	b
Dichlorodiphenylsilane (96%)	b
Methyltrichlorosilane (98%)	b
Silicon tetrachloride (99%)	a
1,1,1-trifluoro-2,4-pentanedione (95%)	c
1,1,1-trifluoro-2,4-hexanedione (bp 121-126°)	c
1,1,1-trifluoro-6-methyl-2,4-heptanedione (bp 70-72°/49 mm)	c
1,1,1-trifluoro-7-methyl-2,4-octanedione (bp 55-65°/4 mm)	c
4,6-nonanedione (bp 79-80°/8 mm)	c
2,4-hexanedione (bp 152-153°)	c
2,4-pentanedione (Reagent grade)	d
1-benzoylacetone (Aldrich Analyzed)	b
Ethylacetoacetate, sodium salt (Aldrich Analyzed)	b
Sodium hydroxide (Reagent grade)	d
Perchloric acid (72%)	d
Sodium sulfide (Reagent grade)	d
Boron trichloride (C.P)	e
Hydrogen chloride	e

Table 2, cont'd.

ii) Solvents	Supplier
Dichloromethane (Reagent ACS)	f
Hexanes (Practical)	d
Ethanol (95%)	d
Cyclohexane (Certified Spectroanalyzed)	d
Methanol (Reagent ACS)	f
Chloroform (Reagent grade)	d
Acetone (Reagent grade)	d
Diethyl ether (Anhydrous)	d

a: Alfa Inorganics

b: Aldrich

c: Eastman Kodak

d: Fisher Scientific Co. Ltd.

e: Matheson

f: Anachemia

In the case of the syntheses of pyrylium salts, the crude product was precipitated by the addition of practical hexanes to the volume-reduced solution. Filtering through a medium porosity filter funnel and drying by passage of nitrogen gas resulted in the desired crude product. The sublimation was carried out under a continuous vacuum, and at approximately 85-90° on an oil-bath with either ice or cold water as a coolant.

The fractionation of the crude product obtained in the pyran synthesis was carried out using the apparatus pictured below:
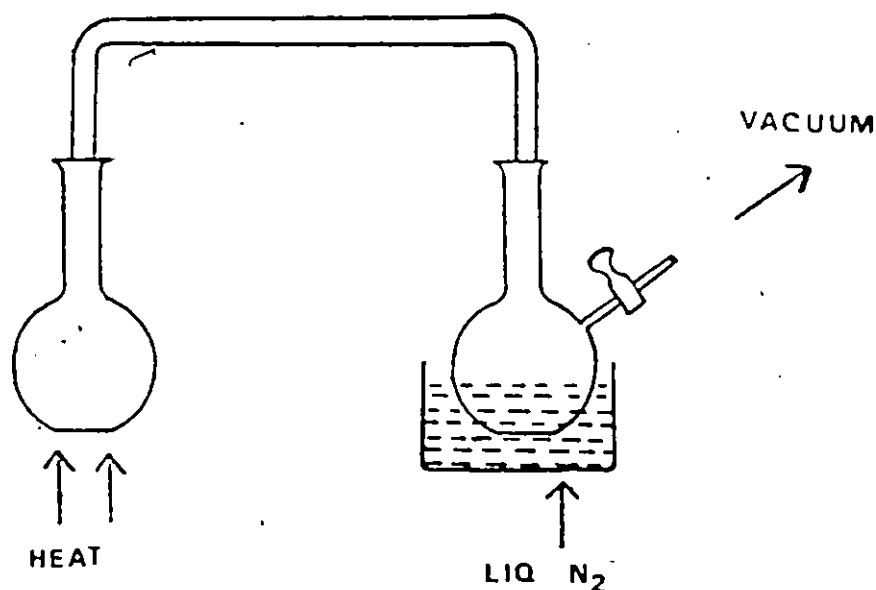
The crude product was heated in an oil-bath in vacuo with collection of the product in the liquid nitrogen flask.

All pure samples were stored in vials under a nitrogen atmosphere and placed in a freezer (-10°) in the dark.

Melting points of the pure products were obtained on a Gallenkamp Melting Point Apparatus. The capillaries were packed under a nitrogen atmosphere in a glovebag and sealed with modelling clay. The reported melting points are uncorrected.

A Metrohm E300B pH meter with a 20.00 ml Multi-Dosimat buret in conjuction with a combination glass calomel electrode was used in the acid-base titrations.

II.C. SPECTRA

Infrared spectra were run on a Perkin-Elmer Model 457 Grating spectrometer. All spectra were calibrated against polystyrene film (0.05 mm) at 2850.7, 1601.4 and 1028.0 cm^{-1}. The samples were run as Nujol mulls, unless otherwise stated. Potassium bromide disc cells were used. Sample preparation was carried out under an inert nitrogen atmosphere in a glovebag.

Mass spectra were recorded with a Hitachi-Perkin-Elmer RMU-6E mass spectrometer. Appropriate samples were prepared just prior to the running of the spectra.

Absorption spectra were obtained with either a Perkin-Elmer 323 or an Aminco-Bowman DW2 spectrophotometer. Samples were prepared in a nitrogen atmosphere immediately before the spectra were recorded. Beckman Blue-Label (10 mm) cells were used. Reagent grade or spectroanalyzed solvents,

and de-ionized water were used as solvents. Luminescence spectra were run in water on a Perkin-Elmer MPF3A spectro-fluorimeter.

Nuclear magnetic resonance spectra were recorded with a Varian Model A60-A spectrometer. Unless otherwise stated, all spectra were run in $CDCl_3$ with 1% TMS (tetramethylsilane) as an internal standard. Homonuclear and heteronuclear decoupling of protons was accomplished with a Bruker WH90 spectrometer. Homonuclear triple irradiations and homonuclear Nuclear Overhauser Effect measurements were determined with a Varian HA-100 spectrometer. Heteronuclear Nuclear Overhauser Effect measurements and simultaneous homonuclear and heteronuclear decoupling were recorded with a Varian DP-60 spectrometer.

II.D. X-RAY CRYSTALLOGRAPHY

Weissenberg and precession cameras manufactured by the Charles Supper Company were used in determining the space group of the crystal. Intensities were collected on a Picker Nuclear/FACS-1 diffractometer controlled by a Digital Equipment PDP-8/S mini-computer. Data reduction and refinement of the data were accomplished on Concordia University's CDC 6400 computer.

II.E. SYNTHESES

II.E.1. 2,4-PENTANEDIONE, THALLIUM SALT

This compound was prepared according to literature methods[100] by reacting thallous carbonate with 2,4-pentane-dione in refluxing ethanol.

II.E.2. 2,4-PENTANEDIONE, SODIUM SALT

The reaction of metallic sodium with 2,4-pentane-dione in diethyl ether resulted in the production of the sodium salt of 2,4-pentanedione.[101]

II.E.3. 2,4-DIMETHYL-6-(2'-HYDROXY-1'-PROPENYL)PYRYLIUM

CHLORIDE

(a) Tl(acac) and $(CH_3)_2SiCl_2$

In a 50 ml Erlenmeyer flask, fitted with a side-arm, dimethyldichlorosilane (2.00 ml, 0.0166 mol) was mixed with 25 ml of dry dichloromethane. To this solution was added the thallium salt of 2,4-pentanedione (3.00 g, 0.00988 mol). Almost instantly, a dark-red solution with a white precipitate formed. The stoppered flask was removed from the glovebag, and the mixture was stirred for 1 hr at ambient temperature.

A medium-porosity filter funnel was utilized in the removal of the white precipitate (TlCl). The volume of the dark-red filtrate was reduced _via_ a rotary evaporator to approximately 10 ml. Dry hexanes (10 ml) was added to precipitate the required crude product. The flask was placed in a freezer (-4°) for 1 hr to complete precipitation. An orange solid was isolated by filtration on a fine-porosity filter funnel, and the solid was dried _in vacuo_ for _not more_ than 30 min. The solid was sublimed at 90° under a continuous vacuum. The required yellow product was washed from the cold-finger with dry dichloromethane, and subsequently recovered by precipitation with hexanes. The bright yellow solid was dried _in vacuo_ for 15 min. Yield 0.23 g (23% of theoretical). Mp 155-156^O(dec).

(b) Na(acac) and $(CH_3)_2SiCl_2$

Dimethyldichlorosilane (2.27 ml, 0.0188 mol) was added to 40 ml of dichloromethane in a 125 ml Erlenmeyer flask, fitted with a side-arm. The sodium salt of 2,4-pentanedione (2.30 g, 0.0188 mol) was then slowly added to this solution. Within 5 min, a dark-red color had developed. The mixture was stirred at ambient temperature for 15 min. The solvent was completely removed by passing dry N_2 gas over the surface of the solution, and the dry residue (dark-red product containing sodium chloride) was sublimed in the same manner as in Synthesis II.E.3.a. The desired yellow product was collected from the cold-finger.

A yield of 0.08 g (4% of theoretical) was obtained.
Mp 155-156°(dec).

(c) Hacac and $(CH_3)_2SiCl_2$

Dimethyldichlorosilane (4.53 ml, 0.0375 mol) was
added to 30 ml of dichloromethane in a 50 ml Erlenmeyer
flask, fitted with a side-arm. 2,4-pentanedione (2.50 ml,
0.0244 mol) was added to this solution which was subsequently
refluxed for 2.5 hr resulting in a dark-red solution. The
bulk of the solvent was removed by passing dry N_2 gas over
the surface of the solution and precipitation of the product
was effected by the addition of hexanes. The precipitate
was collected on a medium-porosity filter funnel, and was
dried for 10 min under a nitrogen atmosphere. The orange
solid was sublimed as in Synthesis II.E.3.a. Yield 0.10 g
(4.1% of theoretical). Mp 155-156°(dec).

(d) Tl(acac) and $(C_6H_5)_2SiCl_2$

To 80 ml of dichloromethane in a 250 ml Erlenmeyer
flask, fitted with a side-arm, diphenyldichlorosilane
(11.85 g, 0.0468 mol) was added. The thallium salt of 2,4-
pentanedione (5.68 g, 0.0187 mol) was slowly added to the
solution. A pale, red solution formed within 2 min. The
mixture was stirred for 20 min at ambient temperature.
Work-up of the solution resulted in a dark-red powder which
was dried in vacuo for 30 min. The sublimation of this
product was carried out as in Synthesis II.E.3.a. Yield

0.11 g (5.3% of theoretical). Mp 155-156^O(dec).

(e) Tl(acac) and CH$_3$SiCl$_3$

Methyltrichlorosilane (3.00 ml, 0.0256 mol) was added to 75 ml of dichloromethane in a 250 ml Erlenmeyer flask, fitted with a side-arm. To this solution was added the thallium salt of 2,4-pentanedione (3.00 g, 0.00989 mol). The mixture was stirred for 30 min; only a slight yellow coloration formed. Refluxing for 30 min resulted in a dark-red solution. The solution was worked-up in the usual manner, with the recovery of a dark-red powder. Sublimation yielded a bright yellow compound in a yield of 0.03 g (3% of theoretical). Mp 155-156^O(dec).

(f) Tl(acac) and (CH$_3$)$_3$SiCl

The reaction between chlorotrimethylsilane (2.58 ml, 0.0203 mol) and the thallium salt of 2,4-pentanedione (3.08 g, 0.0102 mol) in 50 ml of dichloromethane resulted in no color change of the solution. The solution appeared to turn white, but this was a result of the unreacted 2,4-pentanedionato salt. The mixture was refluxed for 2 hr. Work-up of the solution produced no desired product.

(g) Hacac and BCl$_3$

To 125 ml of dry diethyl ether in a 250 ml Erlenmeyer flask was dissolved boron trichloride (2.86 g, 0.025 mol), according to the method of Serpone and Fay.[102] This solution

was filtered and to the filtrate was added 2,4-pentanedione

(5.3 ml, 0.051 mol). The mixture was stirred for 90 min

with a resulting dark-red solution. Filtration of the

precipitate followed by dissolution in dichloromethane, in

the open air, produced a dark-red solution. Subsequent

stirring in the open air for 30 min and work-up in the

usual manner resulted in a dark-red solid. Sublimation

produced a yellow coloration on the cold-finger;

unfortunately, owing to the very minute amount of product

formed precluded the use of instrumentation to determine

the nature of the yellow product.

II.E.4. 2-ETHYL-4,5-DIMETHYL-6-(2'-HYDROXY-1'-PROPENYL)

PYRYLIUM CHLORIDE

In a 50 ml Erlenmeyer flask, fitted with a side-

arm, containing 20 ml of dichloromethane was added 2,4-

hexanedione (2.60 g, 0.0228 mol). To this solution was

added dimethyldichlorosilane (4.12 ml, 0.0342 mol). Refluxing

for 6 hr produced a dark-red solution. Work-up of the

solution resulted in a yellow-green solid. Sublimation at

50° and under a continuous vacuum yielded a very unstable

yellow compound. The yield of this partially decomposed

product was 0.05 g (2% of theoretical).

II.E.5. 2,4-DI-n-PROPYL-5-ETHYL-6-(2'-HYDROXY-1'-PENTENYL)

PYRYLIUM CHLORIDE

4,6-nonanedione (3.54 g, 0.0227 mol) was added to

20 ml of dichloromethane in a 50 ml Erlenmeyer flask, fitted

with a side-arm. Dimethyldichlorosilane (4.1 ml, 0.0340 mol)

was then added and the solution refluxed for 25 hr. Removal

of the solvent and sublimation (using the apparatus pictured

in Section II.B.) in an oil bath at 90° resulted in the

collection of a brown product. Recrystallization from di-

chloromethane and hexanes produced an oil. This oil was

'sublimed' at 60°. A yellow-green product was collected, and

then isolated in dichloromethane. Work-up of this solution

resulted in a small amount of yellow product. Also,

evaporation of the mother liquor produced a small amount of

product. Yield ca. 1% of theoretical.

II.E.6. 6-TRIFLUOROMETHYL-4-METHYL-2-TRIFLUOROACETYL-

PYRANYLIDENE

To a solution of 1,1,1-trifluoro-2,4-pentanedione

(3.77 g, 0.0245 mol) and 20 ml of dichloromethane in a 50 ml

round-bottomed flask was added silicon tetrachloride (1.40 g,

0.0122 mol). Refluxing for 5 hr resulted in a dark-red

solution. The solvent was removed and the remaining dark-

red oil was fractionated at a temperature of 30° and under

a continuous vacuum. Bright yellow crystals were obtained in a yield of 0.55 g (16.5% of theoretical). Mp 45–46°.

II.E.7. 6-TRIFLUOROMETHYL-4-ETHYL-3-METHYL-2-TRIFLUORO-ACETYL-PYRANYLIDENE

1,1,1-trifluoro-2,4-hexanedione (4.07 g, 0.0242 mol) was added to a 50 ml round-bottomed flask with 30 ml of dichloromethane. To this solution was added silicon tetra-chloride (1.38 ml, 0.0121 mol). Refluxing for 24 hr produced a dark-red solution. The solvent was removed, and fractionation of the resulting oil at 60° and under a continuous vacuum yielded large yellow crystals. Yield 0.12 g (3.5% of theoretical). Mp 70–72°.

II.E.8. 6-TRIFLUOROMETHYL-4-ISOBUTYL-3-ISOPROPYL-2-TRI-FLUOROACETYL-PYRANYLIDENE

Several attempts at isolating the desired pyran proved unsuccessful. A brief description of these attempts will be presented. In all cases, the silicon tetrachloride was added to the 1,1,1-trifluoro-6-methyl-2,4-heptanedione in dichloromethane in a ratio of 1:2. Reflux times were varied between 1 and 72 hr, and in each synthesis a dark-red oil was recovered after solvent removal. Upon

fractionation, the starting β-diketone was isolated along with some uncharacterizable residue. The fractionation methods used were vacuum distillation, and extractions involving hexanes and dichloromethane, pentane and di-chloromethane, and methanol and water.

II.E.9. 6-TRIFLUOROMETHYL-4-ISOPENTYL-3-ISOBUTYL-2-TRI-FLUOROACETYL-PYRANYLIDENE

Dichloromethane (25 ml) was added to a 50 ml round-bottomed flask containing 1,1,1-trifluoro-7-methyl-2,4-octanedione (5.39 g, 0.0256 mol). To this solution was added silicon tetrachloride (1.47 ml, 0.0128 mol). Reflux for 88 hr yielded a dark-red oil after solvent removal. Fractionation produced a bright yellow semi-solid product. Isolation of this product was accomplished by dissolution in chloroform with subsequent evaporation. A yield of =0.03 g (0.1% of theoretical) resulted.

II.E.10. REACTION OF BENZOYLACETONE AND LEWIS ACIDS

Attempts at the condensation and cyclization of benzoylacetone to produce the pyrylium cation proved unsuccessful. To a 125 ml Erlenmeyer flask fitted with a side-arm was added dimethyldichlorosilane (3.9 ml,

0.0324 mol) and dichloromethane (30 ml). Addition of

benzoylacetone (3.50 g,0.0216 mol) followed by refluxing

for 4 hr, resulted in a dark-red solution, similar to the

color of the solution in Synthesis II.E.3.a. The removal

of the solvent yielded a large amount of dark-red crystalline

matter. The melting point, and infrared spectrum and nuclear

magnetic resonance spectrum indicated that benzoylacetone

was present in large quantities in the dark-red matter.

Sublimation of the product resulted in a white crystalline

product which was identical to benzoylacetone, and an

intractable dark-red oil. A similar reaction using sodium

benzoylacetonate yielded the same product, that is, benzoyl-

acetone.

II.E.11. REACTION OF THE SODIUM SALT OF ETHYLACETOACETATE

AND LEWIS ACIDS

Several attempts were made at producing the pyrylium

cation from sodium ethylacetoacetate. On addition of the

sodium ethylacetoacetate to a dichloromethane solution

containing dimethyldichlorosilane, vigorous frothing took

place. The mixture was either stirred (1-3 hr) or refluxed

(21 hr) with the solution changing color from yellow to a

brown-orange. Removal of the solvent was accomplished via

a water aspirator, followed by drying in vacuo for 1 hr.

The golden-brown product obtained was always slightly moist

in appearance. Sublimation of this golden-brown product produced a clear liquid on the cold-finger of the sublimation apparatus. The odor and nuclear magnetic resonance spectrum indicated that ethylacetoacetate was collected. The residue turned into a black oil at the end of the sublimation. In some cases, fuming of the collected product was observed, and this was attributed to unreacted dimethyldichlorosilane. Benzene was also used as a solvent, but as above, only ethylacetoacetate and a dark oil resulted.

II.F. REACTIONS OF THE PYRYLIUM SALTS AND OF THE PYRANS

II.F.1. 2,4-DIMETHYL-6-(2'-HYDROXY-1'-PROPENYL)THIAPYRYLIUM CHLORIDE

The preparation of the thiapyrylium salt followed the method of Wizinger and Ulrich.[103] A solution of the pyrylium salt (0.10 g, 0.00049 mol) in acetone (40 ml) was added to a solution of sodium sulfide (0.5 g, 0.0064 mol) in water (10 ml). The solution was shaken periodically over a period of 30 min with a color change from a deep-red to orange. Addition of a 20% hydrochloric acid solution (10 ml) produced a yellow solution. The solution was allowed to stand for 2 hr, but no crystallization occured. Extraction of the product using dichloromethane and hexanes produced but a small amount of unknown product.

II.F.2. 2,4-DIMETHYL-6-(2'-PROPANONE)PYRIDINE

To a solution containing the pyrylium salt (0.65 g, 0.00324 mol) dissolved in water (10 ml) was added concentrated aqueous ammonia (10 ml). The solution immediately turned from a yellow-orange to a bright orange color. Gentle heating for 10 min to ensure reaction resulted in a deep-orange color. The solution was filtered through glass-wool and the filtrate was extracted with ether. Evaporation of the ether via passage of dry N_2 gas over the surface of the solution resulted in a crude product. Recrystallization from dichloromethane and hexanes produced a small amount of the pyridine derivative. Yield 0.15 g (29% of theoretical).

II.F.3. PROTONATION OF 6-TRIFLUOROMETHYL-4-METHYL-2-TRI-
FLUOROACETYL-PYRANYLIDENE TO PRODUCE THE PYRYLIUM
SALT DERIVATIVE

Attempts to protonate the pyran using perchloric acid, anhydrous hydrogen chloride, or concentrated hydrochloric acid failed. The general procedure involved dissolving the pyran in some solvent, usually methanol or chloroform, followed by the addition of the acid. Infrared spectra in the regions 2600-2300 cm^{-1} and 1700-1500 cm^{-1} were taken to monitor the protonation. However, no new bands appeared in this region.

II.G. pK OF 2,4-DIMETHYL-6-(2'-HYDROXY-1'-PROPENYL)PYRYLIUM

CHLORIDE

II.G.1. TITRATION METHOD

A stock solution of the pyrylium chloride in water (50.00 ml, 0.0492 mol) was prepared. Two 25.00 ml aliquots were diluted to 50 ml with water. The pH titrations were carried out with 0.1113 N sodium hydroxide (standardized against potassium acid phthalate according to Dick[104]). The first sample was titrated slowly in order to avoid over-shooting the end-point. The second sample was titrated according to established procedures.[104] The value of the pK was lower than had been anticipated from UV-visible spectral observations (pK≈4).

A second experiment was carried out to determine the pK of pyrylium chloride. In this experiment, three samples were titrated against standardized sodium hydroxide (0.1064 N). The average value for this experiment was higher than the anticipated value (pK≈4).

The third attempt at obtaining the pK value of the pyrylium salt involved standardizing the pH meter with a buffer of approximately the same pH as that of the acid solution. The value of the pK was obtained from the pH of a solution of the pyrylium chloride (0.04592 M).

II.G.2. SPECTROPHOTOMETRIC METHOD[105]

A stock solution of the pyrylium salt in water/
hydrochloric acid was prepared (0.0026 g/100 ml, NaCl —
1.0 $\underline{M}$). Aliquots of this solution were taken and the
absorbance of each solution was recorded at λ·398 nm. The
'working' solution was made up by adjusting the concentration
of the pyrylium salt solution in water such that it has an
absorbance of =1.0 at λ 398 nm. The absorbance and pH of
the 'working' solution, and those of several solutions in
which a small amount of dilute hydrochloric acid was added,
were recorded. The pK of the pyrylium salt was consistent
with that of the third determination of the titration
method in II.G.2.

II.H. CRYSTAL STRUCTURE OF 6-TRIFLUORMETHYL-4-ETHYL-3-
METHYL-2-TRIFLUOROACETYL-PYRANYLIDENE

Crystals of the pyran were grown by slow, gentle
heating in vacuo in a sealed tube. The crystals were
individually sealed in capillary tubes in the presence of
Silicone grease (Dow Corning) to ensure no movement of the
crystal during handling. However, the crystal appeared to
dissolve in this grease, and subsequently glue (Glyptal
Cement - General Electric) was substituted for the grease.
The capillary tube was mounted on a goniometer head for the

space group and unit cell parameter determinations.

Preliminary Weissenberg and precession photographs were taken with Mo K$_\alpha$ (λ=0.71069 Å) radiation in order to check for any defects in the crystal and to determine probable space groups. Accurate cell dimensions were obtained via the diffractometer. Least-squares refinement of the unit cell parameters and the crystal orientation matrix were carried out from the values of 2θ, ω, χ, and ϕ. These values were obtained for 12 Bragg reflections centred at 2θ, both positive and negative, and averaged appropriately. The Picker-Nuclear Co. supplied the programs for this procedure.

Intensity data were collected using a θ-2θ scan on the diffractometer. An asymmetric unit of intensity data was collected such that the angular limits were chosen to include all of the relatively strong reflections. Instrument stability was monitored after every fifty cycles by measuring the intensity of a standard reflection and also by the measurement of the intensity of reciprocal axis reflections with negative and positive indices both before and after data collections.

A locally written program* PREP, was employed in data reductions. An approximate scale factor and overall isotropic thermal parameters from reflection statistics were determined using the Wilson plot. Reflection intensities, I, and standard deviations, $\sigma(I)$, were calculated from the

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*Supplied by Dr. P.H. Bird, Concordia University, Montreal.

expressions $I = (N - Bt_s/t_b)$ and $\sigma(I) = \left(N - B(t_s/t_b)^2 + (0.02N)^2 \right)^{\frac{1}{2}}$, where N and B are the total counts accumulated during the scan period, t_s, and the total background counting time, t_b, respectively. Data were rejected for $I < 3\sigma(I)$ and the remaining intensity data were corrected for Lorentz and polarization effects, according to the expression, $(Lp)^{-1} = \sin 2\theta_s (\cos^2 2\theta_m + 1)/(\cos^2 2\theta_m + \cos^2 2\theta_s)$, where $2\theta_m$ and $2\theta_s$ are diffraction angles at the monochromator and sample crystal, respectively. Corrections for absorption were not applied. The structure factor amplitude, F, was obtained from the expression, $F = \sqrt{I/Lp}$, and standard deviations were computed according to the expressions, $\sigma(F) = \sigma(I)/\sqrt{I/Lp}$ if $I < \sigma(I)$, or $\sigma(F) = F - \left(I - \sigma(I)/Lp \right)^{\frac{1}{2}}$ if $I > \sigma(I)$. The scattering power of each atom for each reflection $(f_{i,\theta})$ was computed from the expression,

$$f_{i,\theta} = \sum_{j=1} a_{ij} \exp\left(-b_{ij} \frac{\sin^2 \theta}{\lambda^2}\right) + c_j$$

where a, b, c are empirical constants.

Program EGEN was used to calculate the normalized structure factors, E, from the observed structure factors, F_{obs}, according to the expression, $E^2 = |F_{obs}|^2 / \epsilon \sum_i f_i^2$, where ϵ is an integer (usually 1) which may vary for special sets of reflections. The Wilson plot was repeated in order to optimize the scale factor and overall isotropic parameters, and distribution of the E's into parity groups was also accomplished with this program.

The MULTAN program was composed of three parts:
a) SIGMA2; b) CONVERGE;and c) FASTAN.

a) SIGMA2 sets up all the Σ_2 phase relationships in the form $\phi = \phi_{h'} + \phi_{h-h'}$, where ϕ_h is the phase of F_h. A weight was given by $K_{hh'} = 2\sigma_3 \sigma_2^{-3/2} |E_h E_{h'} E_{h-h'}|$, where $\sigma_n = \sum_{j=1}^{N} z_j^n$ and z_j is the fraction of the scattering power represented by the ith atom. The strongest relationships were retained later for use in the tangent formula. The right-hand side of Sayre's equation, $S(F_h) = S(F_{h'}) \cdot S(F_{h-h'})$, where S means the 'sign of' and $=$ means 'is probably equal to', was set up for these reflections.

b) CONVERGE compute the probabilities of the signs of the centric reflections _via_ the Σ_1 formula, $\phi_{h'} = \phi_{h-h'}$. Generally, the high E's will affect the Σ_1 probabilities the most and thus these were used. These 'best' reflections were used to define the origin and other reflections which appeared to provide a reasonably good starting point for the phase determinations. The formula used was

$$\alpha_h^2 = \left(\sum_{h'} K_{hh'} \cos(\phi_{h'} + \phi_{h-h'}) \right)^2 + \left(\sum_{h'} K_{hh'} \sin(\phi_{h'} + \phi_{h-h'}) \right)^2$$

where, $K_{hh'}$ is defined previously and provides a measure of the reliability with which the phase ϕ_h may be determined.

c) FASTAN determines the phases of the reflections by means of the tangent formula,

$$\tan\phi_h = \frac{\sum_h w_{h'} w_{h-h'} |E_{h'} E_{h-h'}| \sin(\phi_{h'} + \phi_{h-h'})}{\sum_h w_{h'} w_{h-h'} |E_{h'} E_{h-h'}| \cos(\phi_{h'} + \phi_{h-h'})} = \frac{T_h}{B_h}$$

where w_h is the weight applied to the phase ϕ_h and this weight was computed from

$$w_h = \tanh(\tfrac{1}{2}\alpha_h)$$

and

$$\alpha_h = |E_h|(T_h^2 + B_h^2)^{\frac{1}{2}}$$

Program EXPAND prepares the data for the Fourier synthesis which was carried out by the subprogram, FFT,

$$\rho(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_l F_{hkl} \cos 2\pi(hx + ky + lz - \alpha'_{hkl})$$

where, $\rho(x,y,z)$ is the electron density, V is the volume of the unit cell and $2\pi\alpha'_{hkl}$ is the phase angle. PKSRCH subprogram searches for the largest peaks from FFT and attempts to organize them into fragments of the structure using symmetry relationships. A 20% excess of atoms were added as input to this program. DRAW plotted the atom positions in the portion of the unit cell specified in the input.

SFC and SFLS were used to calculate the F (and E) from a partial structure that was inputed into the program. The phases of E were calculated and compared to the observed E values. The output resulted in a Fourier map in all of x,

one-half in y, and one-half in z. The SFLS program used a least-squares refinement of the molecule as a means of obtaining structure.

II.I. PROTON NUCLEAR MAGNETIC RESONANCE SPECTRA OF 2,4-DIMETHYL-6-(2'-HYDROXY-1'-PROPENYL)PYRYLIUM CHLORIDE IN WATER, ACID, AND BASE

The pyrylium salt under study has an acidic proton in the propenyl side-chain. A low temperature ^{1}H nmr spectrum[83] (in CDCl$_3$/TMS) indicated the presence of a fast keto-enol type exchange in this side-chain. Literature sources[106] indicated that in the presence of OH$^-$ there is a likelihood that reaction with a pyrylium salt will produce a phenyl derivative. In addition, titration with OH$^-$ (Section II.G.1.) produced inconclusive results. This experiment was undertaken in order to observe changes in the nmr spectra corresponding to the changes that the pyrylium salt undergoes with changing the pH of the solution.

The first spectrum recorded was that of the pyrylium salt in water. The same solution was acidified with 1.0 M HCl and the spectrum was recorded. Addition of 1.0 M NaOH to the acidic solution resulted in a color change from yellow to orange. A spectrum was recorded.

II.J. ^{13}C NUCLEAR MAGNETIC RESONANCE AND ^{1}H DECOUPLING

EXPERIMENTS OF 2,4-DIMETHYL-6-(2'-HYDROXY-1'-PROPENYL)

PYRYLIUM CHLORIDE

The X-ray crystallographic structure determination of pyrylium chloride indicates the two oxygen atoms are trans.[83] ^{13}C nmr experiments are able to differentiate, in some cases, the orientation of molecules. The pyrylium chloride was analyzed by ^{13}C nmr and ^{1}H decoupling experiments to determine the nature of this pyrylium salt in solution.

^{13}C nuclear magnetic resonance spectra were recorded on the pyrylium chloride in CDCl$_3$/TMS solution at ambient temperature. ^{1}H decoupling experiments were performed on all the protons of the pyrylium chloride to determine the proximity of the protons or alkyl groups to the heteronuclear oxygen atom, and to determine a probable structure in solution.

II.K. ^{1}H, ^{13}C AND ^{19}F NUCLEAR MAGNETIC RESONANCE SPECTRA OF

6-TRIFLUOROMETHYL-4-METHYL-2-TRIFLUOROACETYL-

PYRANYLIDENE

An attempt was made to determine the positions of the methyl- and trifluoromethyl groups with respect to the ring oxygen via a crystal structure determination of 6-trifluoro-methyl-4-ethyl-3-methyl-2-trifluoroacetyl-pyranylidene

(Section II.I.). However, the structure of the molecule could not be solved and, therefore, nuclear magnetic resonance spectroscopy was used.

The problem of assigning the relative positions of the trifluoromethyl- and methyl groups was tedious. Several nmr techniques were required to determine the position of the methyl group (and trifluoromethyl group) with respect to the ring oxygen. The ^{1}H nmr spectrum of the pyran under study (in $CDCl_3$/TMS) was recorded at a frequency of 90 MHz. Decoupling experiments were performed to determine the positions of the protons and neighboring proton groups in the molecule. The decoupled group(s) and the frequency at which measurements were recorded are listed in Table 3.

The ^{19}F nuclear magnetic resonance spectrum of the pyran was recorded at a frequency of 56.4 MHz. The proton at δ5.9 ppm was decoupled, and the spectrum was recorded at 84.66 MHz.

[13]C nmr spectra were recorded at a frequency of 22.62 MHz. In a similar manner to the ^{1}H nmr spectra several decoupling experiments were performed. Table 3 contains a listing of the actual experiments performed on the pyran.

Homonuclear and heteronuclear Nuclear Overhauser Effect (NOE) measurements were performed on the pyran solution to distinguish between the two possible structures. In the homonuclear NOE measurements, the methyl group was irradiated and several scans of the signal at δ8.1 and 6.5 ppm were taken. The low-field fluorine resonance signal was

irradiated and several scans of the signals at δ8.1 and 6.5 ppm were taken (heteronuclear NOE).

Table 3. Decoupling experiments of 6-trifluoromethyl-4-
methyl-2-trifluoroacetyl-pyranylidene in $CDCl_3$/TMS solution.
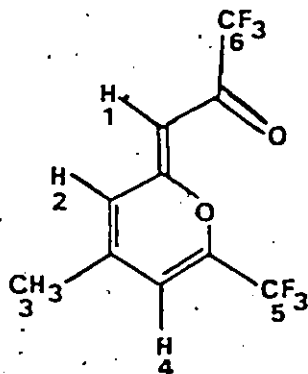
Nucleus	Recording Frequency (MHz)	Nucleus/Nuclei Decoupled
^1H	90	(CH_3)
^1H	90	H(2)
^1H	100	(CH_3) and H(1)
^1H	58.3	(CF_3) (5)
^1H	58.3	(CF_3) (6)
^1H	58,3	(CF_3) (5) and CH_3
^1H	58.3	(CF_3) (5) and H(2)
^{13}C	22.62	proton coupled
^{13}C	22.62	proton decoupled
^{13}C	22.62	(CH_3)
^{13}C	22.62	H(2)
^{13}C	22.62	H(4)

III. RESULTS AND DISCUSSION

III.A. PYRYLIUM SALTS

III.A.1. SYNTHESIS

The usefulness of silicon complexes in preparative organic chemistry has been described earlier (cf. Section I.A.3.). It was observed in this laboratory[83] that the reaction between an organohalosilane and a β-diketone in dichloromethane resulted in the isolation of oxygen hetero-cycles, either a pyrylium salt or a pyran, depending on the nature of the β-diketone. Discussion of the pyran (synthesis, structure, etc.) will follow that of the pyrylium salt.

It is instructive at this point to briefly review the synthesis of pyrylium salts to facilitate an understanding of the reaction between the Lewis acid and the β-diketone. Addition of the β-diketone (as a pure β-diketone, or as the thallium or sodium salts) to a solution of an organohalo-silane (e.g., $(CH_3)_2SiCl_2$) in dichloromethane with stirring and/or refluxing results in the isolation of a pyrylium salt (the salt was isolated by subliming the reaction residue).

Table 4. Summary of the different Lewis acids used in the
synthesis of 2,4-dimethyl-6-(2'-hydroxy-1'-propenyl)pyrylium
chloride with the yields produced.

Lewis acid	Yield (%)
$(CH_3)_3SiCl$	no reaction
$(CH_3)_2SiCl_2$	23
CH_3SiCl_3	$=10$
$(C_6H_5)_2SiCl_2$	$=10$
BCl_3	trace

The Lewis acids used in the preparation and the yields of
the pyrylium salts obtained using 2,4-pentanedione as the
β-diketone are summarized in Table 4. It can be seen that
for the reaction to produce a pyrylium salt there must be
present in the silicon complex at least two replaceable
chlorine atoms. The reaction of $(CH_3)_3SiCl$ with 2,4-pentane-
dione or salts of 2,4-pentanedione fails to produce the
pyrylium salt; this organohalosilane has only one replaceable
chlorine atom. However, compounds such as $(R')_2SiCl_2$ or
$RSiCl_3$, where R' is CH_3 or C_6H_5 and R is CH_3, react with
2,4-pentanedione to produce pyrylium salts in yields of up
to 23%. These complexes have at least two replaceable
chlorine atoms. Thus, it may be concluded that two replace-
able chlorine atoms on the organohalosilane (Lewis acid) are
required in order for the reaction to form the pyrylium salt.

The silicon atom in (XXXI) may be required to orientate the acac ligahds into a favorable position for reaction.

CH$_3$ H O
O—C=C—C—CH$_3$

R$_2$Si

O—C=C—C—CH$_3$
CH$_3$ H
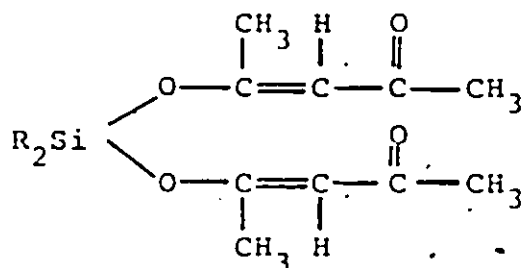
XXXI

It should be noted that the configuration of the acac ligands shown in (XXXI) may be misleading. If such appropriate orientation were not needed, the condensation and cyclization reaction should have proceeded in the absence of an organo-halosilane. There is no evidence of this taking place, although in a recent paper[96] the condensation and cyclization of 2,4-pentanedione is believed to proceed with the aid of hydrochloric acid, but only in the presence of a Lewis acid containing a heavy metal.

Returning to the discussion on the condensation and cyclization reaction, failure to obtain the pyrylium salt from the reaction between $(CH_3)_3SiCl$ and acac$^-$ indicates that two such ligands bonded to the silicon atom are required.

In all of the reactions with 2,4-pentanedione and an organohalosilane the product was the same pyrylium salt, 2,4-dimethyl-6-(2'-hydroxy-1'-propenyl)pyrylium chloride. This may indicate, again, that the silicon moiety is required to prevent the acac unidentate ligands from being randomly arranged. If this were not the case, other isomers could be

formed and could possibly be detected. However, no other structures were found from the nuclear magnetic resonance spectra, both ^{13}C and ^{1}H. It should be noted that in a recent publication[96] Fowles, Rice and Shanton reacted 2,4-pentanedione with several heavy-metal Lewis acids and produced a pyrylium salt that was different from the one reported herein. Also, Oldham and Ketteringham[96] have prepared the same pyrylium salt as Fowles and co-workers,[96] albeit from different Lewis acids. In both cases the compound was identified as the 2,4,6-trimethyl-3-acetylpyrylium cation. How the Lewis acids used are involved in the condensation and cyclization of the 1,3-diketone was not given.[96,97] The counter-ion was usually a complex ion of the Lewis acid. It is interesting to note that reactions of organohalosilanes and $acac^-$ produce one type of pyrylium salt (this work), while reaction of $PtCl_4$, or other heavy-metal Lewis acids, with 2,4-pentanedione produce a different pyrylium salt. The platinum complex and other heavy-metal complexes, as well as silicon compounds, should affect the reaction path. Earnest and Brown[99] have demonstrated the use of Pt in some condensation and cyclization reactions of cyclopropanes. They have proposed that intermediates exist as platinum-stabilized carbonium ions. This is the only reference which illustrates how the Lewis acid is involved in these reactions.

The time of reaction between 2,4-pentanedione and $(CH_3)_2SiCl_2$, $(C_6H_5)_2SiCl_2$, and CH_3SiCl_3 was found to be

approximately: $(CH_3)_2SiCl_2$ (1 hr) < $(C_6H_5)_2SiCl_2$ (1.5 hr) < CH_3SiCl_3 (2 hr). As mentioned earlier the species that lead to the formation of the pyrylium salt possess a unidentate diketonate ligand. Compounds such as $C_6H_5SiCl_3$ and CH_3SiCl_3 react with 2,4-pentanedione to give six-coordinated silicon complexes.[70] This fact explains the rather slow reaction of CH_3SiCl_3 with 2,4-pentanedione to form the pyrylium chloride. When compounds such as $(CH_3)_2SiCl_2$ and $(C_6H_5)_2SiCl_2$ react with 2,4-pentanedione, the open-chain complexes are formed, i.e., the 2,4-pentanedionate ligand is unidentate.[70] The reaction times of these two dichlorosilanes are different. This may be attributed to the large size of the phenyl group in comparison to the methyl group. The reactivity at Si-X (X is a halogen) bonds is determined mainly by steric hindrance.[107] The larger phenyl groups may impede the course of the reaction to a greater extent than the much smaller methyl group.

The criterion used in determining the completion of the reaction was the color of the reaction mixture. The 'completion' of the reaction was taken to be when the color of the solution was deep red. It was found that if the reaction mixture was stirred for longer periods, for example until it turned a dark-brown color, only trace amounts of the pyrylium chloride were recovered. If the reaction was allowed to occur over a shorter time, that is, until the solution was bright red, also no pyrylium chloride was isolated. Thus, the production of the pyrylium salt is very

sensitive to the reaction time: too long or too short a reaction time produced no pyrylium salt. Completion of the reaction was difficult to assess. This difficulty may have had an effect on the yields of each synthesis. It was possible to approximate whether or not a good yield was forthcoming by the addition of the hexanes. A dark-red or brown precipitate resulted in a low yield, but the lighter the brown color, that is, approaching the yellow color of the pyrylium salt, the less the impurity and, thus, a higher yield. In some cases, these slight impurities had little effect on the experiments being performed. In the reaction between 2,4-pentanedione and $(CH_3)_2SiCl_2$ in refluxing di-chloromethane, it was observed that an almost pure product (pyrylium chloride) was recovered. On subliming the crude product, there was very little residue. The melting point was the same as the pure pyrylium chloride and only a slight impurity was present in the ^1H nuclear magnetic resonance spectrum. This synthesis was the main source of the pyrylium chloride owing to the simplicity in the experimental procedure. Both the silane and the 2,4-pentanedione are readily available liquid reagents. There is no need to prepare the Tl or Na salts of 2,4-pentanedione.

It was initially thought that the pyrylium chloride was unstable in the air; later it was found that most solutions could be prepared in the open air. This was demonstrated by obtaining ^1H nmr spectra with samples prepared in the same way but one in a glovebag under nitrogen

and the other in the open air. The spectra were identical. However, storage of the pyrylium salt was in the cold, in the dark, and under a nitrogen atmosphere. Decomposition was observed as a change in color from a bright yellow to a dark-green color. Once the salt was in solution, the pyrylium chloride was stable for indefinite periods of time in the dark. Light appears to have a marked effect on the solution. Depending on the concentration of the salt in water, the solution slowly loses its color until it forms a colorless solution. The light source was either laboratory fluorescent lighting or sunlight. In either case the weak solutions $(10^{-5}$ $\underline{M})$ lose their colors in less than 12 hr, whereas the concentrated solutions $(10^{-3}$ $\underline{M})$ lose their color in about 4 days. Storing the pyrylium chloride in the dark for an indefinite period resulted in no color loss.

Several β-diketones, other than 2,4-pentanedione, were used in syntheses, but most of the syntheses ended in some degree of failure. Each will be discussed in some detail. In the reaction between 4,6-nonanedione and $(CH_3)_2SiCl_2$ in refluxing dichloromethane, only a small amount of pyrylium salt was recovered (less than 1% of theoretical). This β-diketone is symmetrical in a manner similar to 2,4-pentane-dione. The small amount of product was unexpected. Apparently, the bulkiness of the intermediate formed (XXXII) prevents formation of reasonable amounts of product. Longer reflux times (25 hr) compared to 2,4-pentanedione (2.5 hr) did not improve the yield of the product. Also, it is possible the

$$CH_3-CH_2-CH_2$$
$$R_2Si \begin{array}{c} O-C=C-C-CH_2-CH_2-CH_3 \\ \\ O-C=C-C-CH_2-CH_2-CH_3 \end{array}$$
$$CH_3-CH_2-CH_2$$
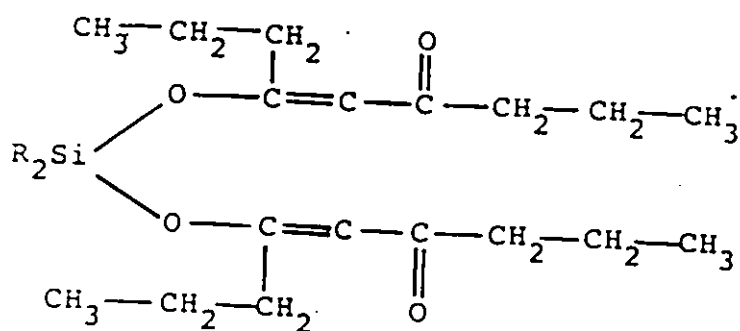
<u>XXXII</u>

longer reflux times lead to decomposition of the formed pyrylium salt. Another reason for the low yield may be that attainment of the correct configuration for reaction is difficult due to the bulkiness of the complex (<u>XXXII</u>). As can be seen from the structure, a $-CH_3$ group is now replaced by a $-CH_2CH_2CH_3$ group. One last point concerning this reaction is that the reaction does not appear to be reproducible. Several attempts to produce this pyrylium salt failed, even though the same reaction conditions were used. In all cases that ended in failure, a dark-red colored solution was observed for the reaction, but only a small amount of the dark-red precipitate was recovered. Sublimation produced no pyrylium salt.

A β-diketone similar to 2,4-pentanedione, benzoyl-acetone, was reacted as the pure β-diketone and also as the Tl and Na salts with $(CH_3)_2SiCl_2$ but no pyrylium salt was isolated. In all three forms (Tlbzac, Nabzac, or Hbzac) used in the reaction a dark-red solution was worked up to give a

dark-red solid. Subliming this solid resulted in the collection of pure benzoylacetone, even when the starting materials were the Tl or Na salts of the β-diketone. The important intermediate may have one or more of the three possible forms (XXXIIIa, b, c), due to the unsymmetrical nature of the ligand.
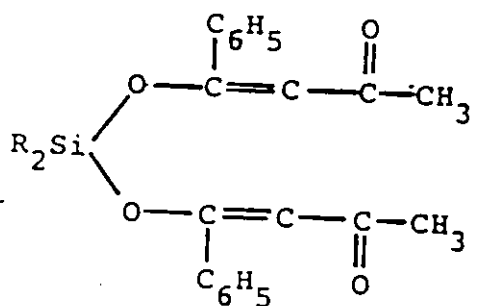
(a)
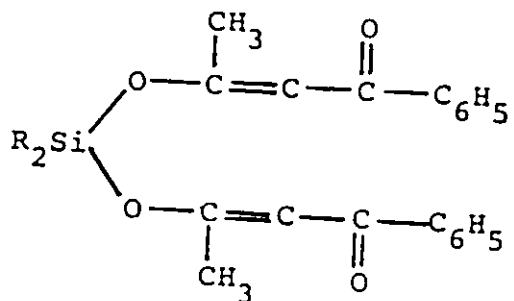
(b)
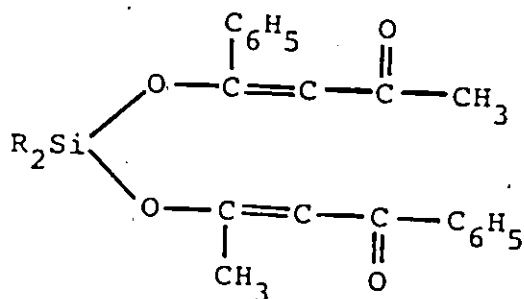
(c)

XXXIII

If one considers the difference between (XXXIIIb) and (XXXI), it lies in the nature and size of the phenyl groups at the terminal carbon of the unidentate ligands. Referring to structures (XXXIIIa) and (XXXIIIc), the phenyl group(s) are adjacent to the oxygen(s) bound to the silicon atom. This could have a considerable effect on the electronic structure

of the complexes and thus interfere in the reaction process. The precipitate that was obtained in the reaction was analyzed by melting point, ^{1}H nmr, IR, and mass spectrometry; each method indicated that a large portion of the product was, indeed, pure benzoylacetone. It is conceivable that the condensation reaction product is very reactive (unstable) or very difficult to attain. Cyclization to produce the pyrylium salt would be favorable inasmuch as a large electron source, like the phenyl group, should stabilize the pyrylium cation.[91] Thus, it appears that the condensation reaction may be the slow step in the reaction.

A β-ketoester, the sodium salt of ethylacetoacetate, was employed in the attempt to synthesize a pyrylium salt. However, no success was realized in this reaction. A color change from yellow to brown-orange was observed, but on removal of the solvent, only the neat β-ketoester was recovered. As in the discussion above, this β-ketoester is unsymmetrical compared to 2,4-pentanedione and several configurations are possible (XXXIV). Complex (XXXIVa) is similar to complex (XXXIIIb). The -OC$_2$H$_5$ group is larger than the -CH$_3$ group but smaller than the phenyl group. It was expected that complex (XXXIVa) would give a condensation product, but apparently complex (XXXIVa) is not produced in the reaction. Complexes (XXXIVb) and (XXXIVc) are conceivable but because of the -OC$_2$H$_5$ group attached close to the Si atom, the ethoxy group may cause a large change in the electronic structure at the Si centre and prevent

$$
\begin{array}{c}
\text{CH}_3 \quad\quad\; \text{O} \\
\text{O}-\text{C}=\text{C}-\text{C}-\text{OC}_2\text{H}_5 \\
\text{R}_2\text{Si} \\
\text{O}-\text{C}=\text{C}-\text{C}-\text{OC}_2\text{H}_5 \\
\text{CH}_3 \quad\quad\; \text{O}
\end{array}
$$

(a)

$$
\begin{array}{c}
\text{C}_2\text{H}_5\text{O} \quad\quad\; \text{O} \\
\text{O}-\text{C}=\text{C}-\text{C}-\text{CH}_3 \\
\text{R}_2\text{Si} \\
\text{O}-\text{C}=\text{C}-\text{C}-\text{CH}_3 \\
\text{C}_2\text{H}_5\text{O} \quad\quad\; \text{O}
\end{array}
$$

(c)

$$
\begin{array}{c}
\text{CH}_3 \quad\quad\; \text{O} \\
\text{O}-\text{C}=\text{C}-\text{C}-\text{OC}_2\text{H}_5 \\
\text{R}_2\text{Si} \\
\text{O}-\text{C}=\text{C}-\text{C}-\text{CH}_3 \\
\text{C}_2\text{H}_5\text{O} \quad\quad\; \text{O}
\end{array}
$$
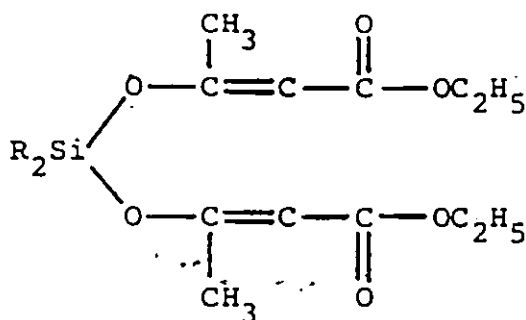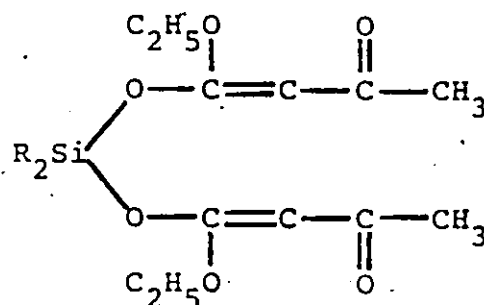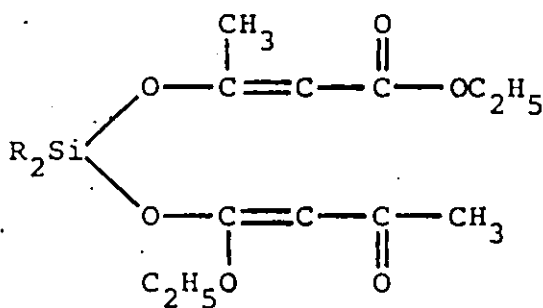
(b)

<u>XXXIV</u>

condensation to occur. The product collected from the reaction mixture was analyzed by ^{1}H nmr and IR spectroscopies, and was confirmed to be the pure β-ketoester.

Boron trichloride also was used as a Lewis acid in the condensation and cyclization of 2,4-pentanedione. The procedure was similar to that outlined by Fay and Serpone.[102]

The characteristic dark-red color was observed on exposing the reaction mixture to the air. Work-up of the solution and isolation of the product resulted in a slight yellow coloration on the cold finger of the sublimation apparatus. The coloration was very similar to that obtained in other syntheses of pyrylium salts. Only a small amount was recovered, not enough to characterize the product further.

The synthesis of the pyrylium salt from 2,4-hexane-dione and $(CH_3)_2SiCl_2$ results in a very unstable pyrylium salt. The salt was characterized by mass spectroscopy. The sample had the characteristic yellow color while under vacuum, but when a sample was prepared for nuclear magnetic resonance studies the sample immediately decomposed. The unsymmetrical nature of this ligand compared to 2,4-pentane-dione may result in some difficulty in obtaining the pyrylium salt. The possible precursor complexes formed are given in (XXXV). The $-C_2H_5$ group is larger than the $-CH_3$ group and this may affect the reaction. The electronic effects are very similar. There may be a competition in the three possible complexes resulting in a mixture of pyrylium salts that may be formed, but this does not explain the instability. There is no explanation for the inability of the 2,4-hexane-dione to condense and cyclize to form a pyrylium salt, even though there is a very strong resemblance between the nature of the two β-diketones.

(a)

(b)

(c)
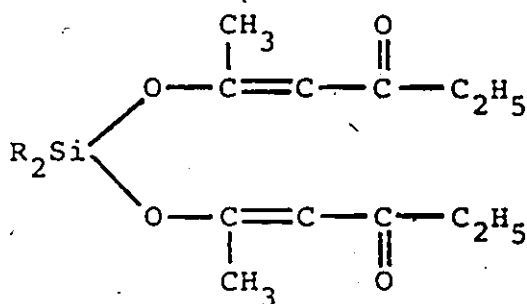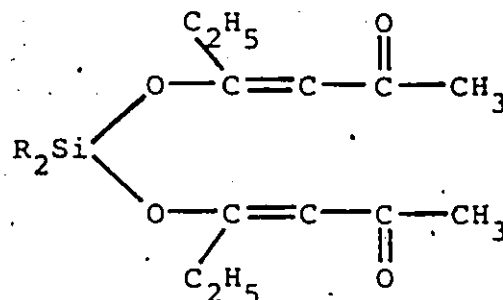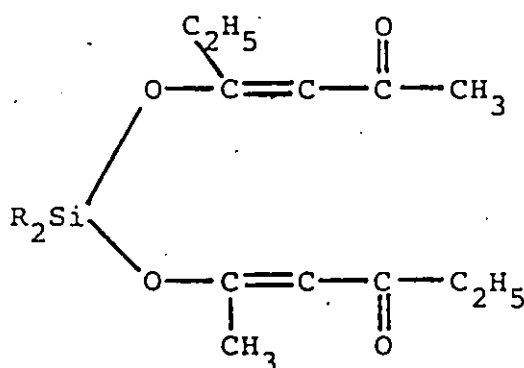
XXXV

III.A.2. ACIDITY OF PYRYLIUM CHLORIDE

The acidity of a weak organic acid may be determined by several techniques, of which the most popular are pH acid-base titrations and spectrophotometric techniques. Before delving into these experimental techniques, a little should be said about what the pK of a weak acid is. The derivation and detailed explanation of the equations used may be found in any analytical chemistry textbook.[104]

The addition of a weak acid, HA, to water results in the reaction

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$
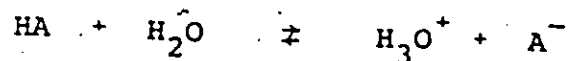
The resulting expression for the equilibrium in this system is:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

where K_a is the dissociation constant of the acid, HA, and A^- is the concentration of the dissociated acid. Thus, the pH gives the pK_a of HA under the condition that $[HA]=[A^-]$.

The acid dissociation constant, pK_a, of pyrylium chloride in water (1.0 $\underline{M}$ NaCl) was determined by pH and spectrophotometric techniques. The pK_a's are listed in Table 5 and are 2.98 and 5.69 for the pH titration method, 3.76 for the spectrophotometric method and 3.86 for the pH determination of the pyrylium chloride solution.

Calibration curve data for the spectrophotometric method is presented in Table 6. The concentration of the pyrylium salt ranges from 0.52×10^{-5} g/cc to 1.89×10^{-5} g/cc with the corresponding absorbances ranging from 0.325 to 0.890. The calibration curve (Absorbance $\underline{vs}$ Concentration) is presented in Figure la. pK_a's from the spectrophotometric

Table 5. The pK$_a$'s of 2,4-dimethyl-6-(2'-hydroxy-1'-propenyl)
pyrylium chloride in water as determined by pH and spectro-
photometric techniques.

Method	pK$_a$
a) pH titration	2.98[a]
	5.69[a]
b) pH of a solution of the pyrylium chloride	3.86
c) spectrophotometric	3.76

Ave. = 3.81

[a] Not used in the final calculation of the pH value (see text).

Table 6. The concentration of 2,4-dimethyl-6-(2'-hydroxy-1'-
propenyl)pyrylium chloride in water (1.0 $\underline{M}$ NaCl) and the
corresponding absorbance at λ=398 nm.

Concentration (10^5 g/cc)	Absorbance
1.69	0.890
1.56	0.868
1.30	0.760
1.04	0.626
0.78	0.485
0.52	0.325

method were determined both mathematically (Table 7) and graphically (Figure 1b). In both cases, the pK_a was determined to be 3.76.

The pH acid-base titration curves of the pyrylium chloride and sodium hydroxide are presented in Appendix A.

Table 7. Log $[A^-]$ / $[HA]$ as a function of the pH of 2,4-dimethyl-6-(2'-hydroxy-1'-propenyl)pyrylium chloride in water (1.0 $\underline{M}$ NaCl).

pH	$[A^-]$ $(10^5$ g/cc)	$[HA]$ $(10^5$ g/cc)	$\log[A^-]$ / $[HA]$	pK_a
3.20	6.211	2.243	0.442	3.64
3.39	5.509	2.940	0.273	3.66
3.55	4.958	3.488	0.153	3.70
3.72	4.257	4.186	0.007	3.73
4.00	3.005	5.432	-0.257	3.74
4.61	1.853	6.588	-0.551	4.06
				ave. 3.76 ± 0.15[a]

[a] Mathematically determined value.

The first method to be discussed will be the acid-base titration technique. A known amount of the weak acid (pyrylium chloride) was dissolved in distilled water. The

Figure 1. Calibration curve (a) and the plot of pH versus log $[A^-]/[HA]$ (b) required for the pK_a determination of pyrylium chloride in water.

(a)

(b)

Absorbance

Conc.(g/cc ×10⁵)

0.50   150

0.2   0.4   0.6   0.8

pH

3.00   4.00   5.00

log[A⁻]/[HA]

-0.6 -0.4 -0.2   0   0.2   0.4

pK VIA pH MEASUREMENT   3.86

pK VIA SPECTROPHOTOMETRIC   3.72

METHOD

66
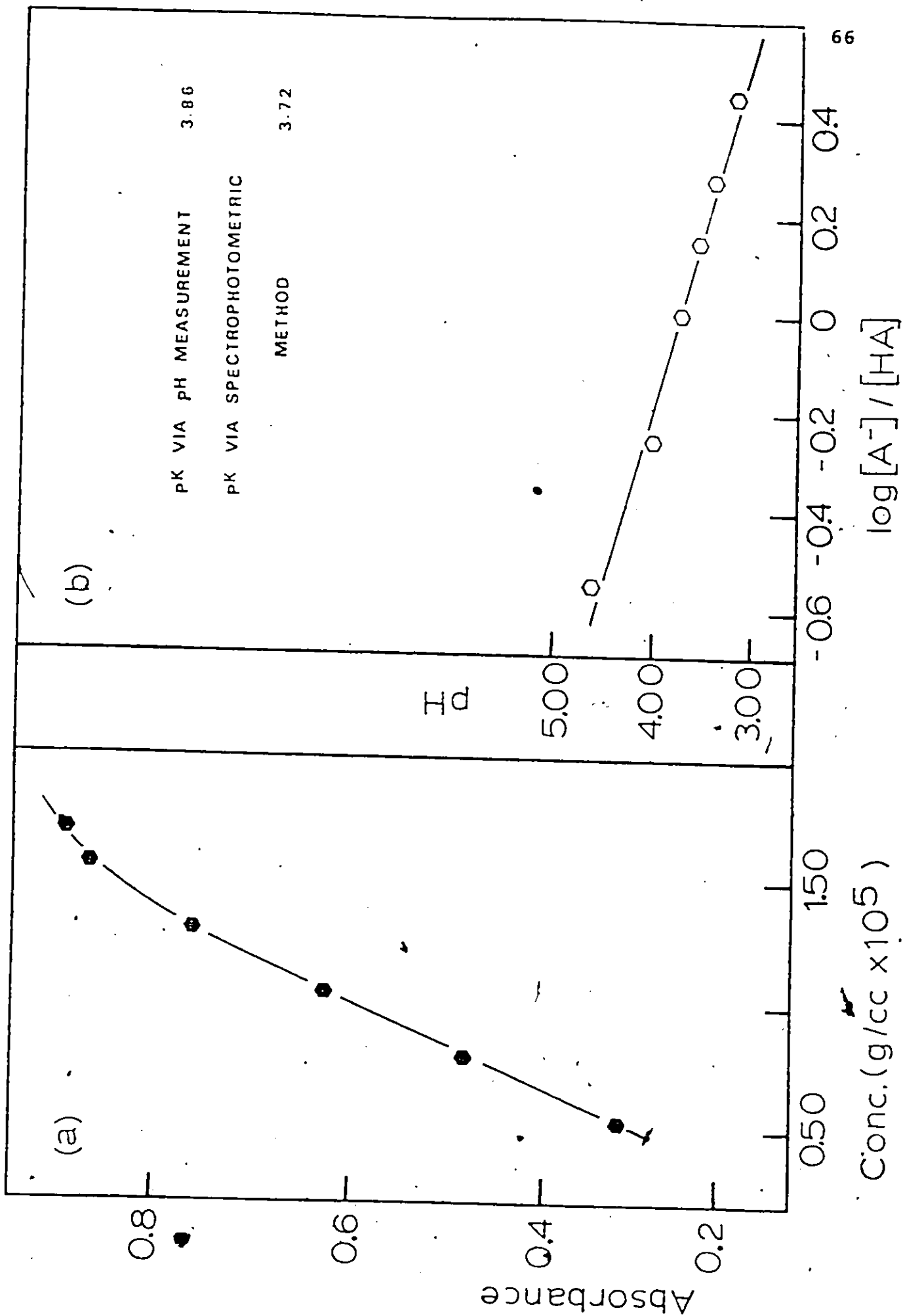
samples were titrated with a standardized sodium hydroxide solution. After each aliquot of sodium hydroxide added, the pH of the solution was recorded. A plot of the pH _vs_ ml of titrant yielded a value of the pH at the equivalence point (Appendix A). The K_a was calculated from the expression:

$$C_s = \frac{V_a M_a}{V_a + V_b} \qquad\qquad [H_3O^+] = \sqrt{\frac{K_a K_w}{C_s}}$$

where C_s is the concentration of the salt, V_a and V_b are the volume of the acid and base, respectively, M_a is the molarity of the weak acid, $[H_3O^+]$ is the concentration of the acid obtained from the pH at the equivalence point and K_w is the ionization constant of water (1.0×10^{-14}).

The two values of the pK_a obtained from the titration method at two different times with fresh solutions are 2.98 and 5.69. The reason for the large discrepancy between the two values is attributed to a possible reaction between the weak acid and OH^-. When these titrations were performed, it was believed that the neutralization reaction would be the predominant reaction. However, the results show that this was not the case.

The reaction between the pyrylium chloride and hydroxide was believed to proceed according to Scheme 7:
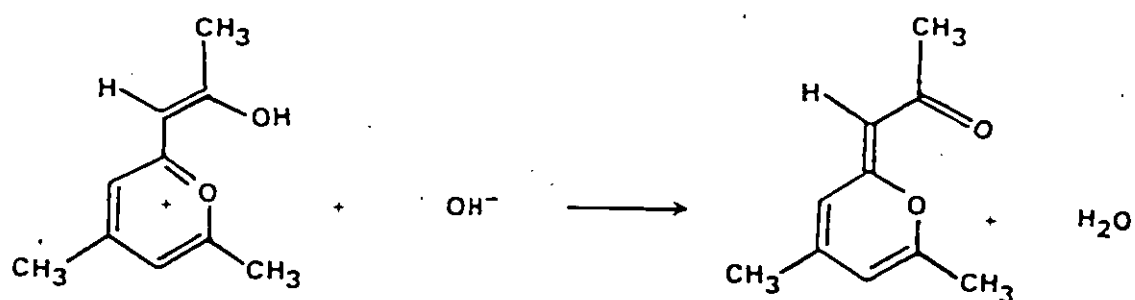
SCHEME 7

The other reaction that is well known in pyrylium salt chemistry[106] is presented in Scheme 8:
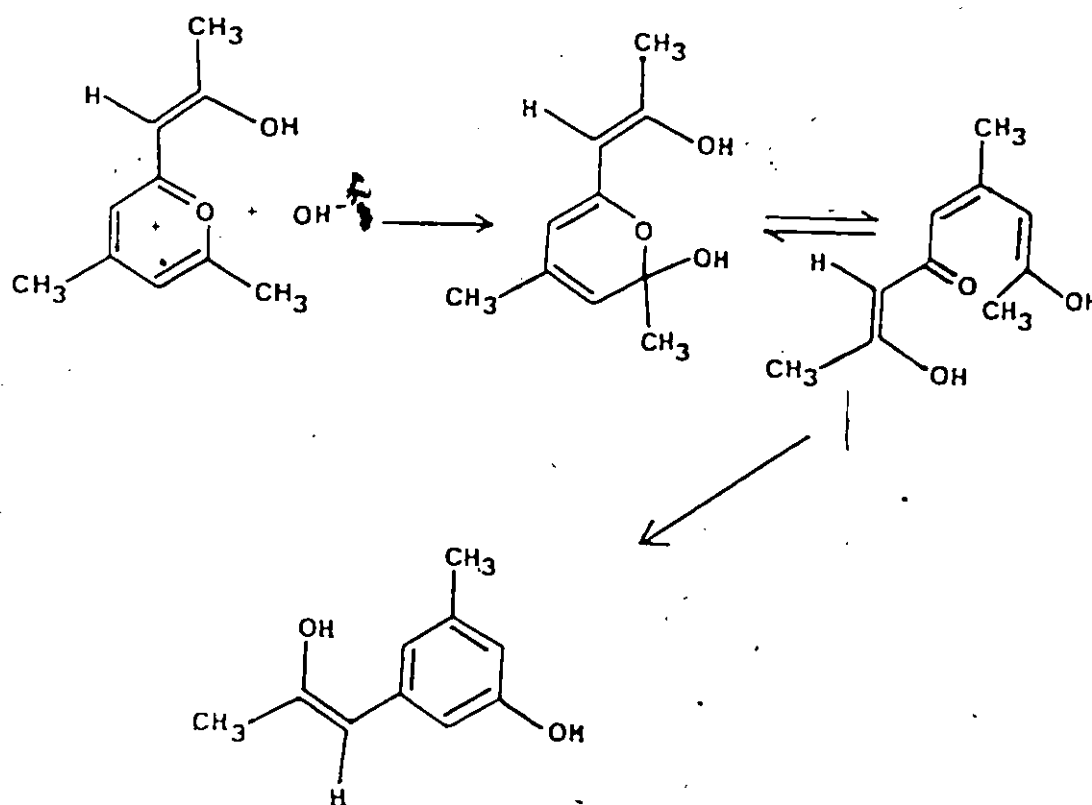
SCHEME 8

The reaction depicted in Scheme 8 predominates and probably causes the differences in the pK_a values. During the titration the OH^- must decide which site is more energetically favorable, the acidic site or the 2-position on the ring; it appears that the phenol formation interferes to a marked degree.

A technique that is a variation of the acid-base titration method is one that involves a measurement of the pH of a known amount of the weak acid in water. From a knowledge of the pH of the solution, a simple mathematical treatment gives the value of the pK_a from the expression:

$$[H_3O^+] = \frac{-K_a \pm \sqrt{K_a^2 + 4K_a C_a}}{2}$$

where $[H_3O^+]$ is obtained from the pH of the solution, and C_a is the concentration of the weak acid in water. This method avoids the use of base, which may cause unwanted side reactions. This procedure necessitates calibrating the pH meter with buffer solutions near the pH of the solution containing the weak acid. Thus, the first reliable value of the pK_a was recorded. A value of 3.86 was obtained which agrees with the preliminary result of ≈4 obtained from absorption spectra in acidic solutions.

This brings us to the third and final method used in the pK_a determination of pyrylium chloride. The pyrylium salt is stable in weak acid solutions. Thus, there appeared

to be no interfering aspects in this experiment. A stock solution of the weak acid in water (and 1.0 $\underline{M}$ NaCl) was prepared. The calibration curve was prepared by making successive dilutions of the stock solution with dilute acid. Subsequent addition of acid (very small amounts) to a solution in the upper region of the calibration curve followed by measurements of the absorption and the pH of the solution resulted in the raw data required to determine the pK_a. The pK_a was determined in two ways: the first was graphical and the pK_a was obtained by plotting pH $\underline{vs}$ log $[A^-]/[HA]$, with the pH at the intercept being the pK_a. The second method involved substitution into the equation

$$pK_a = pH + \log [HA]/[A^-]$$

In both cases the value of the pK_a was 3.76.

The acid dissociation of pyrylium chloride in water may be represented as that shown in Scheme 9:
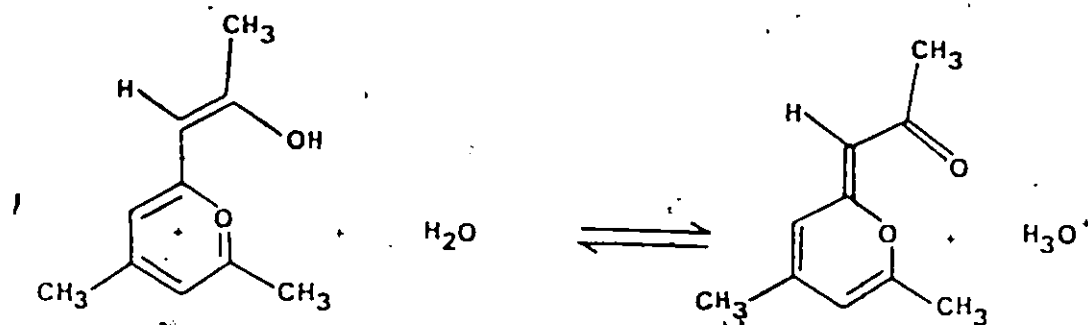
SCHEME 9

Thus, the pyran is the conjugate base of the pyrylium salt, as was expected.

III.A.3. REACTIONS OF PYRYLIUM CHLORIDE

The importance of pyrylium salt research lies in the relative ease of converting the pyrylium salt into other heterocyclic or benzenoid molecules. The pyrylium cation can undergo three basic types of reactions:[106]

a) recyclization

b) changes in the substituents on the aromatic ring

c) reactions which retain the ring

The addition of nucleophilic agents to cyclic cations results in the destruction of the aromaticity which frequently leads to ring opening. There is a possibility of the open-chain compound to recyclize or remain open. Only those reactions in which the open-chain recyclizes will be discussed.

Pyridine, pyridinium salts, and pyridine-N-oxides can be prepared from pyrylium salts by their interaction with ammonia and its derivatives. Several workers have investigated these reactions,[108-112] and have reported that the yields are almost always quantitative. Aqueous and alcoholic ammonia solutions,[108,110] or ammonium acetate in acetic acid[113] are generally employed in the conversion of pyrylium salts to pyridine. The mechanism of the reaction involves nucleophilic attack by ammonia at the 2-position

of the pyrylium ring (Scheme 10). This leads to ring-opening and subsequent closure to form the pyridine ring.[114]
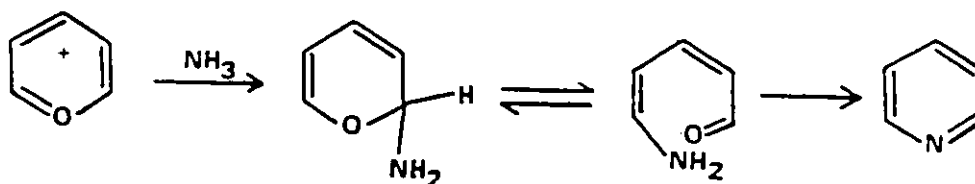
SCHEME 10

Similarly, primary aliphatic and aromatic amines react with pyrylium salts to form N-alkyl- and N-aryl-pyridinium salts.[115] This method is used to produce pyridinium salts which would be otherwise difficult to prepare by other methods.[108,109,112,115]

The conversion of pyrylium chloride into 2,4-dimethyl-6-(2'-propanone)pyridine was accomplished by adding concentrated aqueous ammonia to an aqueous solution of pyrylium chloride. Extraction with ether followed by recrystallization from dichloromethane and hexanes yielded the desired product. This pyridine was an oil.

The ^{1}H nuclear magnetic resonance spectrum of the pyridine derivative in $CDCl_3$/TMS solution is redrawn as a bar graph in Figure 2. Chemical shifts of this compound are presented in Table 8. All signals are singlets. There is one signal in the aromatic region (δ 6.89 ppm), three signals in the methyl region (δ 2.23, 2.30, 2.50 ppm) and one methylene resonance (δ 3.86 ppm).

Figure 2. Nuclear magnetic resonance spectrum of 2,4-dimethyl-6-(2'-propanone)pyridine in $CDCl_3$ solution.

TMS

0   1.0   2.0   3.0   4.0   5.0   6.0   7.0   8.0

δ PPM

4

2

1

3

A,B

CH_3^2

H^B

H^A

CH_3^1

CH_2^3—C—CH_3^4

O
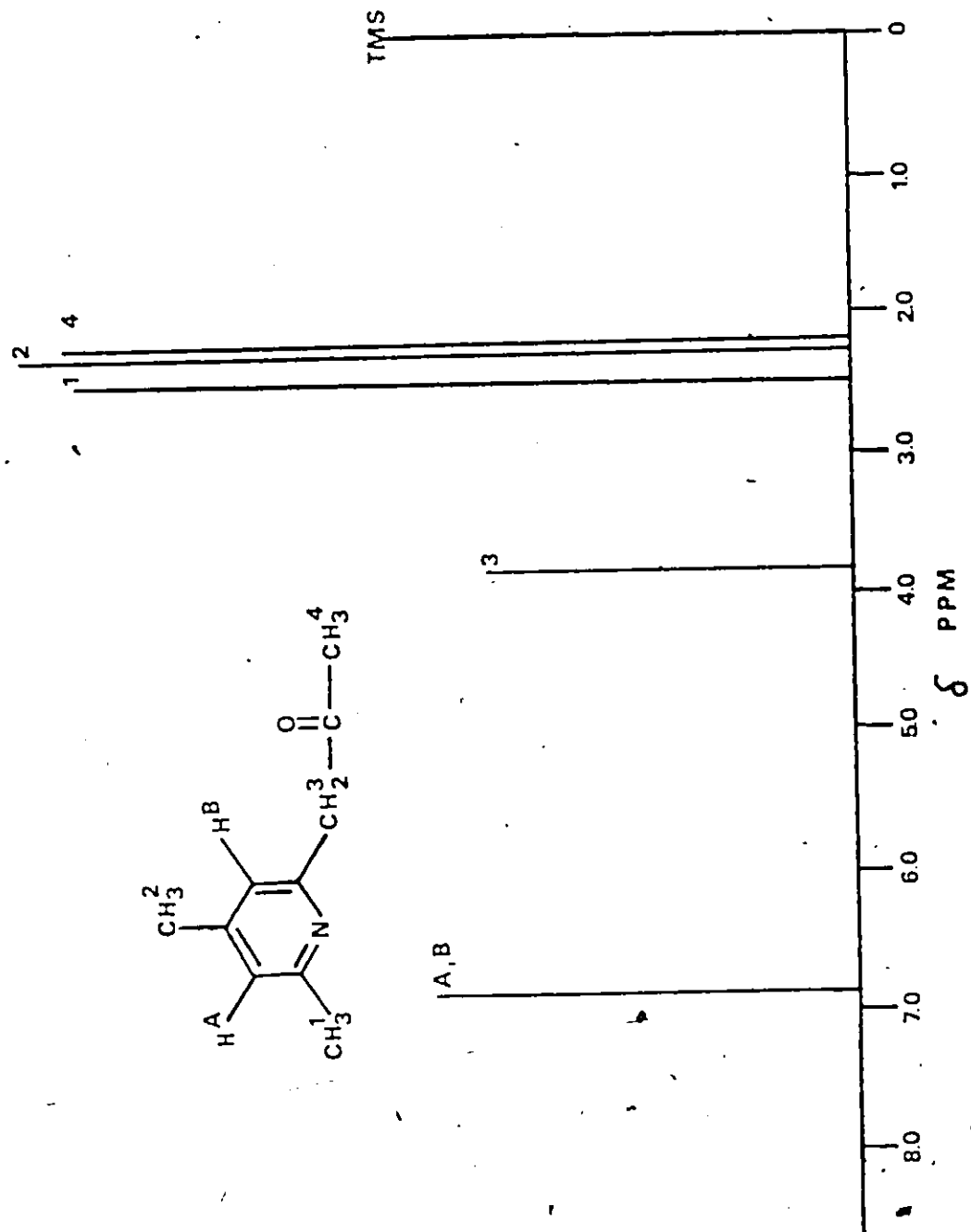
Table 8. Chemical shifts of substituted pyridine compounds.
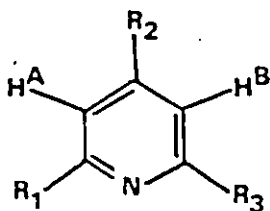
Compound	Substituent	Chemical shift (δ ppm)	Solvent	Reference
1	R^1 CH$_3$	2.50	CDCl$_3$	116
	R^2 CH$_3$	2.29		
	R^3 H	8.35		
	H^a	6.99		
	H^b	6.97		
2	R^1 R^3 CH$_3$	2.52	CDCl$_3$	116
	R^2 H	7.45		
	H^a,H^b	6.97		
3	R^1 R^3 CH$_3$	2.37	CCl$_4$	
	R^2 CH$_3$	2.18		
	H^a,H^b	6.59		
4	R^1 CH$_3$	2.50	CDCl$_3$	—
	R^2 CH$_3$	2.30		
	H^a,H^b	6.89		
	R^3 CH$_2^c$COCH$_3^d$	(c) 3.86; (d) 2.23		

Solvent effects are critical in the nmr spectra of pyridines.[117] The two ring protons in the pyridine derivative (compound 4) were recorded as a singlet at δ 6.89 ppm. This is in agreement with the literature for substituted pyridines in $CDCl_3$.[116] The ring methyl group in the 2-position (R^1) and 4-position (R^2) are assigned to the signals at δ 2.50 ppm and 2.30 ppm, respectively, in accordance to the chemical shifts reported.[116] The carbonyl methyl group chemical shift is located at δ 2.23 ppm, in agreement with carbonyl methyl group chemical shifts obtained from standard spectroscopy textbooks.[118] Methylene groups attached to aromatic rings are observed in the nuclear magnetic resonance spectrum at ≈δ 4 ppm,[119] in agreement with the methylene group signal at δ 3.86 ppm.

The infrared spectrum of the pyridine derivative was recorded in $CDCl_3$/TMS solution in NaCl sealed cells (0.1 mm) in the region 1900-800 cm^{-1} (Figure 3). Major absorption bands are listed in Table 9 with possible assignments. The band at 1705 cm^{-1} is assigned the C=O stretching frequency. There are several absorption bands in the 1600-1400 cm^{-1} region indicating the presence of a pyridine ring (Table 9), and based on the similarity of the two pyridine infrared spectra (the pyridine derivative and the pyridine from the literature) it may be concluded that a pyridine ring is present in the molecule.

The mass spectrum of the pyridine derivative is presented in Figure 4 with the major fragment ions listed

Figure 3. Infrared spectrum of 2,4-dimethyl-6-(2'-propanone)
pyridine in the region 1900-800 cm^{-1} in $CDCl_3$ solution.
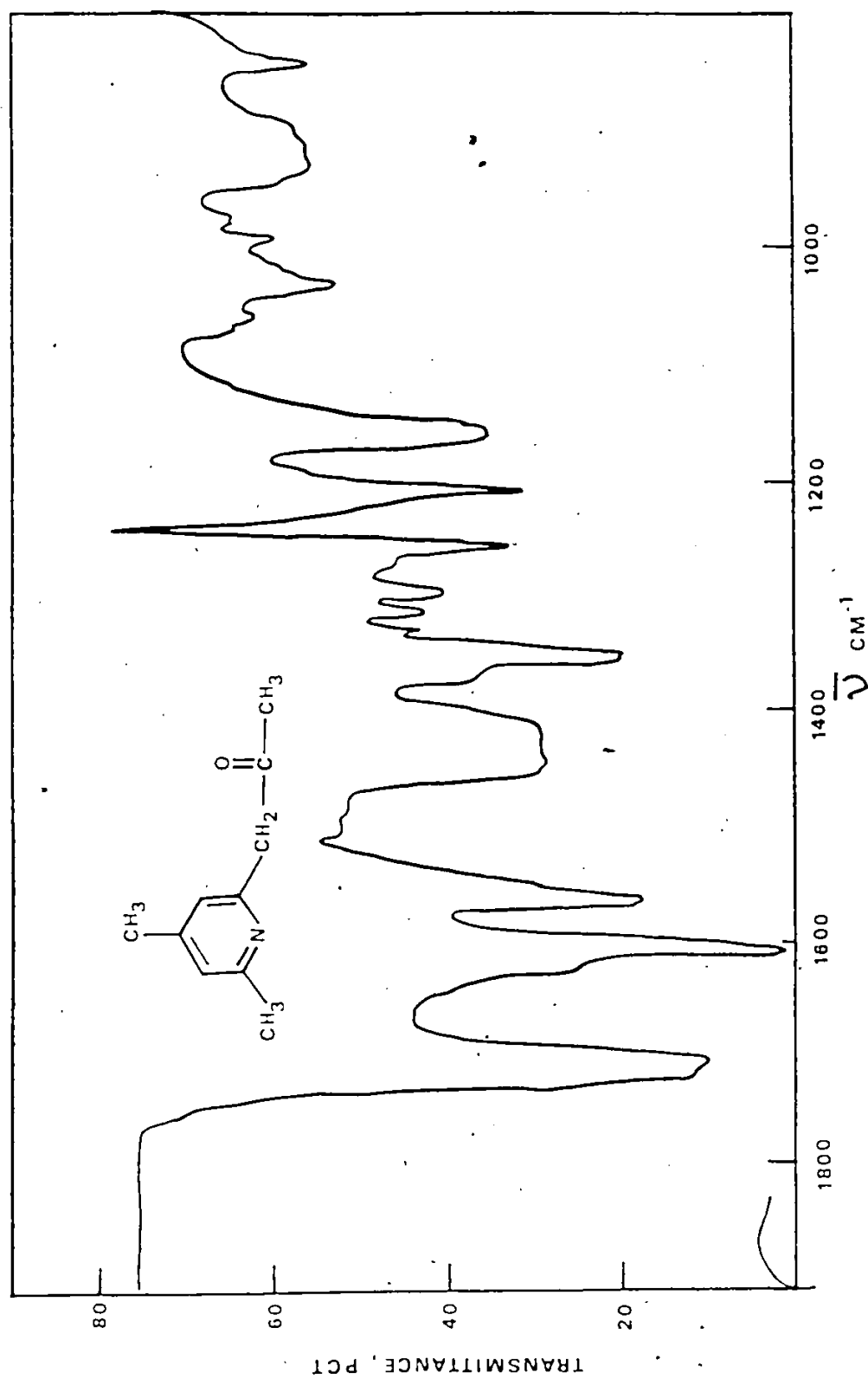
Table 9. Infrared absorptions of 2,4-dimethyl-6-(2'-propanone)pyridine in $CDCl_3$ solution.

$\bar{\nu}$ (cm^{-1})	Possible modes	$\bar{\nu}$ (cm^{-1}) [a]
1705	C=O	–
1605	ring vibration	1583
1560	ring vibration	1572
1450	ring vibration	1482
1355	ring vibration	1375

[a] Ring vibrations of pyridine from ref. 120.

in Table 10. In the mass spectrum of the pyridine derivative two points are noteworthy: the simplicity of the mass spectrum and the presence of the molecular ion (in contrast to the mass spectrum of the pyrylium salt). The molecular ion ($C_{10}H_{13}NO^{\cdot+}$) is located at m/e 163. Loss of a methyl group (m/e 15) and a HCN group (m/e 27) results in the formation of the ion $C_8H_9O^+$ (m/e 121).[121] Another process which leads to the m/e 121 involves the loss of $CH_2CO^{\cdot}$ (m/e 42). Cleavage at the α-carbon on a chain is a highly probable process.[118] The fragmentation pattern of the pyridine derivative is presented in Scheme 11.

Figure 4. Mass spectrum of 2,4-dimethyl-6-(2'-propanone)
pyridine.
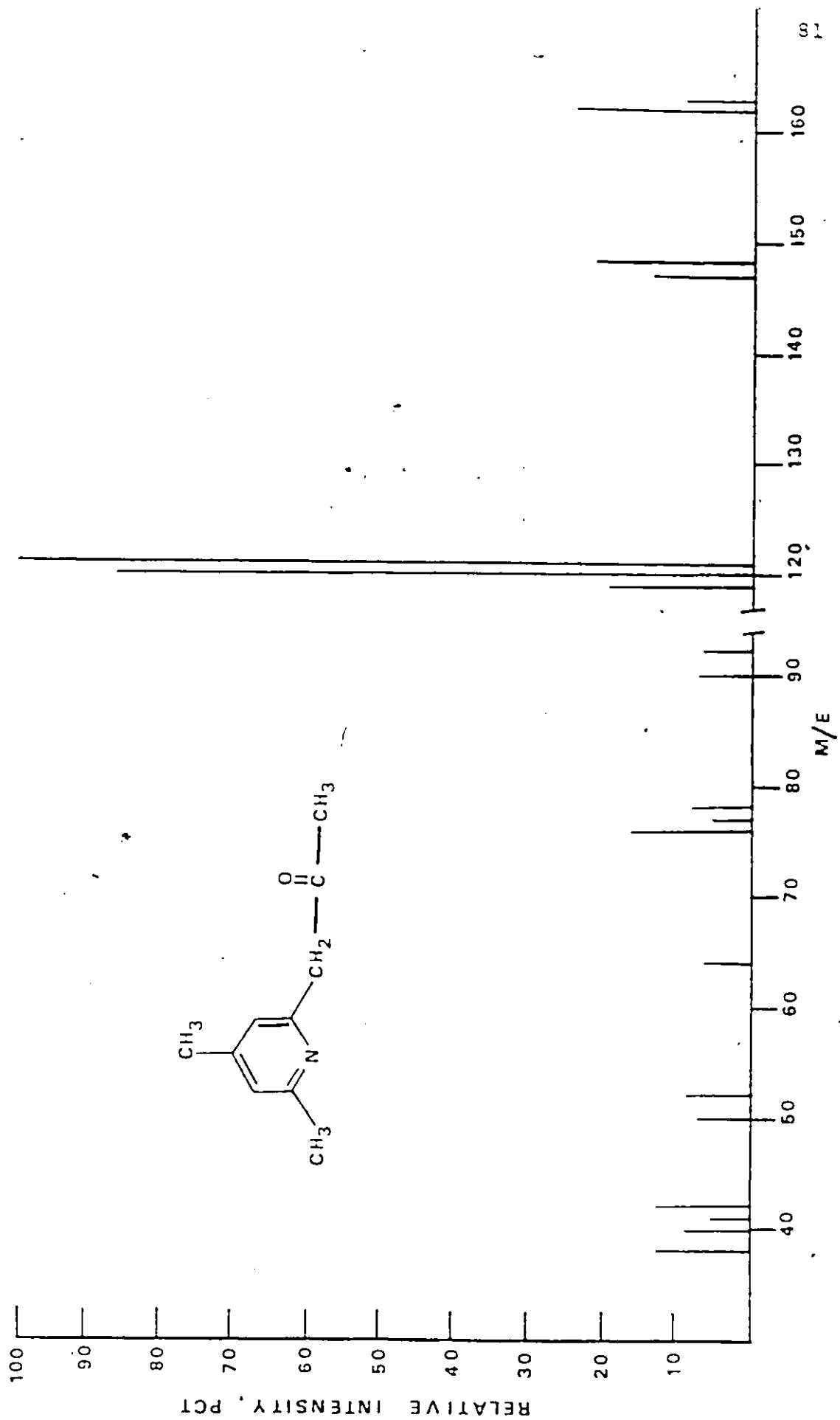
Table 10. Relative intensities of some major fragment ions of 2,4-dimethyl-6-(2'-propanone)pyridine.

m/e (amu)	Relative Intensity(%)	Fragment
163	9.4	$C_{10}H_{13}NO^{+\cdot}$
162	24.0	$C_{10}H_{12}NO^{+}$
148	20.8	$C_9H_{10}NO^{+}$
147	14.1	$C_9H_9NO^{+\cdot}$
121	100.	$C_8H_{11}N^{+}$
		$C_8H_9O^{+}$
120	84.9	$C_8H_{10}N^{+}$
119	17.4	$C_8H_9N^{+}$
76	15.9	$C_5H_2N^{+}$

All the instrumental techniques indicate the synthesis of the pyridine derivative of pyrylium chloride produced the expected product.

As far as the thiapyrylium salt synthesis is concerned, addition of sodium sulfide to a pyrylium salt also results in ring opening (Scheme 12):

$$C_{10}H_{13}NO^{+\cdot}$$
$$(163)$$

$$\dot{C}H_3 + C_9H_{10}NO^+ \qquad CH_3CO^{\cdot} + C_8H_{10}N^{+\cdot} \qquad \dot{C}H_2CO^{\cdot} + C_8H_{11}N^{+\cdot}$$
$$(15) \quad (148) \qquad\qquad (43) \qquad (120) \qquad\qquad (42) \qquad (121)$$

$$HCN + C_8H_9O^+ \qquad\qquad\qquad\qquad\qquad\qquad \dot{C}H_3 + C_7H_8N^{+\cdot}$$
$$(27) \quad (121) \qquad\qquad\qquad\qquad\qquad\qquad\qquad (15) \quad (106)$$

$$\dot{C}H_3 + C_6H_5N^{+\cdot}$$
$$(15) \quad (91)$$

$$\dot{C}H_3 + C_5H_2N^{+\cdot}$$
$$(15) \quad (76)$$
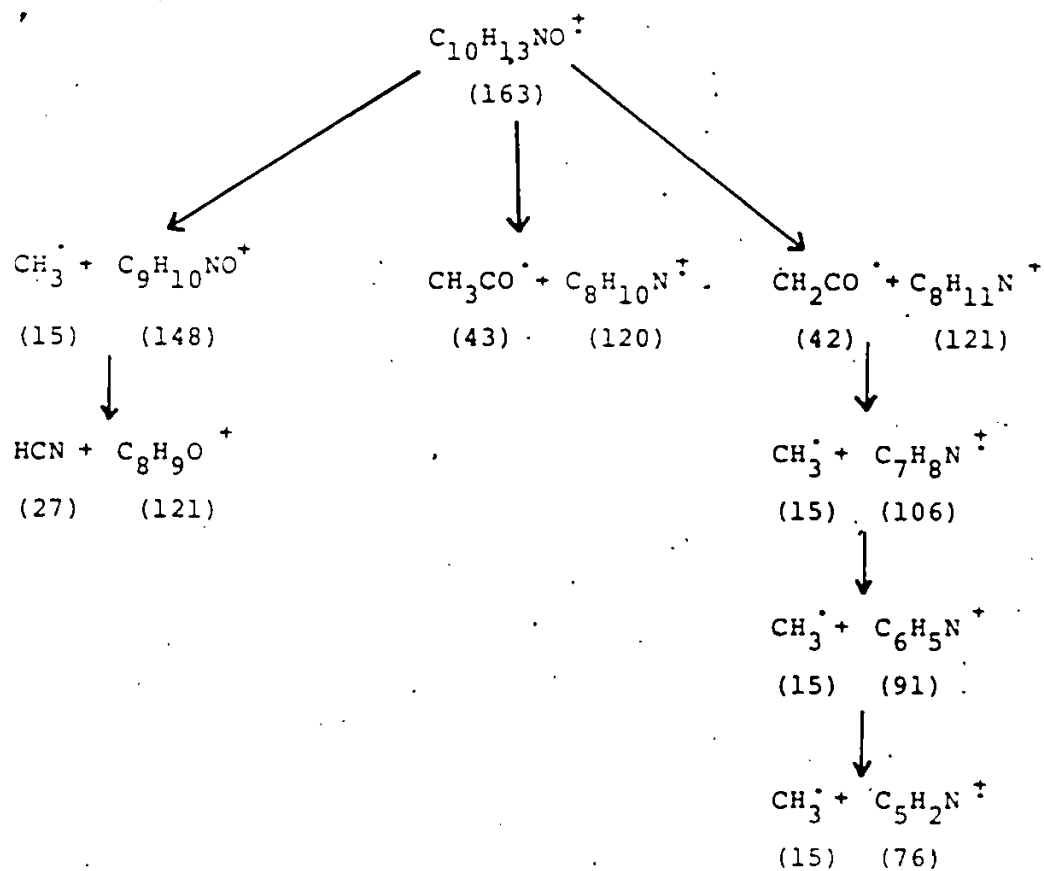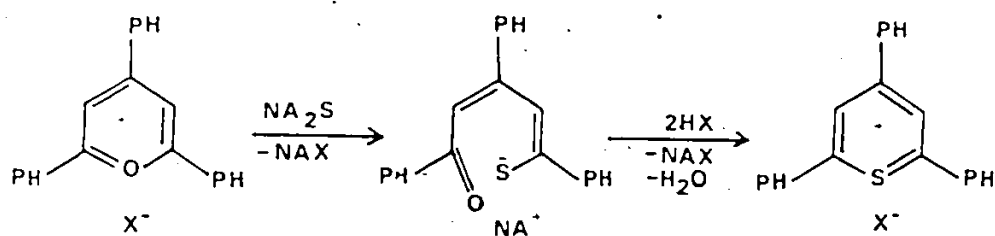
Scheme 11

SCHEME 12

Wizinger and Ulrich[103] proposed that in the presence of an inorganic acid the ring closes to form the thiapyrylium salt.

The method used to prepare the thiapyrylium salt derivative of pyrylium chloride was that of Wizinger and Ulrich.[103] However, all attempts to produce the desired thiapyrylium salt proved unsuccessful. The reason for this failure lay in the structure of the pyrylium chloride (see Scheme 7, A). In order for this reaction to proceed, a phenyl group in the 2-position is required.[106] There is no known example of the reaction of a pyrylium salt proceeding to a thiapyrylium salt without a phenyl group in the 2-position. No explanation was given[106] for the purpose of the aryl group; apparently the electronic structure of the aryl group somehow stabilizes the intermediate formed.

III.A.4. NUCLEAR MAGNETIC RESONANCE SPECTRA OF PYRYLIUM SALTS

Since nuclear magnetic resonance experiments have become a routine analytical method, there is a large amount of information on the proton chemical shifts of pyrylium salts. A general survey of the proton chemical shifts of pyrylium salts are presented (Table 11).

Earnest and Brown[99] have prepared several alkyl substituted pyrylium salts and have characterized them by nmr spectroscopy. All spectra were recorded as CD_3CN solutions and the proton resonances are listed in Table 11. The aromatic

Table 11. Nuclear magnetic resonance spectral data of substituted pyrylium ions.[99]
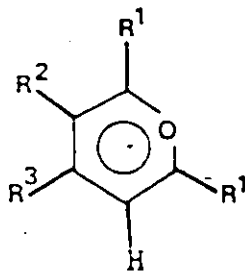
R^1 (δR^1, ppm)	R^2 (δR^2, ppm)	R^3 (δR^3, ppm)	Aromatic Protons
CH_3 (2.84) (2.87)	CH_3 (2.40)	CH_3 (2.63)	8.02
CH_3 (2.96)	——	C_2H_5 (1.32,t)[a] (3.02,q) (J 7.6 Hz)	7.99
C_2H_5 (1.41,t) (3.20,q) (J 7.5 Hz)	——	C_2H_5 (1.36,t) (3.10,q) (J 7.5 Hz)	8.00
CH_3 (2.90)	CH_3 (2.42)	C_2H_5 (1.27,t) (3.01,q) (J 8.0 Hz)	7.90
C_2H_5 (1.50,t) (3.32,q) (J 7.5 Hz)	CH_3 (1.67)	CH_3 (2.58)	——

[a] t, triplet; q, quartet.

protons of the pyrylium hexachloroplatinates are found in the regions δ 7.80-8.06 ppm. The 2-alkyl protons absorb in the region δ 2.84-2.96 ppm, the 4-alkyl proton signals occur in the region δ 2.58-2.78 ppm, and the 3-alkyl protons at δ 1.67-2.42 ppm. The other alkyl groups (ethyl and iso-propyl) have their characteristic splitting patterns as well as agreement with the resonance positions reported by Balaban and co-workers.[122]

In a very recent paper on the synthesis of pyrylium salts by the condensation of 2,4-pentanedione, Fowles, Rice and Shanton[96] reported that the nmr spectra of all species studied were identical in a given solvent. The nuclear magnetic resonance spectral results of 3-acetyl-2,4,6-trimethylpyrylium salts are listed in Table 12. In CD_3CN, two of the proton resonances overlap as compared to CF_3COOH where all signals are clearly separate. Assignments were based on the criterion that CH_3 (C-2) and CH_3 (C-6) are adjacent to the ring oxygen and that because CH_3 (C-2) is adjacent to the acetyl group, this signal will occur at a higher δ value. The other assignments were obtained by comparison with analogous compounds.

The nuclear magnetic resonance spectrum of pyrylium chloride in $CDCl_3$ solution consists of four signals (Figure 5), two each in the aromatic (at δ 8.10 and 6.73 ppm) and in the methyl (at δ 2.45 and 2.57 ppm) regions (Table 13). In the low temperature (-44.8°) nmr spectrum,[83] two additional proton signals appear at δ 5.6 and 14.3 ppm.

Table 12. Nuclear magnetic resonance spectral data of 3-acetyl-2,4,6-trimethylpyrylium cation in CF_3COOH and CD_3CN solutions.[96]

1. CF_3COOH

X^- —— $ZnBr_6^{2-}$	δ 2.76 ppm	CH_3	(C-2)
	δ 2.84 ppm	CH_3	(C-6)
	δ 2.94 ppm	CH_3	(C-4)
	δ 3.01 ppm	CH_3	(acetyl)
	δ 7.90 ppm	H	(C-5)
X^- —— $(WCl_2O_2(CH_3CO)_2CH)$	δ 2.76 ppm	CH_3	(C-2)
	δ 2.84 ppm	CH_3	(C-6)
	δ 2.94 ppm	CH_3	(C-4)
	δ 3.01 ppm	CH_3	(acetyl)
	δ 7.90 ppm	H	(C-5)

2. CD_3CN

X^- —— $TaCl_4O$	δ 2.65 ppm	CH_3	(C-2,6)
	δ 2.80 ppm	CH_3	(C-4)
	δ 2.99 ppm	CH_3	(acetyl)
	δ 7.93 ppm	H	(C-5)

Figure 5. Nuclear magnetic resonance spectrum of pyrylium chloride in $CDCl_3$.
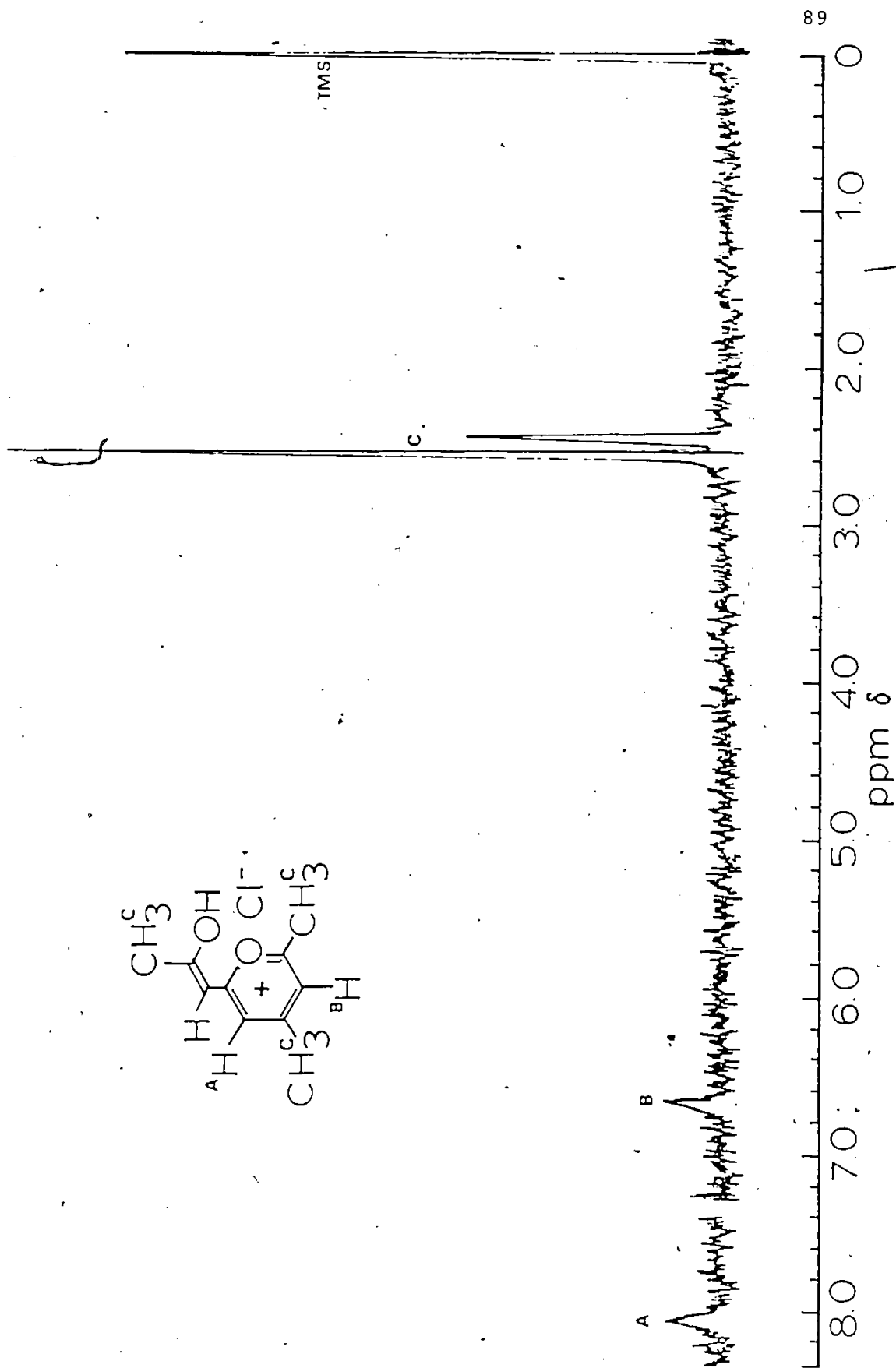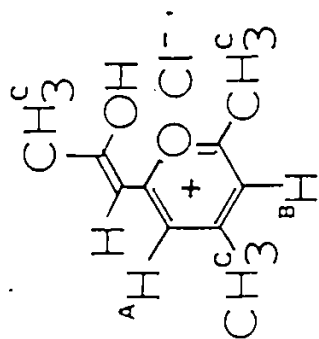
Table 13. Proton magnetic resonance chemical shifts of
pyrylium salts in $CDCl_3$.

$R^1 = R^2 = R^3 = CH_3$	δ 2.45–2.57 ppm
$R^4 = H$	δ 8.10 ppm
H^A	δ 5.6 ppm
H^B	δ 14.3 ppm
H^C	δ 6.73 ppm
$R^1 = R^2 = R^3 = C_3H_7$	
$R^4 = C_2H_5$	δ 0.75–1.40, 1.40–2.08, 2.30–3.00 ppm
H^C	δ 6.53ppm .

These two signals are attributed to the rapidly exchanging
protons (keto-enol tautomerism) present in the propenyl
side chain (Scheme 13), where R is the substituted pyrylium
ring. The high acidity of pyrylium chloride (pK_a of 3.76)
is seen from the nmr signal at δ 14.3 ppm. This region
indicates that an acidic proton is present. The signal at
δ 5.6 ppm is characteristic of the alkene proton resonance
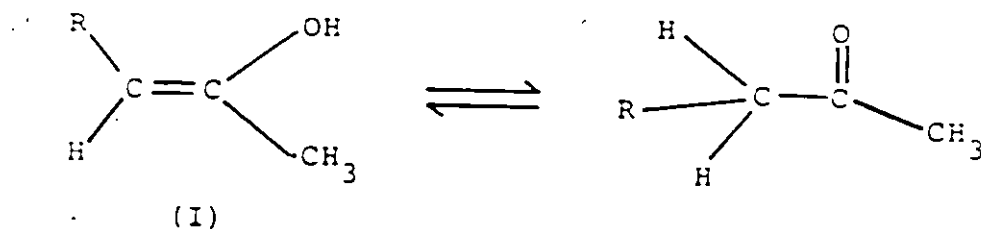
Scheme 13

region, which supports the presence of structure (I) in Scheme 13. Assignment of the other signals were obtained from the following argument The 2-methyl group and the methyl group adjacent to the hydroxyl group in the side chain have similar environments and have been assigned to δ 2.57 (6H) ppm. Due to the large amount of double-bond character present in the hydroxyl group, as observed from the X-ray crystallographic experiment,[83] the two methyl groups are in similar environments (Scheme 14):
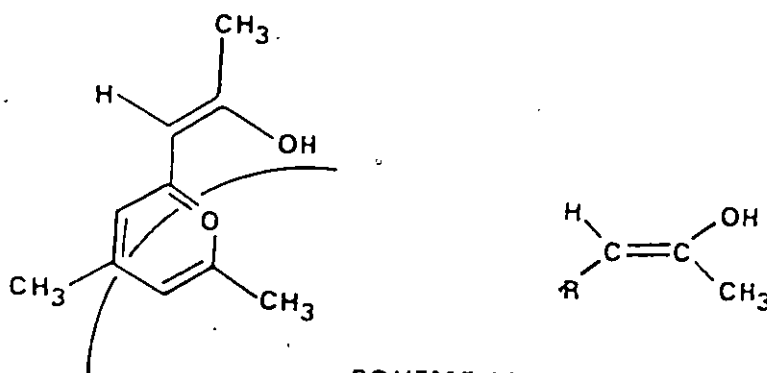
SCHEME 14

The third methyl group, the 4-methyl, is assigned as δ 2.45

(3H) ppm. However, because this signal integrates to three protons and is upfield from the signal at δ 2.57 ppm, assignment was somewhat less ambiguous. The aromatic protons were assigned by comparison with the other pyrylium salt synthesized in this laboratory. The pyrylium salt obtained from the 4,6-nonanedione synthesis contained only one aromatic proton at δ 6.53 ppm. Thus, the 3-position proton signal (adjacent to the 2-methyl group) in pyrylium chloride was assigned as δ 6.73 ppm. The proton adjacent to the propenyl side chain was assigned the signal at δ 8.10 ppm, since the aromatic proton is deshielded by the propenyl group which causes the proton signal to shift to lower field.

The assignment of the nmr spectrum of the pyrylium salt obtained from 4,6-nonanedione was more difficult than the preceding pyrylium chloride. This is due to the presence of propyl and ethyl groups (Figure 6). The ethyl group produces the characteristic triplet and quartet in the regions δ 1.0 and 2.5 ppm, respectively, and the propyl group has the characteristic triplet (δ 1.0 ppm), sextet (δ 1.5 ppm), and triplet (δ 2.5 ppm). There is a large amount of overlap in the alkyl region, which makes it difficult to make assignments. The one assignment that is possible is that of the aromatic proton with a chemical shift of δ 6.53 ppm (Table 13).

The nuclear magnetic resonance spectrum of pyrylium chloride in $CDCl_3$ was discussed earlier, and it was noted that four signals are present. However, in distilled water,

Figure 6. Nuclear magnetic resonance spectrum of 2,4-di-
n-propyl-5-ethyl-6-(2'-hydroxy-1'-pentenyl)pyrylium chloride
in $CDCl_3$.

94
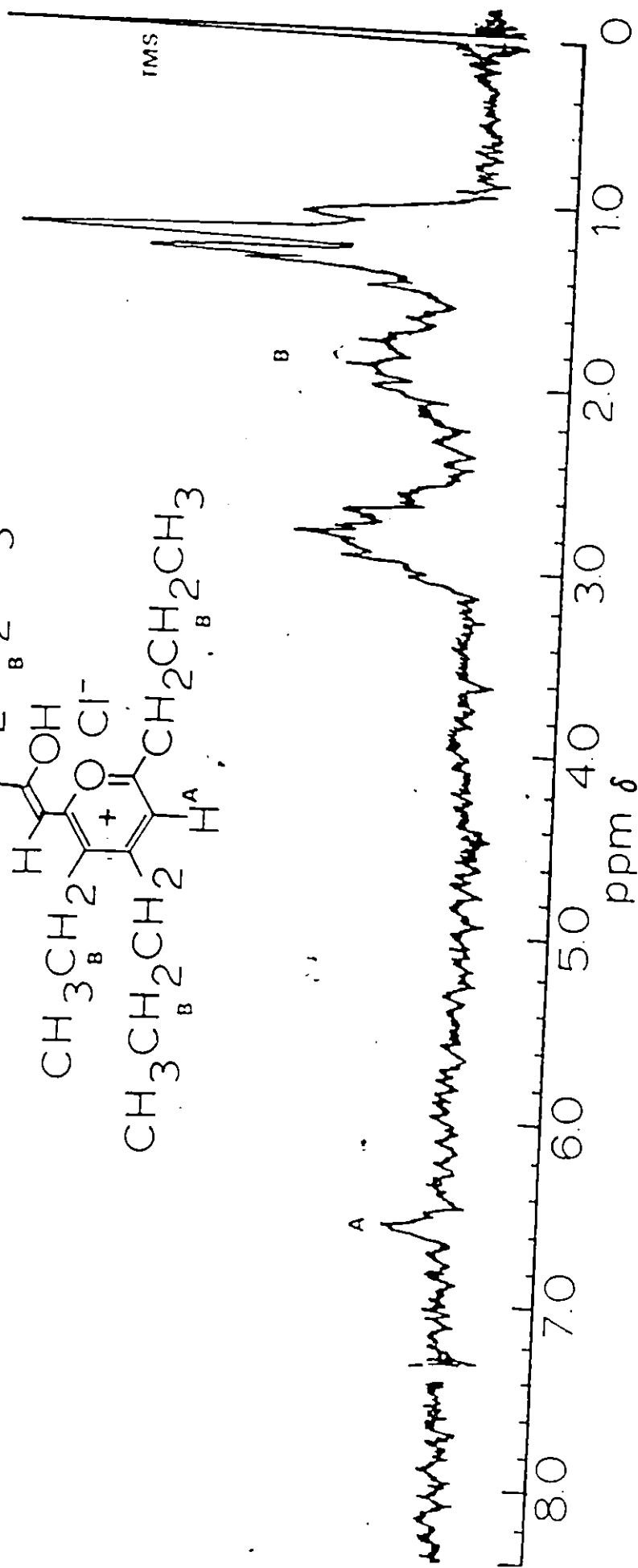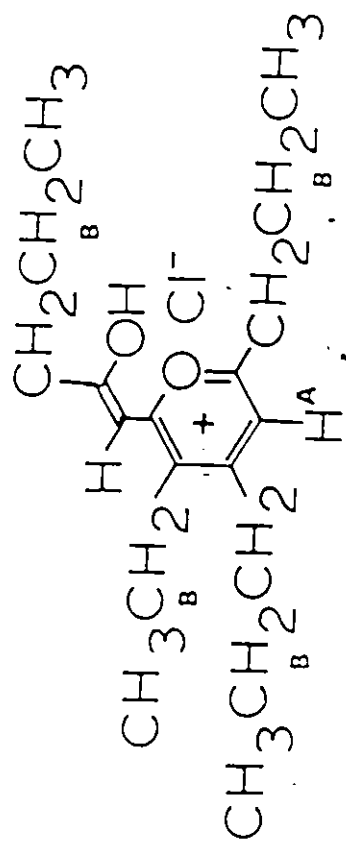
·the same pyrylium salt produces five signals. A schematic
of the spectra is shown in Caption 1. The methyl region
changes from two signals to three signals. The aromatic

H₂O/HCl

H₂O

CDCl₃

TMS

8   6   4   2   0

δ (PPM)
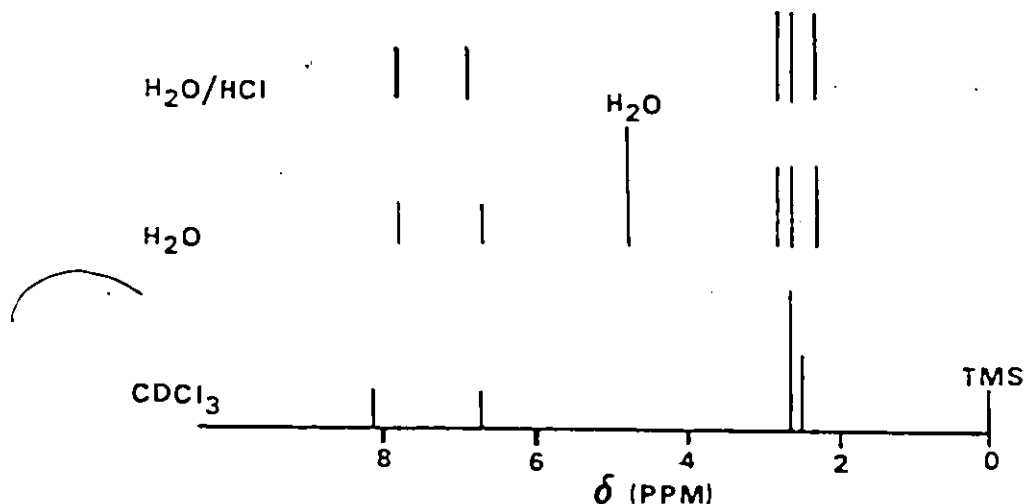
CAPTION 1

region remained the same but, the signal which originally
represented two methyl groups split into two signals. A
reason for this change may be due to the high polarity of
the solvent, water, compared to the organic solvent, $CDCl_3$.
The water may act as a base and affect the methyl group
adjacent to the hydroxyl group in the propenyl side chain.
This effect may cause the resonance signal to shift, that is,
the environment of the 2-methyl and the acetyl type methyl
are sufficiently different to cause the splitting to occur.
However, the purpose of this experiment was not to study
the nmr spectrum in water as to structure determination, but

to study the structural changes that may take place in acidic and basic solutions.

In acidic solution, the nuclear magnetic resonance spectrum is the same as in pure water. The pK_a of pyrylium chloride is 3.76 and addition of hydrochloric acid (1.0 $\underline{M}$) does not affect the spectrum, but the solution changes from a bright yellow to a pale yellow color. It is possible that a fast equilibrium is set up, which is not evident in the room-temperature spectrum. This equilibrium is represented in Scheme 15:

SCHEME 15
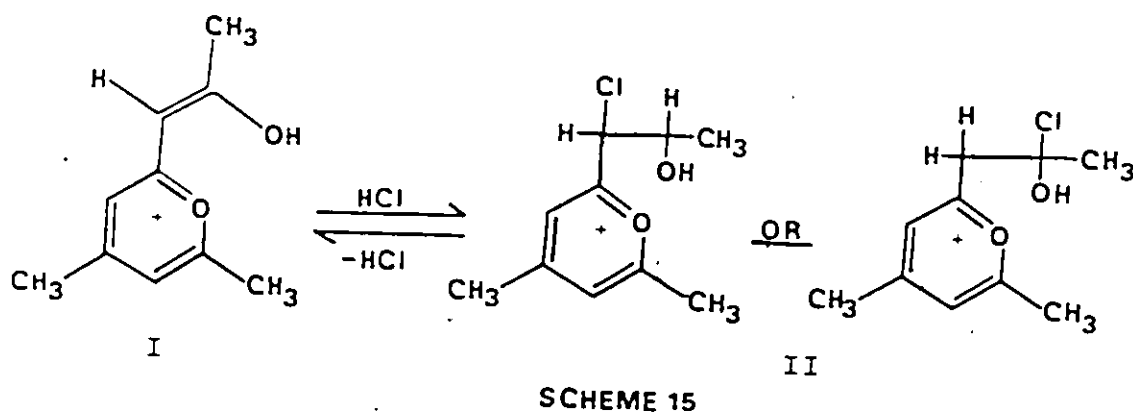
The nmr spectrum would not be altered if the exchange is fast. Because the solvent is water, it may be difficult to record a reliable low temperature spectrum. One can look at the other possibility, that there is a reaction between the hydrochloric acid and pyrylium chloride to form structure (II). It is entirely possible that this entity is a pale yellow color, since the high degree of conjugation initially present is now removed. However, α-haloalcohols are unstable[123]

so that this structure may not be a reality, but only an intermediate in the fast exchange reaction. Therefore, it is difficult to find an explanation for the loss of color.

The addition of base to the pyrylium salt in water results in an orange colored solution. The nmr spectrum of this solution is not given in Caption 1 because of its complexity, that is, there were resonance signals in all regions of the spectrum. It should be remembered that base causes the pyrylium ring to produce the open-chained moiety. Thus, the nuclear magnetic resonance spectrum contains a host of compounds because of a possible reaction occurring in the sample tube. It should be noted that the aromatic signals do disappear, added proof that there is a reaction proceeding.

The addition of acid and base to the nmr sample solution has an effect on the system in solution. A scheme is proposed to account for the changes (Scheme 16). If one considers the enol form of the pyrylium salt, three paths are open. The first (1) is the well known keto-enol tautomerism. The presence of this equilibrium was confirmed by obtaining the nuclear magnetic resonance spectra at ambient and at low temperatures. In the ambient temperature spectrum the rate of exchange between the vinylic and ethylenic protons is faster than the nmr time scale. The low temperature slows down the exchange process such that the time required for exchange and the time scale of the nmr are similar. This results in the appearance of two
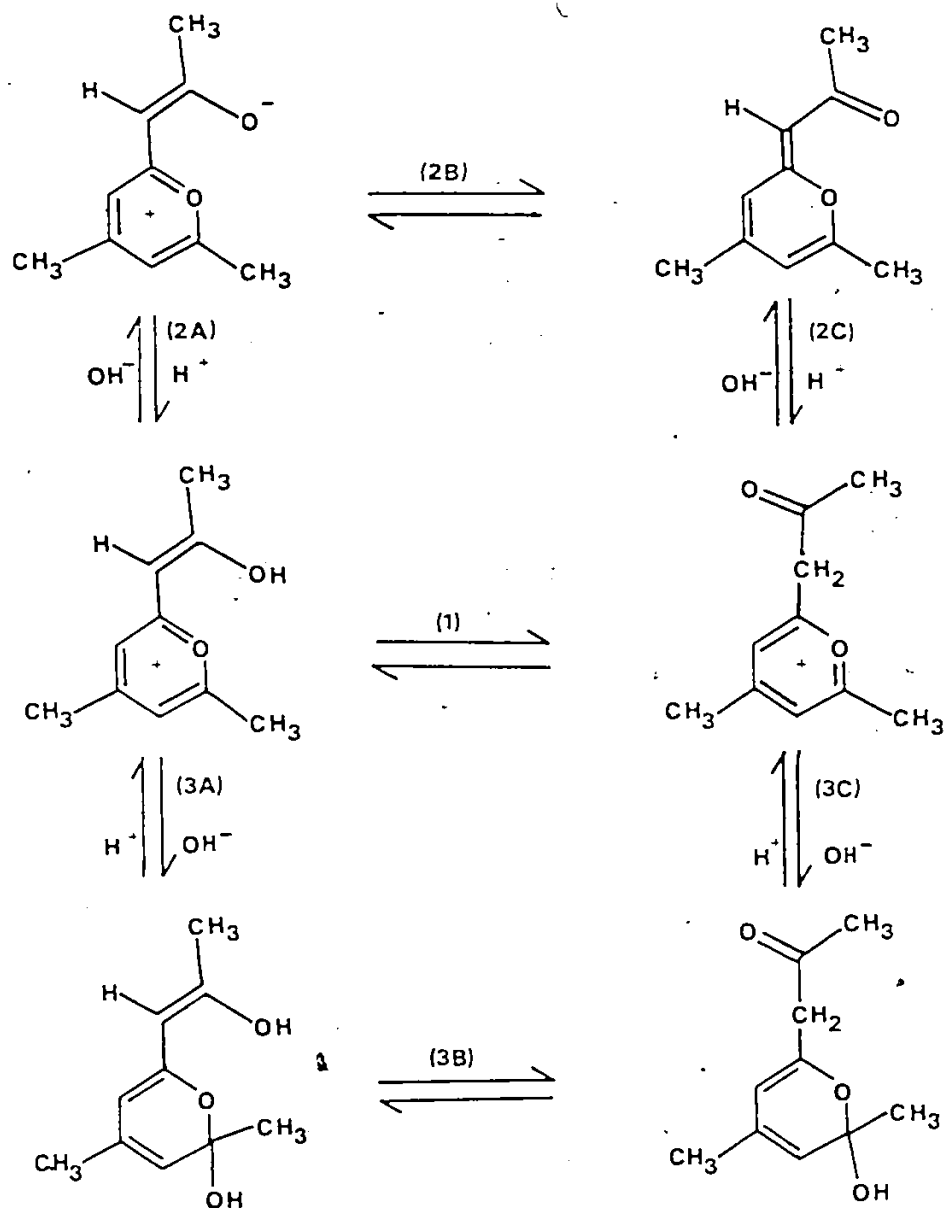
SCHEME 16

additional signals in the low temperature spectrum not present in the ambient temperature spectrum.

The second path involves the addition of base (2A) to a solution of the pyrylium salt in water. A simple acid-base reaction results in the abstraction of the acidic enolic proton. This 'intermediate' may then be set up in an equilibrium (2B) in which the Zwitterion neutralizes itself to form a substituted pyran molecule, which may be a stable species. Addition of acid (2C) results in the keto form of the pyrylium salt, which changes to the starting enol form.

The third path again involves addition of base (3A), but now follows the known conversion of a pyrylium salt to a phenol. An equilibrium (3B) may be set up to give a 2-hydroxy pyran which can be converted to the keto form (3C) of the starting pyrylium chloride. From the nmr data presented, it appears that the reaction observed in acid solution is path (2), and the basic reaction is path (3).

To further elucidate the structure of pyrylium chloride in solution, a series of ^{13}C and ^{1}H decoupling nuclear magnetic resonance experiments were performed. The ^{13}C nmr spectrum of pyrylium chloride was recorded in $CDCl_3$. Chemical shifts in ppm downfield from TMS are presented in Table 14 with references made to 2,4-pentanedione.[124] Certain portions of pyrylium chloride are structurally similar to 2,4-pentanedione. Carbon atoms 8, 9 and 10 of pyrylium chloride are in a similar environment as carbon atoms 8, 9 and 10 of 2,4-pentanedione. The chemical shifts of C-2 and

Table 14. [13]C nuclear magnetic resonance chemical shifts of pyrylium chloride and 2,4-pentanedione[124] in $CDCl_3$/TMS solution.
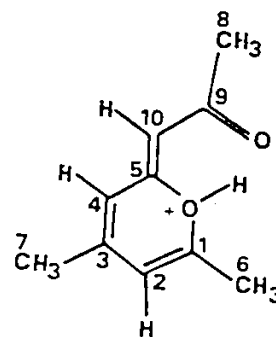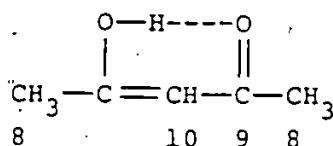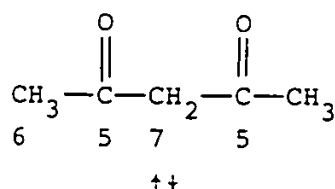
Chemical shift of pyrylium chloride (ppm)	Chemical shift of 2,4-pentanedione (ppm)	Carbon atom
20.2	30.2	6
22.7	58.2	7
24.8	24.3	8
94.6	100.3	10
115.5	–	2
118.7	–	4
163.2	201.4	5
166.3	–	1
172.9	–	3
186.0	191.4	9

C-4 are similar, as are C-1, C-3 and C-5. Actual assignments
of the ^{13}C chemical shifts were performed elsewhere.[*]

The results of the ^1H decoupling experiments performed
on pyrylium chloride are summarized in Table 15. The
decoupling experiments were performed by successively
irradiating each proton or proton group and observing the
effect on the remainder of the protons. In the first part of
the experiment single protons were irradiated. Protons (1)
and (4) are coupled by virtue of a keto-enol tautomerism.[83]
Irradiation of proton (1) or (4) results in the disappearance
of the nuclear magnetic resonance signal of the other. The
aromatic protons, (2) and (3), may be assigned by noting
the effect irradiation of these protons has on neighboring
groups. Irradiation of proton (2) sharpened the nmr signals
of protons (3) and (5) and that of proton (3) sharpened the
nmr signals of protons (2), (5) and (6). This experiment was
performed qualitatively.

The second part of the ^1H decoupling experiments
consisted of observing the effect irradiation of the proton
groups (methyl) has on the aromatic protons. A ^1H nmr
spectrum was recorded with no proton groups irradiated, and
the half-width ratio, referenced to $CHCl_3$, were recorded.
The proton groups were successively irradiated and an effect
on the aromatic protons was observed in the case of proton
groups (5) and (6). Irradiation of proton group (7) resulted

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[*]Dr. M. McGlinchey, McMaster University, Hamilton, Ont.

Table 15. ^{1}H decoupling experiments performed on pyrylium chloride in CDCl$_3$.
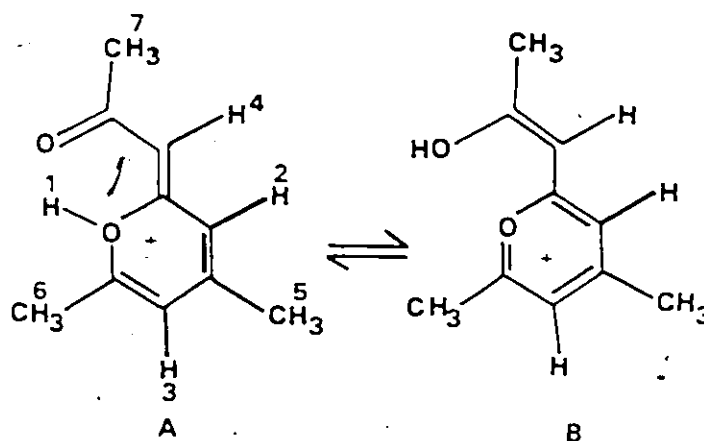
Proton/proton group irradiated	Peak studied	Half-width ratio[a]	Intensity ratio
1	4 (disappears)	–	–
4	1 (disappears)	–	–
2	3,5 (sharpened)	–	–
3	2,5,6 (sharpened)	–	–
none	2	2.11	0.50
none	3	2.11	0.48
5	2	1.82	0.56
5	3	1.82	0.50
6	2	1.94	0.50
6	3	1.72	0.52
7	2	2.00	0.49
7	3	2.12	0.52

Table 15, cont'd.

no decoupling	·2	2.7	1.0
no decoupling	3	·2.1	1.0
no decoupling	5,6,7.	-	2.1
decouple 1	2	2.9	1.0
decouple 1	3	2.5	1.0
decouple 1	5,6,7	-	2.4
decouple 4	2	1.4	1.7
·decouple 4	3	1.6	1.4
decouple 4	5,6,7	-	2.1

[a]Referenced to $CHCl_3$

in proton (2) signal sharpening, but proton (3) was unaffected.

The final part of the decoupling experiments determined the effect irradiation of protons (1) and (4) has on the aromatic protons. As in the second part of the decoupling experiments, a spectrum of the aromatic protons was recorded and the half-width ratios reported. Decoupling proton (1) did not affect either of the aromatic protons which indicates no coupling between proton (1) and protons

(2) and (3). Proton (4), on the other hand, is coupled with protons (2) and (3). This long-range coupling (proton (4)-proton (3)) could occur _via_ proton (2), that is, proton (4) is coupled to proton (2) and proton (2) is coupled to proton (3).

These ^{1}H decoupling experiments provide an unequivocal· assignment of the protons of pyrylium chloride in $CDCl_3$ solution.

In Table 15 an equilibrium is presented and the discussion of the chemical shifts is based on structure (A),. whereas earlier discussions were based on structure (B). Both cases yielded satisfactory results and conclusions. This may be explained by the equilibrium A⇌B passing through an intermediate (Scheme 17) that is required for the reaction to occur. The difference in the two structures (A) and (B)
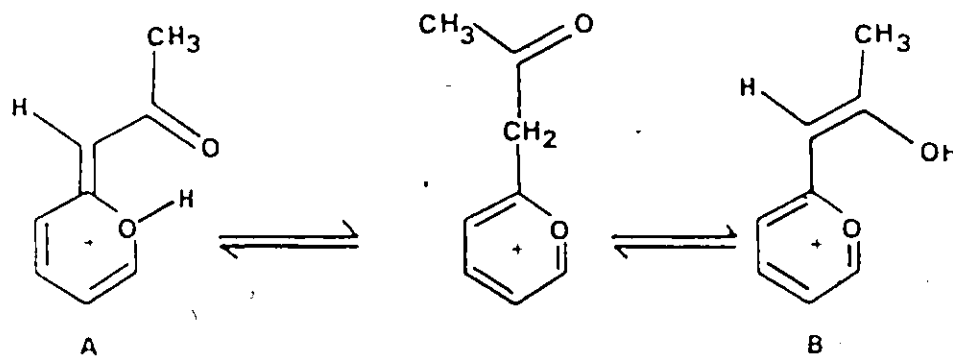
SCHEME 17

lies in the position of the enolic proton: on the side-chain oxygen or on the ring oxygen. In the solid state, the proton

is situated on the side-chain oxygen.[83] It is difficult to say which structure prevails in solution, (A) or (B), but both will be used interchangeably inasmuch as their chemistry is probably very similar.

✦

III.A.5. INFRARED SPECTRUM OF PYRYLIUM CHLORIDE

The infrared spectra of pyrylium salts have certain characteristic absorptions which unmistakably determine the presence of a pyrylium cation. An in depth survey of the infrared spectra of pyrylium salts by Balaban and co-workers[125] has shed much light on the identification of pyrylium ring modes of vibration. Bands assigned to ring stretching modes centred near 1635 cm^{-1} and 1530 cm^{-1}, as well as an absorption near 870 cm^{-1} are characteristic of the pyrylium cation. The counter-ion has little effect on the position of the absorption bands except that they have their own absorptions, and thus obscure some of the pyrylium cation absorptions.

The infrared spectrum of pyrylium chloride was recorded as a Nujol mull in the region 4000-300 cm^{-1}; the important range 2600-800 cm^{-1} is presented in Figure 7 and the major vibrational bands are listed in Table 16. At a first glance, the striking feature of this spectrum is a broad band of medium intensity centred at ca. 2390 cm^{-1}. Other bands which are characteristic of this pyrylium salt

Figure 7. Infrared spectrum of pyrylium chloride as a Nujol
mull in the region 2600-800 cm^{-1}.
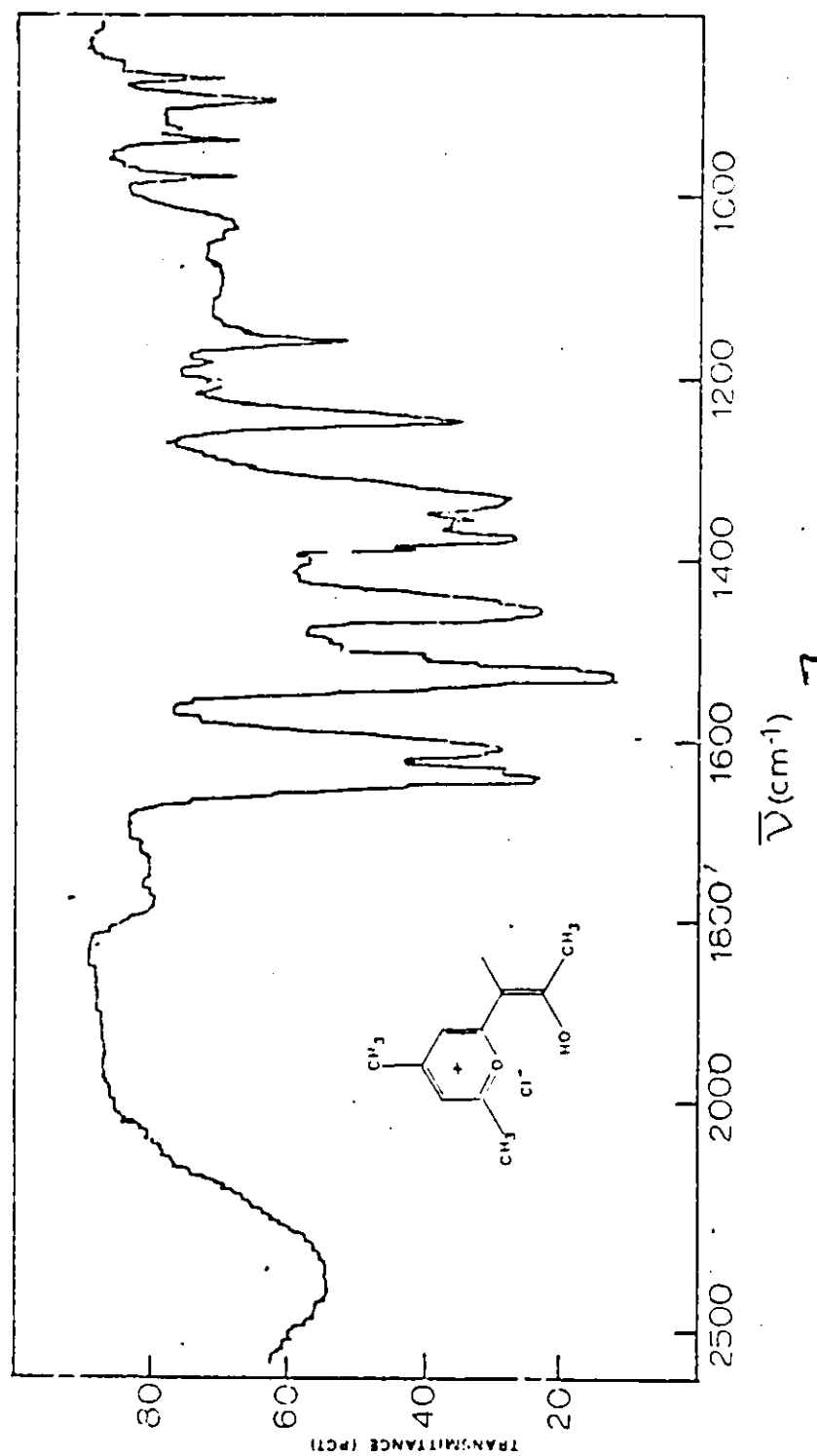
Table 16. Infrared spectral assignments of pyrylium chloride as a Nujol mull.

$\bar{\nu}$ (cm^{-1})	Relative Intensity	Possible Modes
2389	m	O——H
1769	w	C=O
1654	s	ring
1644	s	ring
1618	s	ring
1538	vs	ring
876	w	ring

are a weak band at 1769 cm^{-1}, strong bands at 1654, 1644, 1618, 1538 and a weak band at 867 cm^{-1}.

The rather weak band at ca. 2390 cm^{-1} is assigned as an O-H stretch. The large amount of double-bond character present, as observed from the X-ray crystallographic experiment,[83] shifts the band to lower energy.

The rather weak band at 1769 cm^{-1} is assigned to a carbonyl stretch based on the double-bond character of the C=O-H bond. However, Andrieux and co-workers[126] have noted that the band at 1755 cm^{-1} in their pyrylium salts is due

to the C=O stretch. The only C=O entity in their pyrylium salt is the ring C=O-C (XXXVI). This contradicts what is

XXXVI
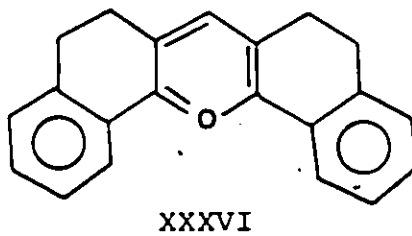
generally accepted,[125] in that the ring C=O vibration occurs at $\approx$1635 cm^{-1} and at $\approx$1530 cm^{-1}, similar to the aromatic vibrations found at 1600 and 1500 cm^{-1}.

It was noted earlier that the synthesis of the thia-pyrylium salt was unsuccessful. The purpose of this synthesis was to shed light as to what vibrational modes are responsible for the absorptions in the infrared spectral region. In the thiapyrylium salt the bands at 1635 cm^{-1} and 1530 cm^{-1} would have been expected to shift to a lower energy because of the increase in mass in going from oxygen to sulfur. This shift would have confirmed that the ring C=O-C vibration is indeed at 1635 and 1530 cm^{-1}. Since the synthesis of the thiapyrylium salt proved unsuccessful, uncertainty in the assignments in Table 16 remains.

III.A.6. MASS SPECTRA OF THE PYRYLIUM SALTS

Mass spectrometry is mainly concerned with chemical reactions, that is, reaction between a molecule and an electron. The vaporized sample is bombarded with low-energy electrons to produce the positive ions which are identified at the detector:

$$M \; + \; e^- \longrightarrow M^+ \; + \; 2e^-$$

These positive ions may further react <u>via</u> fragmentation or rearrangement reactions: thus,

$$ABCD \; + \; e^- \longrightarrow ABCD^+ \; + \; 2e^-$$

$$ABCD^+ \longrightarrow ABC^+ \; + \; D^\cdot$$
$$\quad\quad\quad \hookrightarrow AB^+ \; + \; C \qquad \Big\} \;\; \text{Fragmentation}$$

$$ABCD^+ \longrightarrow ACB^+ \; + \; D \qquad\quad \text{Rearrangement}$$
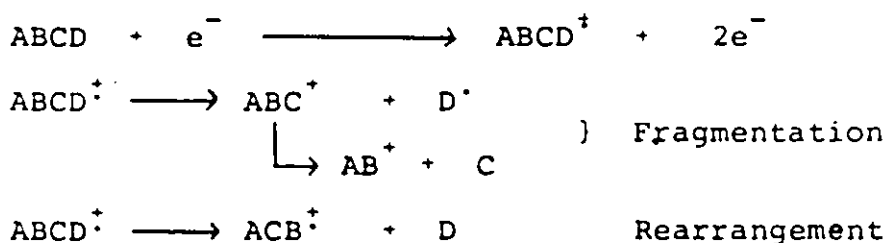
In a publication by Hvistendahl and co-workers[127] on the mass spectroscopic study of pyrylium salts, it was reported that the base peak in the mass spectra of several 2,4,6-triphenylpyrylium salts was the mass of the cation, whereas, in the methyl derivatives, the base peak was found at one unit below the mass of the cation. With respect to the methyl derivatives, it was believed that the volatile component is the anhydro base (B) in Scheme 18. Heating the
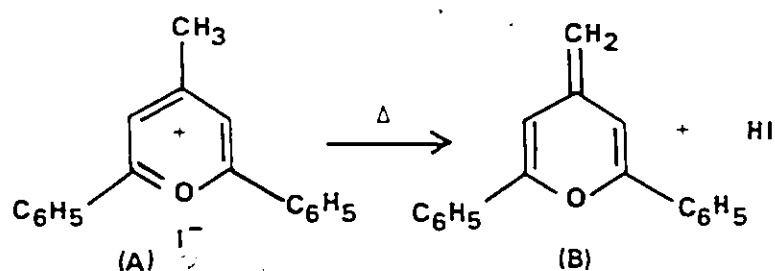
SCHEME 18

pyrylium iodide results in the liberation of hydrogen iodide
and the 4-methylene pyran, which is subsequently vaporized.
This pyran molecule then undergoes the fragmentation and
rearrangement processes characteristic of the molecule. This
also explains the lack of the molecular ion in the mass
spectra of pyrylium salts. It seems reasonable that any
pyrylium salt whose anion is the chloride, bromide or iodide
containing at least one methyl group would give a similar
mass spectrum, that is, the molecular ion peak would be
absent but the peak of the highest mass to charge would be
found at M-HX, where M is the molecular ion and X is one of
the halogens.

The mass spectra of the three pyrylium salts herein
reported are presented in Figures 8 to 10, and the listing
of the major fragment ions of these pyrylium salts is given
in Tables 17 to 19. Firstly, the molecular ion mass peak is
not present in the mass spectrum of any of the pyrylium
salts. This is in agreement with the observations obtained
by Hvistendahl[127] discussed above. The base peak ion in

each mass spectrum is found at a m/e of M-15 or M-43 (M is

the mass of the cation less one unit) where a loss of a

methyl group is the main process in the pyrylium salts

synthesized from 2,4-pentanedione and 2,4-hexanedione. A loss

of a propyl group appears to be the main process in the

fragmentation pattern of the pyrylium salt obtained from

4,6-nonanedione. These points are the general observations

found in comparing the three mass spectra.

The mass spectrum of pyrylium chloride is presented

in Figure 8 and the major fragment ions are listed in Table

17. A fragmentation pattern of the pyrylium salt is presented

in Scheme 19. From the bar graph of the mass spectrum of

pyrylium chloride it can be seen that the most intense mass

peak is located at m/e 165. However, from the discussion

above,[127] the loss of hydrogen chloride results in a peak

at m/e 164. The m/e 165 may be due to the loss of only

chlorine, in addition to the peak due to the different

isotopes present, to give a somewhat large relative intensity

at m/e 165. Getting back to the m/e at 164 (denoted as M),

the loss of the methyl radical from the acetyl side-chain

gives the base peak ion at m/e 149. If one looks at the

structure of M (XXXVII) it is evident that it is the anhydro

base of the pyrylium chloride, as expected.[127] Loss of a CHO

radical (m/e 29) from $C_9H_9O_2^+$ (m/e 149) results in the

formation of $C_8H_8O^{+\cdot}$ (m/e 120). Loss of a second methyl

radical results in the $C_7H_5O^{+\cdot}$ ion (m/e 105). The $C_7H_5O^+$

fragment may lose either a CO molecule or a HCO radical to

Figure 8. Mass spectrum of pyrylium chloride.
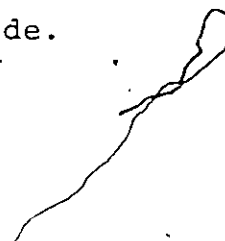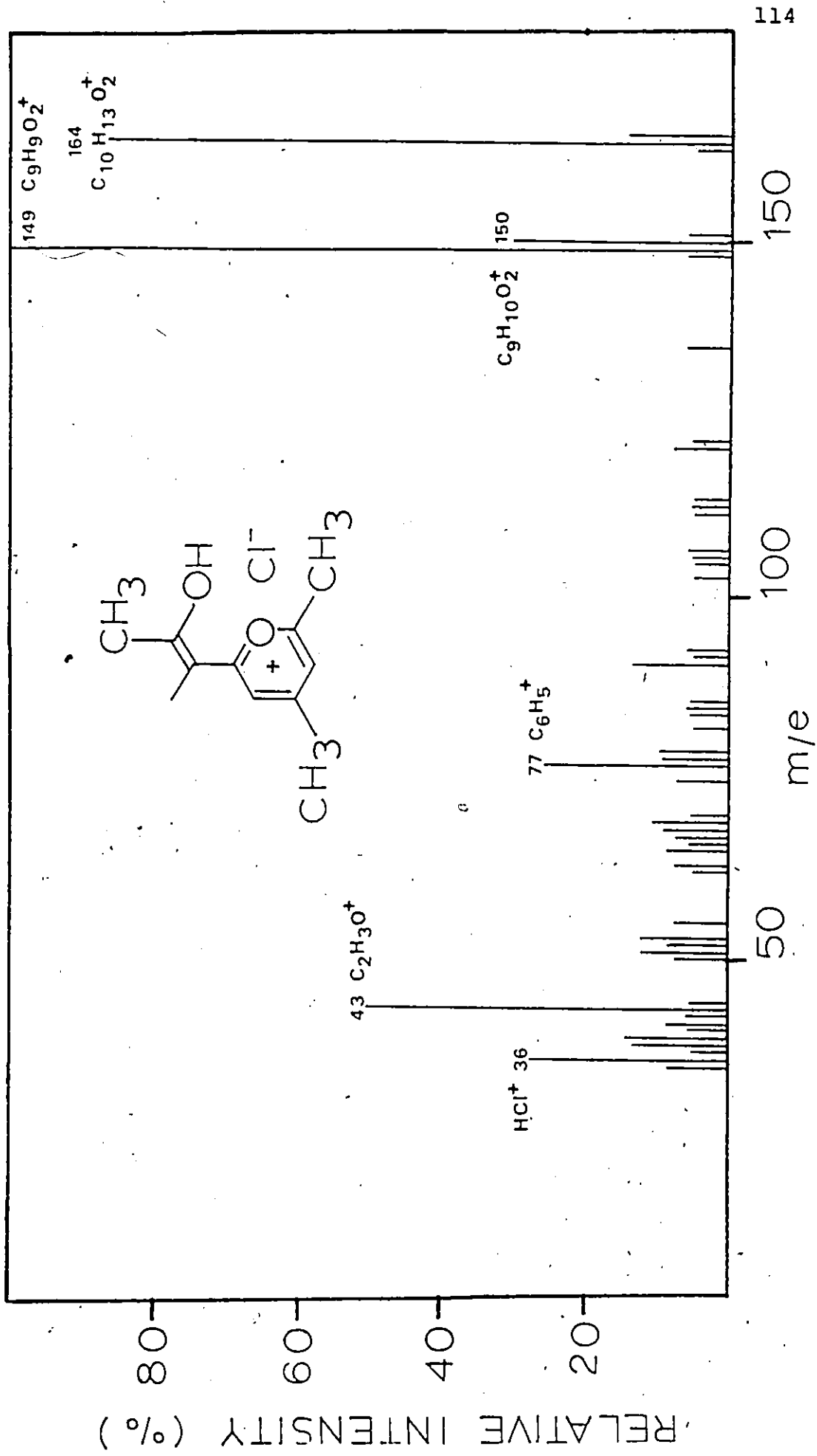
Table 17. Relative intensities of some major fragment ions of pyrylium chloride.

m/e (amu)	Relative intensity (%)	Fragments
165	14.4	$C_{10}H_{13}O_2^+$
164	86.6	$C_{10}H_{12}O_2^+$
150	30.9	$C_9H_{10}O_2^+$
149	100.	$C_9H_9O_2^+$
91	13.9	$C_6H_3O^+$
77	25.8	$C_6H_5^+$
43	50.4	$C_2H_3O^{\cdot}$
38	13.4	$H^{37}Cl$
36	28.1	$H^{35}Cl$

produce the six-membered rings $C_6H_5^+$ (m/e 77) and $C_6H_4^{+\cdot}$ (m/e 76), respectively. Loss of a C_2H_2 molecule (m/e 26) from $C_6H_4^{+\cdot}$ results in the formation of the four-membered

XXXVII

$-HCl$

$-Cl\cdot$

200

164

165

$-CH_3\cdot$

$-CH_3\cdot$

149

150

$-HCO\cdot$

$-HCO\cdot$

$-CO$

120

121

122

$-CH_3\cdot$

$-CH_3\cdot$

$-CH_3\cdot$

105

106

107

$-HCO\cdot$

$-CO$

$-HCO\cdot$

$-CO$

$-HCO\cdot$

$-CO$

76

77

78

79

$-C_2H_2$

$-C_2H_2$

$-C_2H_2$

$-C_2H_2$

50

51

52

53
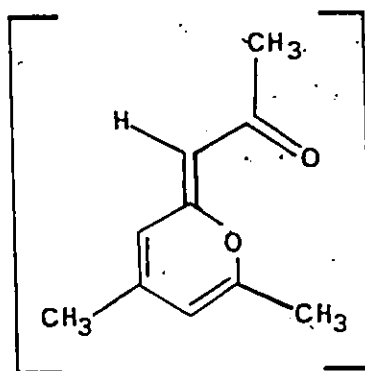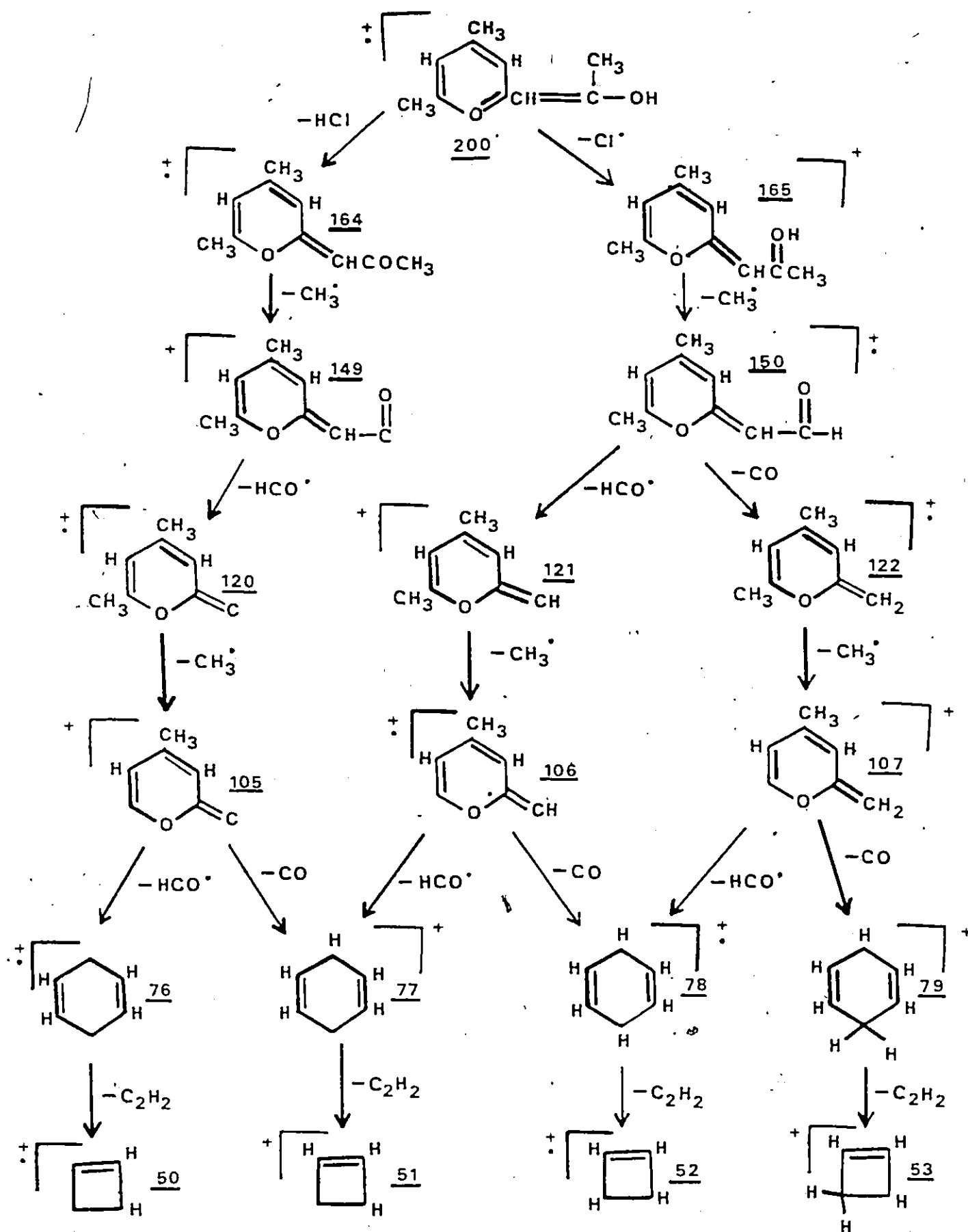
SCHEME 19

ring species, $C_4H_2^{+\cdot}$ (m/e 50). Similarly, loss of a C_2H_2 molecule from $C_6H_5^+$ produces the $C_4H_3^+$ ion (m/e 51).

The fragmentation pattern of pyrylium chloride originating from the $C_{10}H_{13}O_2^+$ (m/e 165) ion is virtually identical to the fragmentation pattern discussed earlier originating from the $C_{10}H_{12}O_2^{+\cdot}$ (m/e 164) ion. Loss of the chlorine radical to produce the $C_{10}H_{13}O_2^+$ species is the main difference.

One last point on the fragmentation pattern involves the loss of the hydrogen chloride. Peaks at a m/e of 36 and 38 in the ratio of 2:1 indicate the presence of hydrogen chloride as $H^{35}Cl^+$ and $H^{37}Cl^+$, respectively.

The fragmentation pattern for pyrylium chloride was postulated _via_ high-resolution mass spectrometry.[*] Hence, the somewhat elaborate fragmentation pattern. On the other hand the two subsequent fragmentation schemes are rather simple, for they are based on low-resolution mass spectrometric experiments.

The mass spectrum of 2-ethyl-4,5-dimethyl-6-(2'-hydroxy-1'-propenyl)pyrylium chloride is presented in Figure 9 and the major fragment ions are listed in Table 18. A fragmentation pattern was devised for this compound and it is presented in Scheme 20. As was stated before, the base peak ion is located at (M-36)-15 and the peak at the highest m/e value is located at M-36, where M is the molecular mass

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[*] Dr. J. Miller, Brock University, St. Catherines, Ont.

Figure 9. Mass spectrum of 2-ethyl-4,5-dimethyl-6-(2'-hydroxy-1'-propenyl)pyrylium chloride.
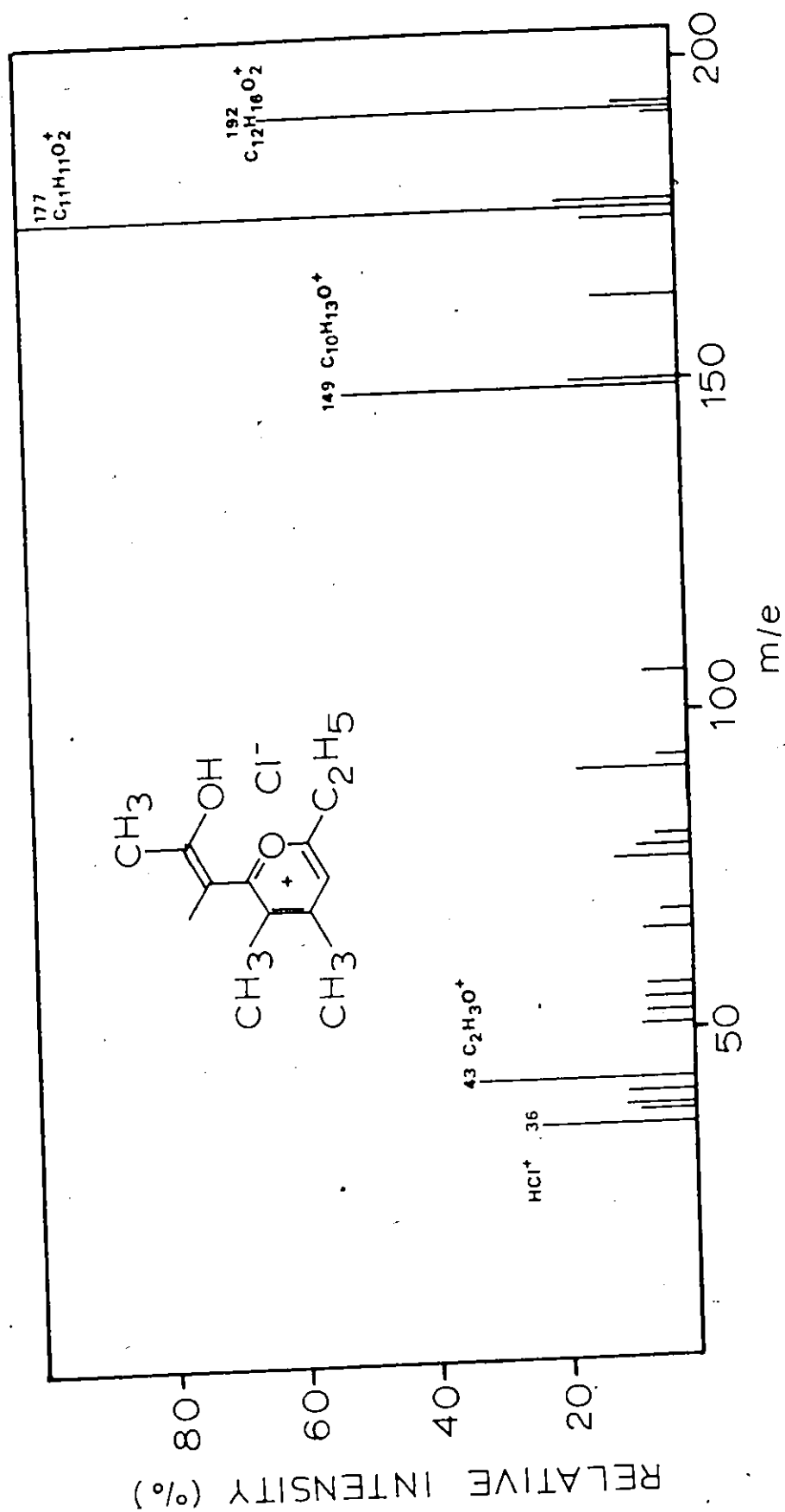
Table 18. Relative intensities of some major fragment ions of 2-ethyl-4,5-dimethyl-6-(2'-hydroxy-1'-propenyl)pyrylium chloride.

m/e (amu)	Relative intensity (%)	Fragments
193	9.8	$C_{12}H_{17}O_2^+$
192	63.6	$C_{12}H_{16}O_2^{+\cdot}$
178	19.3	$C_{11}H_{12}O_2^{+\cdot}$
177	100.	$C_{11}H_{11}O_2^+$
175	14.9	$C_{11}H_{15}O^+$
163	13.4	$C_{10}H_{11}O_2^{+\cdot}$
150	17.1	$C_{10}H_{14}O^{+\cdot}$
149	51.7	$C_{10}H_{13}O^+$
91	17.7	$C_6H_3O^{+\cdot}$
77	12.2	$C_6H_5^+$
43	33.6	$C_2H_3O^\cdot$
38	9.0	$H^{37}Cl$
36	23.7	$H^{35}Cl$

mass of the molecule.

The fragmentation path from the molecular ion to the base peak involves simple loss of a methyl group. There are three methyl groups, not to mention the methyl group

$$C_{12}H_{17}O_2Cl^{\ddot{+}}$$

(228)

$$C_{12}H_{16}O_2^{\ddot{+}} + HCl$$

(192)   (36)

$$C_{10}H_{13}O^+ + CH_3CO^{\cdot} \qquad\qquad C_{11}H_{11}O_2^{+} + CH_3^{\cdot}$$

(149)   (43)   (177)   (15)

-CO (28)

$$C_9H_{10}O^{\ddot{+}} + CH_3^{\cdot}$$

(134)   (15)

$$C_7H_5O^+ + C_2H_5^{\cdot}$$

(105)   (29)

$$C_6H_3O^{\ddot{+}} + CH_2^{\cdot} \qquad\qquad C_6H_5^{+} + CO$$

(91)   (14)   (77)   (28)
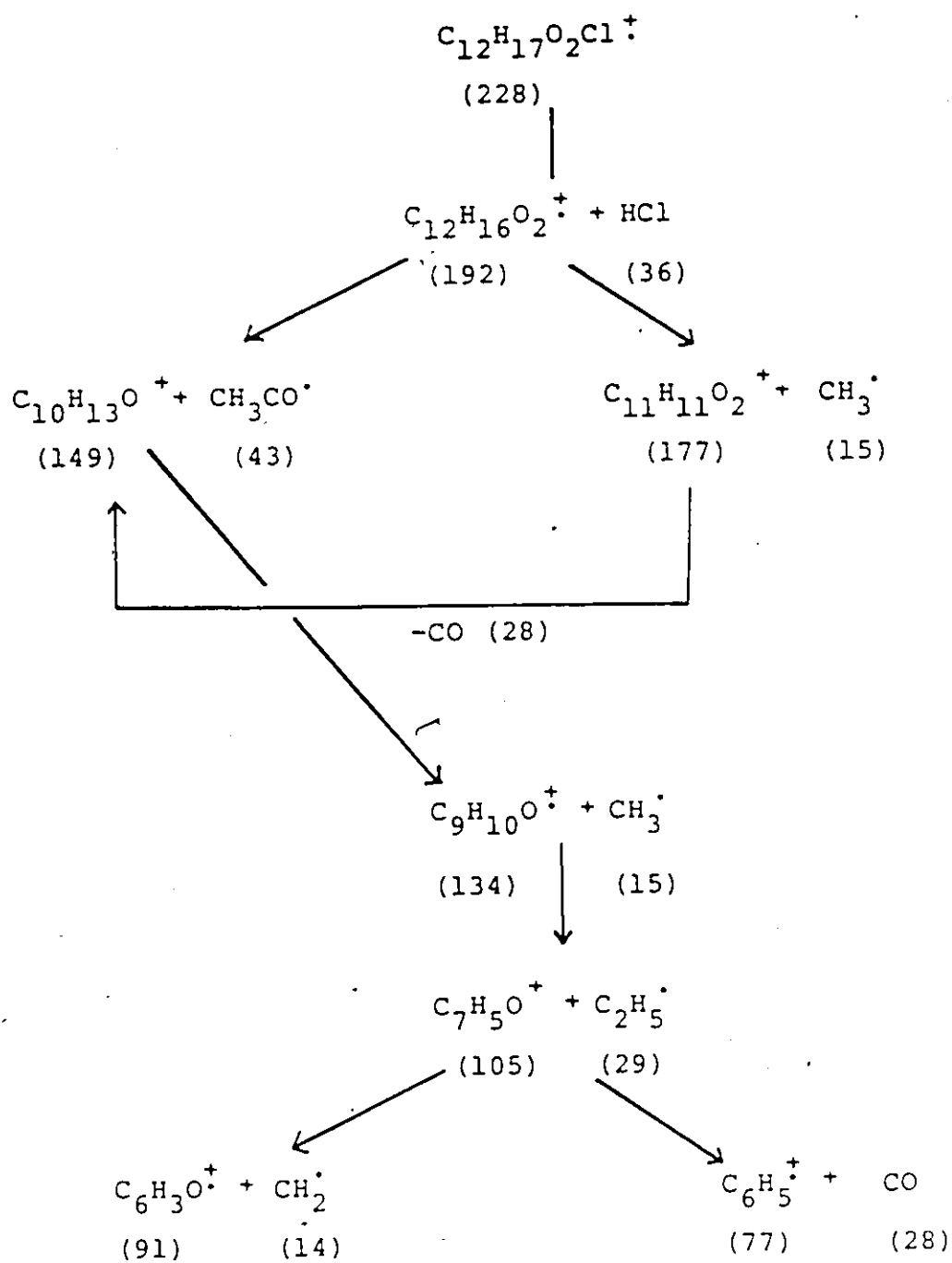
Scheme 20

contained in the ethyl moiety, to choose from. It would be
unlikely that the acetyl methyl group would be lost first,
because this fragment tends to be removed as a single
fragment.[118] This leaves the 4- and 5-methyl groups. Based on
the mass spectrum of pyrylium chloride, and on the relative
reactivity of the two positions, the 4-methyl group would
probably cleave resulting in the base peak ion.

The next step in the fragmentation pattern results in
a peak at m/e 149 with a relative intensity of 51.7%. This
ion fragment can be formed in two ways: the first involves
direct loss of an acetyl group, and the second results from
the loss of CO from the base peak ion.

The remainder of the fragmentation scheme is rather
straightforward. A methyl group is removed, followed by
the last ring substituent, the ethyl group. Subsequent
ring transformations result in $C_6H_3O^+$ (m/e 91) and $C_6H_5^+$
(m/e 77) which are taken as indicative of an aromatic
system.[118]

The final pyrylium salt to be discussed is the
2,4-di-n-propyl-5-ethyl-6-(2'-hydroxy-1'-pentenyl)pyrylium
chloride. Its mass spectrum is presented in Figure 10 and
the major fragment ions are listed in Table 19. The proposed
fragmentation pattern is presented in Scheme 21. Again the
loss of hydrogen chloride prevents the observation of the
molecular ion. In a manner analogous to the fragmentation
pattern of pyrylium chloride (both are similar in structure)
the major fragmentation process probably, also, involves

Figure 10. Mass spectrum of 2,4-di-n-propyl-5-ethyl-6-
(2'-hydroxy-1'-pentenyl)pyrylium chloride.

RELATIVE INTENSITY (%)

80
60
40
20

m/e

50
100.
150
200
250
300

CH₂CH₂CH₃
OH
Cl⁻
C₃H₇
C₂H₅
C₃H₇

$233\ C_{16}H_{26}O^+$

$276\ C_{18}H_{28}O_2^+$

$261\ C_{17}H_{26}O_2^+$

$234\ C_{16}H_{26}O^+$
$247\ C_{16}H_{23}O_2^+$

208
206

$191\ C_{12}H_{15}O_2^+$

$38\ H^{37}Cl^+$
$36\ HCl^+$
$42\ C_2H_2O^+$
$Cl^{+}35$
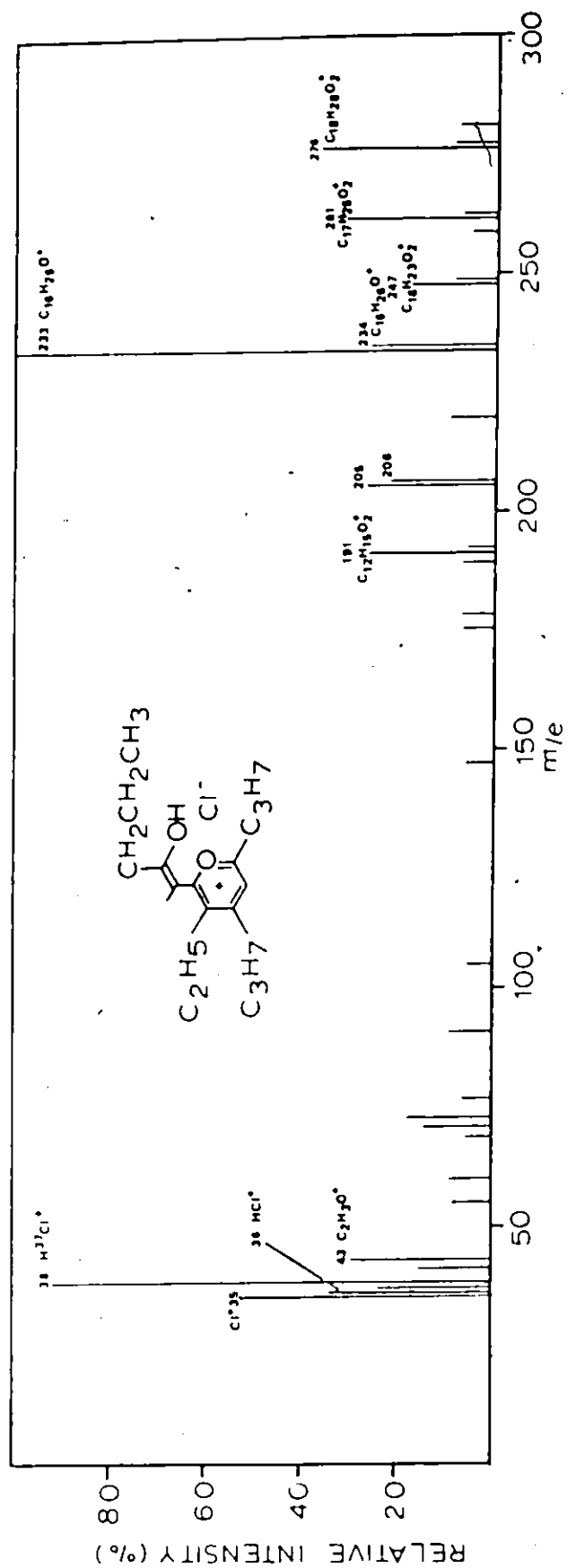
Table 19. Relative intensities of some major fragment ions of 2,4-di-n-propyl-5-ethyl-6-(2'-hydroxy-1'-pentenyl) pyrylium chloride.

m/e (amu)	Relative intensity (%)	Fragments
276	36.7	$C_{18}H_{28}O_2^{+\cdot}$
261	31.2	$C_{17}H_{25}O_2^{+}$
247	17.5	$C_{16}H_{23}O_2^{+\cdot}$
234	25.8	$C_{15}H_{22}O_2^{+\cdot}$
233	100.	$C_{15}H_{21}O_2^{+}$
206	21.4	$C_{14}H_{22}O^{+\cdot}$
205	26.3	$C_{14}H_{21}O^{+}$
191	25.8	$C_{12}H_{15}O_2^{+}$
71	13.9	$C_3H_7CO^{\cdot}$
38	91.1	$H^{37}Cl$
37	23.4	$^{37}Cl^{\cdot}$
36	33.6	$H^{35}Cl$
35	52.3	$^{35}Cl^{\cdot}$

the cleavage of a ring substituent, and in this case, it is the propyl group.

The ion at the highest m/e has three possible

$$C_{18}H_{29}O_2Cl^{+\cdot}$$
(312)

$$C_{18}H_{28}O_2^{+\cdot} + HCl$$
(276)   (36)

$$CH_3^{\cdot} + C_{17}H_{25}O_2^{+}$$

(15)   (261)

$$\dot{C}_3H_7CO^{\cdot} + C_{14}H_{21}O^{+}$$

(71)   (205)

$$CH_2^{\cdot} + C_{16}H_{23}O_2^{+\cdot}$$
(14)   (247)

$$C_3H_6 + C_{11}H_{15}O^{+}$$
(42)   (163)

$$-C_3H_7^{\cdot}$$
(43)

$$CH_2^{\cdot} + C_{15}H_{21}O_2^{+}$$
(14)   (233)

$$C_2H_6 \quad C_9H_9O^{+}$$
(30)   (133)

$$C_3H_6 + C_{12}H_{15}O_2^{+}$$
(42)   (191)

$$C_6H_3O^{+} + C_3H_6$$
(91)   (42)

$$C_3H_6 + C_9H_9O_2^{+}$$
(42)   (149)

$$H_2O + C_6\dot{H}O^{+}$$
(18)   (73)

$$\dot{C}_2H_6 + C_7H_3O_2^{+}$$
(30)   (119)
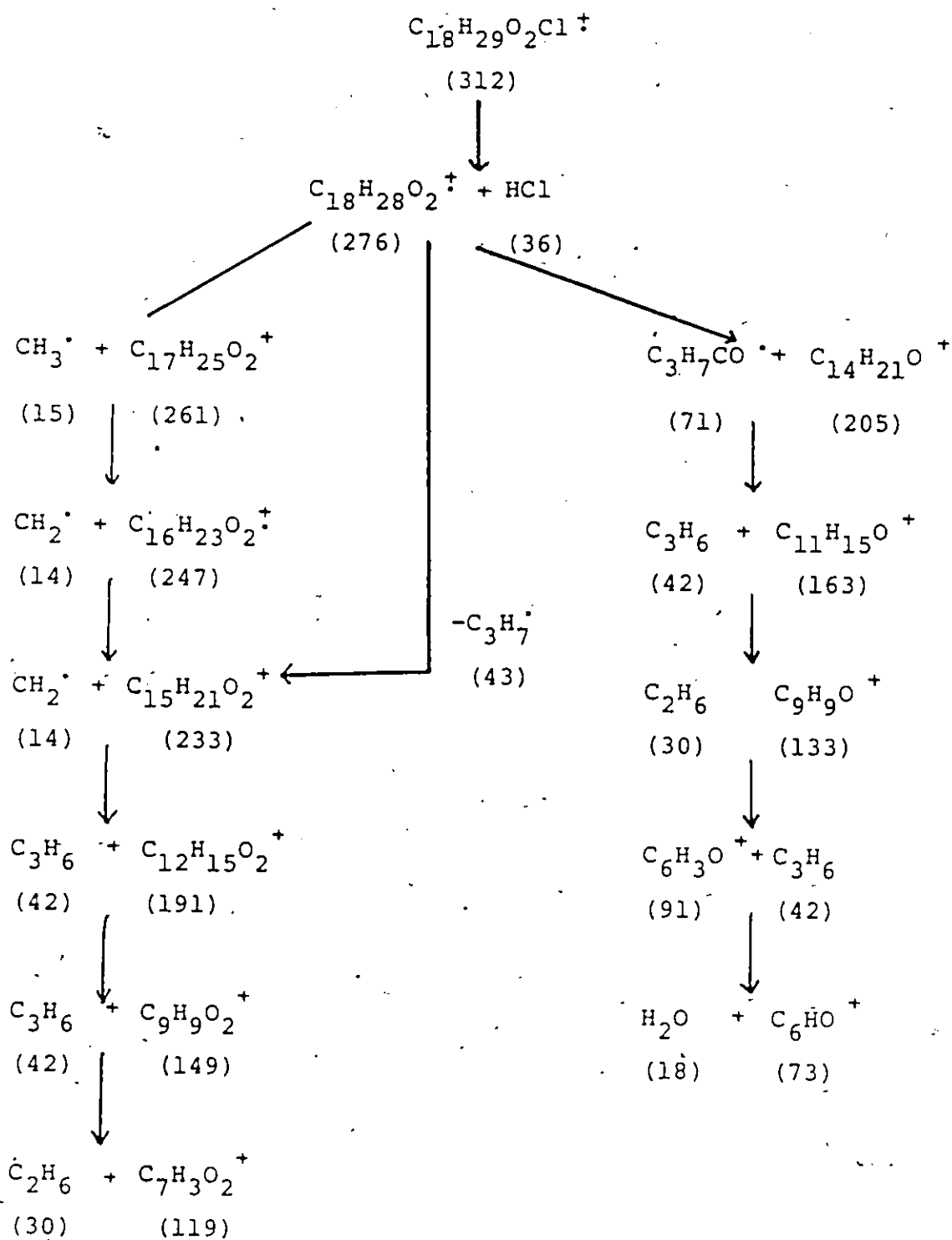
Scheme 21

pathways open for fragmentation. Two of these pathways lead
to the base peak ion. The molecule can lose the propyl group
as one unit or as individual units, that is, the process
can be a one-step or a three-step process. The other process
involves the loss of the $C_3H_7CO^+$ ion to give the $C_{14}H_{21}O^+$
ion (m/e 205). Each of these (the base peak ion and the ion
at m/e 205) can then fragment in separate ways. These ions
fragment in a manner similar to the other two pyrylium
salts already discussed.

III.A.7. ELECTRONIC SPECTRA OF PYRYLIUM CHLORIDE

A brief look at the theory of electronic absorptions
is in order at the present time, but more detailed information
may be found in texts devoted to instrumental analysis of
organic compounds.[118,119]

The absorption peak found in the ultraviolet or
visible spectrum of an organic compound is caused by the
promotion of an electron from a low-lying orbital to a higher
energy orbital. The three types of electrons involved may
be the σ-, the π-, or the n-electrons, where n indicates the
non-bonding type. In most cases, the σ-electron transitions
are of such large energy, that most instruments are not
equipped to handle the recording of the transitions.

There are two types of electronic transitions that
are of great importance to organic chemists:

a) n-π* transitions. These transitions involve the
   excitation of a non-bonded electron (e.g., from
   the oxygen in a carbonyl group) to an unstable
   π-antibonding (π*) orbital. This is represented
   in Scheme 22a.

b) π-π* transitions. These transitions occur from the
   π-orbital, of a carbonyl or alkene-type group,
   to the π*-orbital. This transition is represented
   in Scheme 22b, for the carbonyl group.
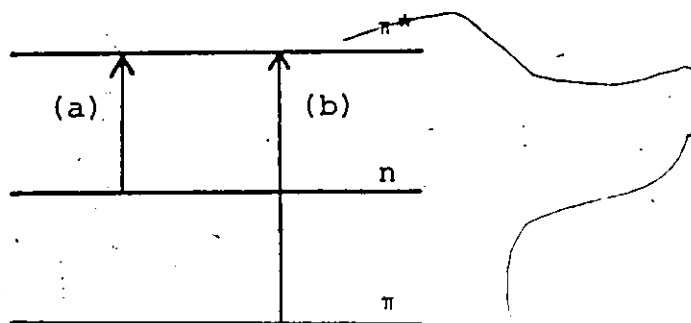
SCHEME 22

There are, generally speaking, two methods used in
characterizing the types of transitions observed in the
electronic spectrum of an organic compound. They are the
molar absorptivities (ε_{max}) and the effect of the polarity
of the solvent on the position of the peak maximum. The n-π*
transitions are characterized by rather small ε_{max}, generally
less than 100, and the large blue-shift (hypsochromic)
in changing from a non-polar to a polar solvent.[118] Hydrogen-

bonding solvents strongly influence the position of the n-π*
band by lowering the n-electron orbital energy level due to
the hydrogen bond formation.[118] All transitions involving n-
electrons are affected in a similar manner.

The π-π* transitions are characterized by the rather
large ϵ_{max}, usually greater than 10^4. Solvent effects cause
the position of the absorption maxima to shift, but not to
the same extent as the n-π* transitions. The π-π* bands red-
shift (bathochromic) on going from non-polar to polar
solvents.[118]

A detailed publication by Balaban and co-workers[128]
on the electronic absorption spectra of alkyl- and phenyl-
substituted pyrylium salts has appeared. The authors have
discussed solvent effects, as well as the effect of alkyl-
and phenyl-groups on the position of the band maxima. It
was observed that in non-acidified solutions a solvolysis
reaction occurs leading to the tautomeric pseudobases (A)
or ethers (B) shown in Scheme 23.[128] In acid solutions, the

Scheme 23
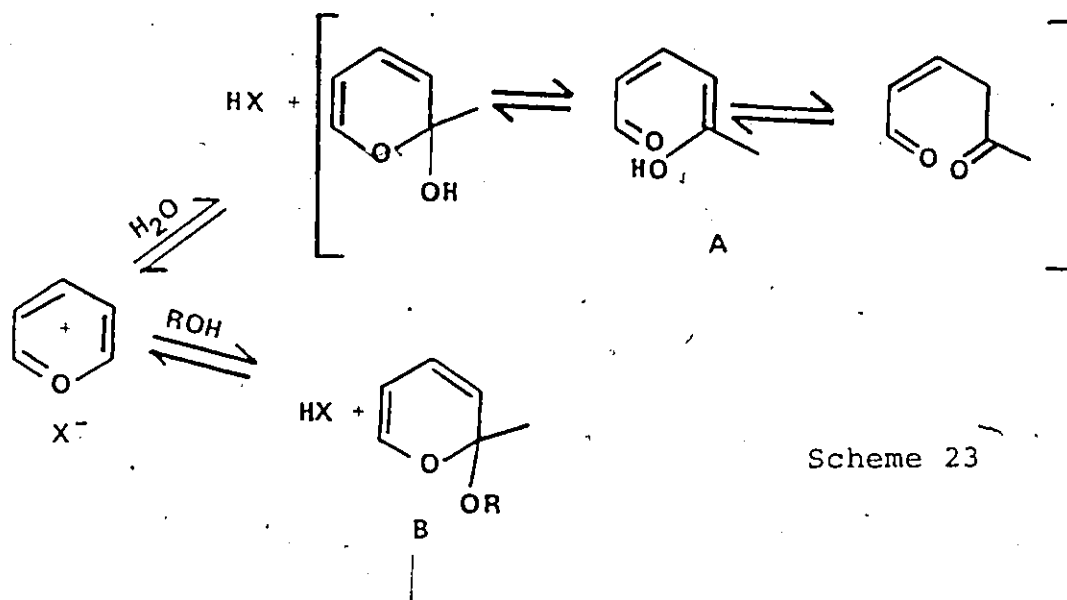
equilibria are shifted toward the left to the pyrylium cation. Also, in acidic solutions the ϵ_{max} was larger than in non-acidic media, which supports partial solvolysis reactions.

Pyrylium salts which contain alkyl groups in the 2-, 4-, and 6-positions have two band maxima in the ultra-violet spectrum, located at 230-235 nm and at 285-290 nm. Alkyl groups affect the band maxima and the ϵ_{max} to only a small degree, that is, the ϵ_{max} ranges from 4.55×10^3 to 6.12×10^3 for the λ_{max} at 230-235 nm, and from 1.16×10^4 to 1.43×10^4 for λ_{max} at 285-290 nm.

Phenyl groups have a marked effect on the electronic spectra of pyrylium salts. As the number of phenyl groups increases (0 to 4) the color of the pyrylium salts changes from colorless to yellow.[128] The band maxima and ϵ_{max} change considerably compared to those of the alkyl substituted pyrylium salts. Whereas the change in ϵ_{max} and λ_{max} for the alkyl groups is less than 30% and 10 nm, respectively, that for the phenyl groups is 300% and 100 nm, respectively. The electronic effects of the phenyl ring stabilize the pyrylium cation more efficiently than the inductive effects of the alkyl groups.

In a more recent article, Wilt, Reynolds and Van Allan[129] have discussed the electronic spectra of alkyl and aromatic pyrylium salts, in a more theoretical manner than before.[128] They have compared the spectra of the alkyl pyrylium salts with the spectra of iso-electronic species,

such as benzene, pyridine and the pyridinium ion. The main
point made was that concerning the absence of the low-energy
n-π* transitions in pyrylium salts. Because the oxygen in
the pyrylium ring has non-bonding electrons, and also because
the n-π* transition is the lowest energy transition in
pyridine, the n-π* transition in pyrylium salts would be
expected to occur at lower energy than the lowest π-π*
transition. However, the band is not observed[129] and the
absence of this n-π* band is explained as resulting from an
electrostatic effect not present in pyridine. The oxygen
atom of the pyrylium cation bears a fraction of the positive
charge. An increase in the positive charge on the oxygen
atom is realized in the n-π* transition, since the non-
bonding electron comes from the oxygen atom. The authors[129]
postulated that this electrostatic effect causes the n-π*
transitions to shift to higher energy.

All the electronic spectra of the pyrylium salts in
this work are restricted to pyrylium chloride because of the
ease of its preparation and stability. The electonic spectra
of pyrylium chloride in methanol and in cyclohexane solvents
are presented in Figure 11; the corresponding λ_{max} and ϵ_{max}
are listed in Table 20. At a first glance, the spectra appear
identical except for the intensities of the corresponding
bands. Bands in the spectrum of pyrylium chloride in cyclo-
hexane reveal a much larger ϵ_{max} for each band compared to
those in the methanol spectrum in the 225-310 nm region,
except for the band at 230 nm. In the visible region, the

Figure 11. Absorption spectra of pyrylium chloride in methanol and in cyclohexane solvents.
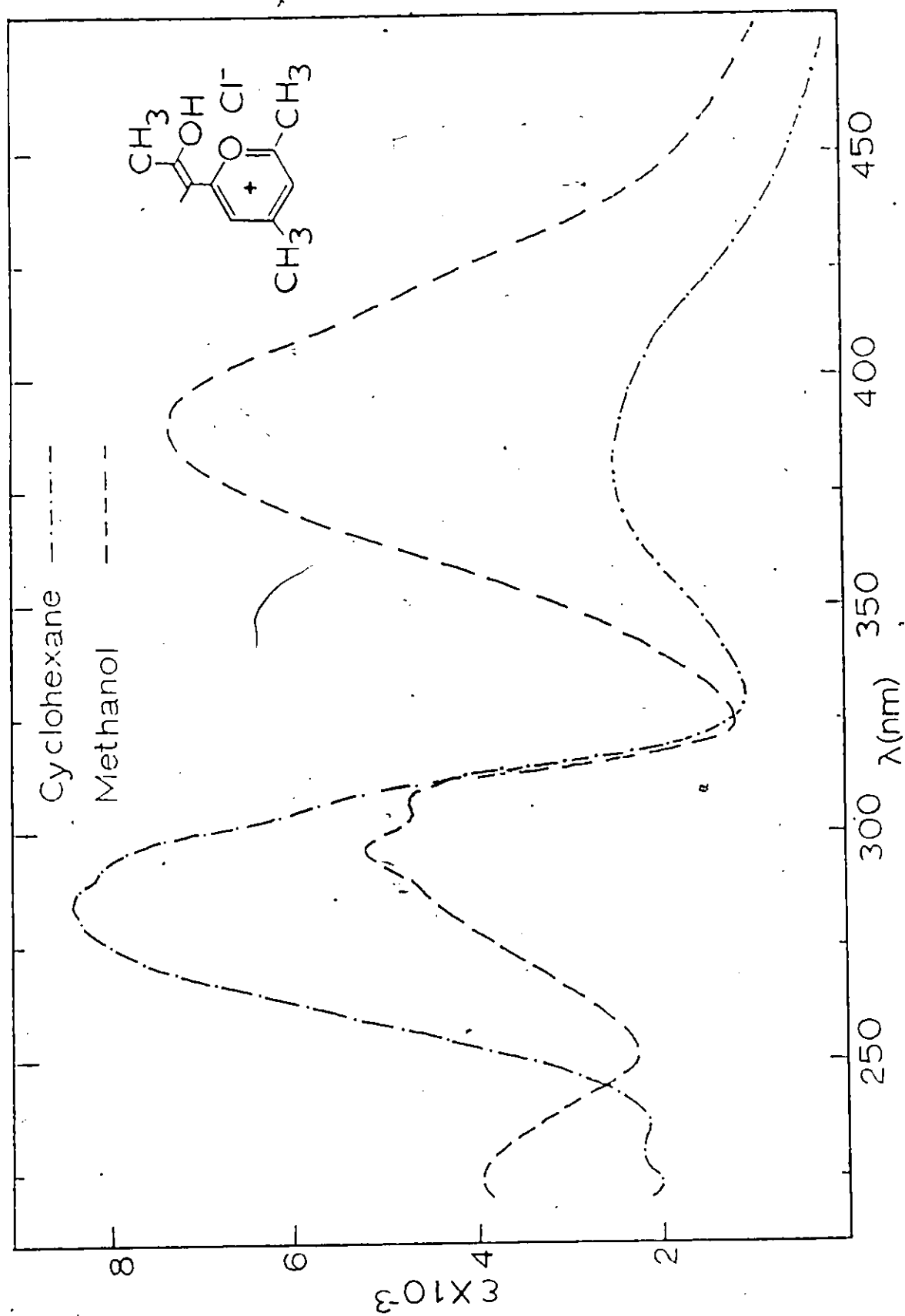
Table 20. Absorption spectra of pyrylium chloride in methanol and in cyclohexane.

Solvent (Concentration, $\underline{M}$)	λ_{max} (nm)	$\varepsilon_{max} \times 10^{-3}$ ($M^{-1}cm^{-1}$)
Methanol	224.0	3.97
	$\approx$287 (sh)	4.71
(8.47×10^{-5})	296.0	5.19
	307.0	4.71
	390.0	7.33
Cyclohexane	230.0	2.21
	284.0	8.40
(3.49×10^{-5})	$\approx$291 (sh)	8.17
	$\approx$306 (sh)	5.73
	380.0	2.46

situation is reversed, in that the band at 380 nm in the cyclohexane spectrum has an ε_{max} which is approximately 33% of the band in the methanol spectrum. This could be due to solvent interactions, in that the polar solvent may stabilize the excited state of the pyrylium salt to a greater degree than the non-polar solvent. The situation is apparently reversed in the 224-310 nm region. By noting the λ_{max} of each band it can be seen that there is a red shift in all the bands, except the band at 230 nm, on going from cyclo-hexane to methanol. This would indicate that the transitions

are π-π* types.[118,119] The lone exception is the band located at 230 nm (cyclohexane) and 224 nm (methanol). This is a blue shift which would indicate an n-π* transition.[118,119] Based on the explanation given by Wilt and co-workers[129] on the position of the n-π* transition, it would appear that we have observed the first n-π* transition in a pyrylium salt.

. The band in the visible region (ca. 385 nm) is assigned to a π-π* transition. Due to the unsymmetrical nature of the envelope there is reason to suspect two bands are present, one assigned to a π-π* transition and the other possibily assigned to an n-π* transition. Unambiguous assignment is difficult because of the intensity of π-π* transitions and the overlap of the two bands.

.⊃The absorption spectra of pyrylium chloride in water and acid solutions are presented in Figure 12 with the corresponding λ_{max} and ε_{max} listed in Table 21. As the acid concentration increases, the ε_{max} at ca. 390 nm decreases, after the initial increase from water to 10^{-4} M HCl, from an ε_{max} of 1.2×10^4 to 600. The change in color from yellow to colorless may result from the loss of conjugation by the increasing acidity,[123] according to the equilibrium presented in Scheme 15.

The electronic spectrum of pyrylium chloride in 10^{-4} M HCl is virtually identical to that in pure water. The pK_a of a weak acid equals the pH of the solution when one-half of the weak acid is in the dissociated form.[104] The pK_a of pyrylium chloride in water is 3.81 (see Table 5). Thus,

Figure 12. Absorption spectra of pyrylium chloride in water and in acid solutions.
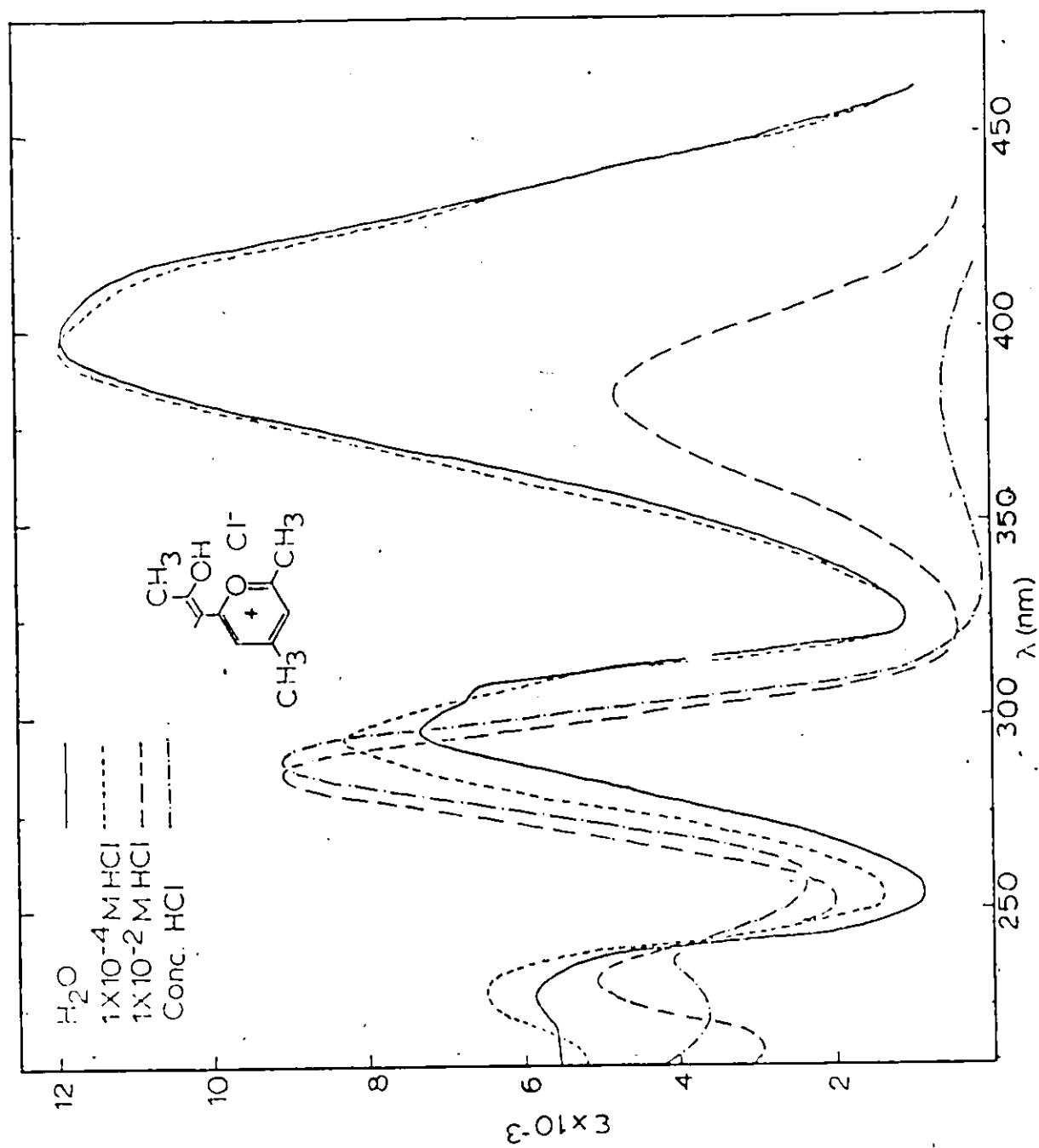
Table 21. Absorption spectra of pyrylium chloride in water and in acid solutions.

Solvent (Concentration, $\underline{M}$)	λ_{max} (nm)	$\epsilon_{max} \times 10^{-3}$ ($M^{-1}cm^{-1}$)
H_2O	227.5	5.89
	296.0	7.35
(1.396×10^{-4})	≈305 (sh)	6.80
	398.0	11.96
10^{-4} $\underline{M}$ HCl	228.5	6.44
	294.0	8.14
(1.196×10^{-4})	≈305 (sh)	6.61
	396.0	12.01
10^{-3} $\underline{M}$ HCl	232.0	5.39
	287.0	8.43
(1.445×10^{-4})	≈310 (sh)	2.70
	389.0	6.84
10^{-2} $\underline{M}$ HCl	232.0	5.10
	284.0	9.16
(1.596×10^{-4})	382.5	4.78
1 $\underline{M}$ HCl	232.0	4.39
	286.0	8.67
(2.093×10^{-4})	382.0	3.12
Conc. HCl	237.0	4.10
	289.0	9.14
(2.442×10^{-4})	383.0	0.63

recording the absorption spectrum of pyrylium chloride in water and in 10^{-4} $\underline{M}$ HCl (pH 4) may produce similar absorption spectra.

There is a gradual shift to longer wavelength of the high energy transition (227.5-237 nm) caused by increasing the concentration of acid. The second band (296-285 nm) gradually blue shifts with increasing ionic strength of the solvent medium, and the lowest energy band (382-396) blue shifts as the ionic strength of the solvent increases. These results (in water and in acid solutions) are in complete reversal to the results obtained from pyrylium chloride on going from cyclohexane to methanol. This is attributed to a large solvent effect present in acidic solutions and probably also to the close proximity of the n,π^* and π,π^* energy states in polar solvents.

Luminescence is a process in which radiation is emitted by molecules that have been excited by the absorption of radiation.[130] Excitations usually originate from the singlet ground state in organic molecules. A schematic state energy level diagram (Scheme 24) illustrares the major
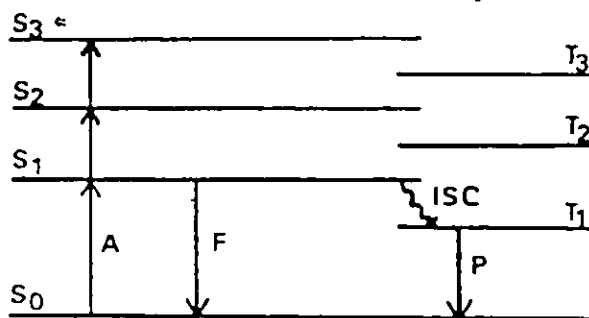
SCHEME 24

transitions occuring in the luminescence processes of organic compounds. Absorption (A), fluorescence (F), phosphorescence (P) and intersystem crossing (ISC) are labelled in the energy level diagram. The multiplicities of the states involved in the fluorescence process are the same, usually the first excited state to the ground state $(S_1 \rightarrow S_0)$, whereas the multiplicities of the states involved in phosphorescence are different, usually from the lowest triplet state (T_1) to the ground state (S_0). There are several other transitions possible (internal conversion, triplet-triplet absorption, etc.), and these are discussed in textbooks dealing with luminescence spectroscopy.[130,131]

The luminescence spectra of pyrylium chloride were recorded in water and in acid solutions (Figure 13, Table 22). Two aspects of the emission spectra are noteworthy on going from water to concentrated acid: the blue shift in the band maxima and the increase in relative intensity of this band (18 to 100%). The lowest energy band in the absorption spectrum of pyrylium chloride is located in the region 383-398 nm and has been assigned as a $\pi-\pi^*$ transition. Two structures of pyrylium chloride in solution were proposed earlier (Scheme 17); the discussion will be based on both of the structures.

The pH of the solution and the hydrogen-bonding ability of the solvent can strongly affect the fluorescence spectra of most aromatic compounds containing acidic or basic functional groups.[131] Hydrogen bonding effects on the

Figure 13. Absorption and luminescence spectra of pyrylium chloride in water and in acid solutions.
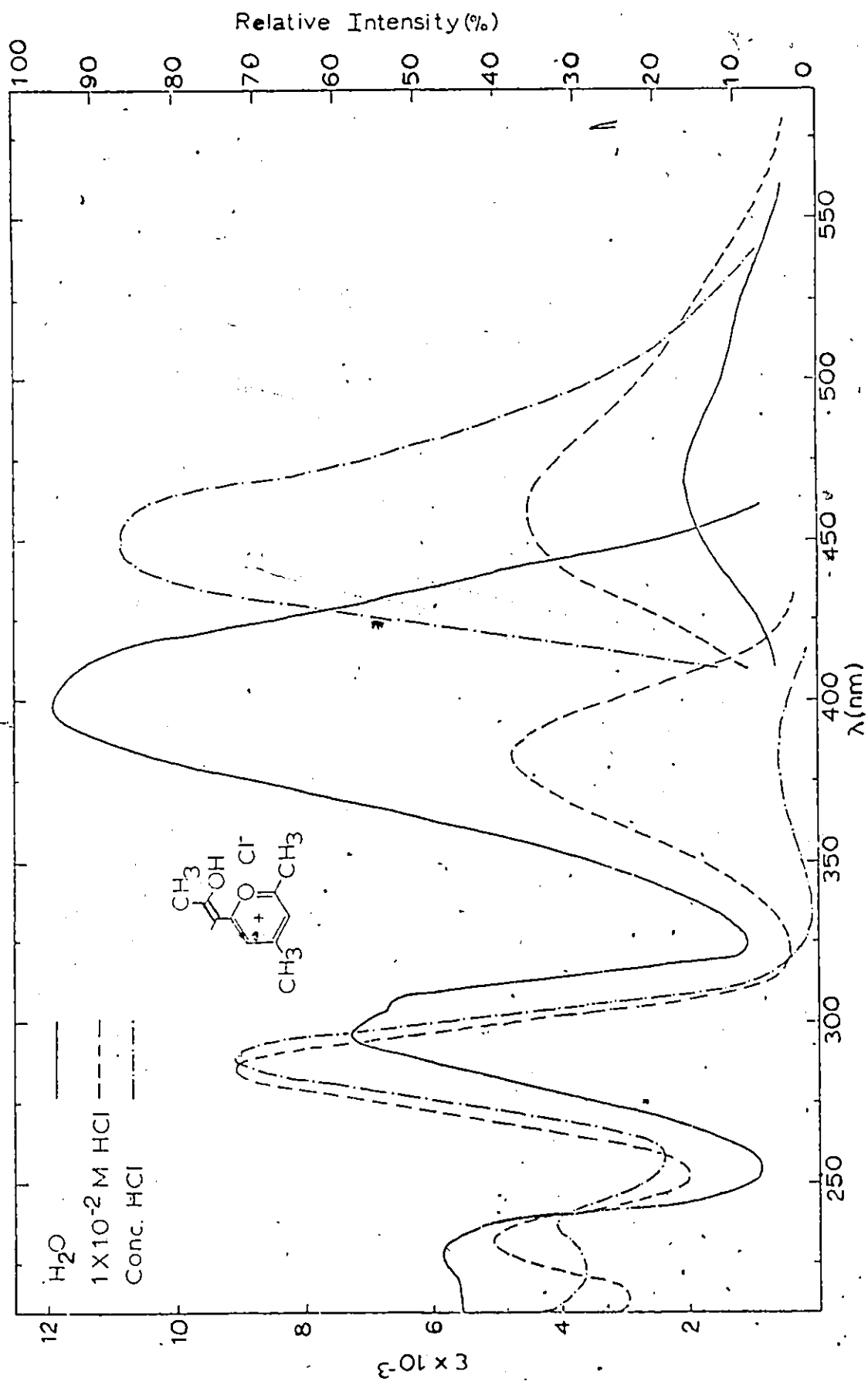
Table 22. Luminescence spectra of pyrylium chloride in water and in acid solutions at λ_{ex} of 386 nm.

Solvent (Concentration, M)	λ_{max} (nm)	Relative Intensity (%)
H$_2$O (1.396 × 10^{-4})	470 ≈520 (sh)	18 11
10^{-2} M HCl (1.595 × 10^{-4})	459 ≈520 (sh)	42 19
Conc. HCl (2.442 × 10^{-4})	450	100

fluorescence spectra are often difficult to predict.[132] Differences in the Bronsted acidity between the ground state and the lowest excited singlet state of organic molecules range from 4 to 9 pK units. Depending on the compound class, the excited state molecules may become either more acidic (phenols) or more basic (ketones and nitrogen heterocycles) with lowest π,π^* singlets.[132,133]

If one studies the excited state of the ring chromophore of structures (A) or (B) (Scheme 17), the acidity

of the ground state is higher than that in the excited state, that is, the excited pyrylium ring is more basic. The excited state of the carbonyl group in (A) is much more basic than in the singlet ground state (S_0), and the hydroxy propene (B) is more acidic in the excited state than in the ground state.[132]

The increase in the relative intensity of the excited state pyrylium chloride on going from pure water to concentrated hydrochloric acid appears to indicate the increased acidity of excited state compared to ground state pyrylium chloride.

III.B. ANHYDRO BASES OF PYRYLIUM SALTS, PYRANS

III.B.1. SYNTHESIS

Silicon tetrachloride and fluorinated β-diketones in refluxing dichloromethane yield the anhydro bases of pyrylium salts. These bases are normally called pyrans. Very little work has been done on simple pyrans (e.g., phenyl- or methyl-substituted pyrans) but a large amount of effort has been spent in studting compounds which contain the pyran ring obtained from natural products. Thus, little information is available that might relate to this work.

To briefly review the synthesis of trifluoromethyl pyrans from fluorinated β-diketones, the diketone was refluxed with silicon tetrachloride in dichloromethane until a deep-red color was present. Evaporation of the solvent via nitrogen gas and a heat gun yielded a gummy residue. This residue was fractionated under vacuum, and yielded bright yellow crystals. The product was used in different experiments without further purification.

In the synthesis involving trifluoromethyl-2,4-pentanedione, a yield of 16.5% was realized. However, due to the nature of the crude product (an oil) it was very difficult to obtain a pure product in the early stages of this study. Several methods ranging from crystallization at low temperatures to fractional crystallization were attempted.

'Subliming' the oil in a sublimation apparatus was attempted, but when the crude product was heated, splattering occured which contaminated the product. Finally, a method was devised in which the crystals were well removed from the crude product. The apparatus utilized is shown in Section II.B. This method optimized the purification of the product. In addition, this technique was clean and efficient. Whereas it took upto one month to recover a small amount of rather impure product previously, it now took less than 24 hr to accomplish complete recovery and purification in one process.

Since both the fluorinated diketone and the Lewis acid ($SiCl_4$) are liquids, they can be handled easily and efficiently. Although the yield was only 16.5%, the amount of product recovered in one synthesis (0.55 g) was large enough to perform all the required experiments needed to characterize this compound fully. This compound had the greatest yield compared to the pyrans obtained from other fluorinated diketones used, as was the case in the synthesis of pyrylium chloride and other pyrylium salts.

In the reaction between trifluoromethyl-2,4-hexane-dione and silicon tetrachloride in dichloromethane, a pyran was recovered from the reaction mixture. The yield was much lower (=4%) than the pyran synthesized from trifluoromethyl-2,4-pentanedione, but the quantity obtained (0.12 g) was adequate to carry out the necessary instrumental analyses required for structure characterization. The reaction time for the synthesis of the pyran obtained from trifluoromethyl-

2,4-hexanedione increased to 24 hr compared to 5 hr for the reaction yielding the methyl pyran. If the reaction time was too short (<20 hr) very little product was obtained, if any; if too long (>28 hr), again very little product was obtained. Depending on the orientation of the substituted methylene side-chain, the methyl group in the 3-position could find itself in a crowded position (XXXVIII). The methyl pyran represents a less crowded structure and the reaction time is
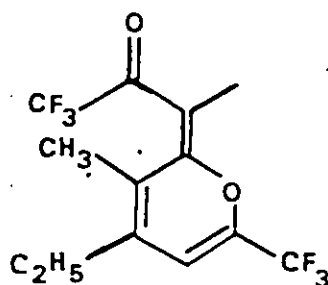
XXXVIII

5 hr compared to 25 hr for the ethyl pyran synthesis.

As more bulky groups are substituted at the 3-position, the yield of the pyran product appears to decrease. On refluxing trifluoromethyl-7-methyl-2,4-octanedione with silicon tetrachloride in dichloromethane for 88 hr, a small amount of the required pyran (0.03 g, 0.1%) was recovered. However, other attempts at the synthesis proved unsuccessful. The long reaction time required can be explained in terms of the size of the substituent that would occupy the 3-position. In this case it is the isobutyl group. This is a very large group compared to the methyl group and hydrogen

which occupy that position in other molecules. The long

reaction time and low yield are not difficult to imagine.

The low yield of the final product gives an indication of

the difficulty in forming the pyran, but intermediates may

also have a large part in the low yield of the reaction. Due

to steric factors, pyrans may be difficult to form. This

aspect will be discussed later.

The final synthesis involving a fluorinated diketone

involves trifluoromethyl-6-methyl-2,4-heptanedione and

silicon tetrachloride in refluxing dichloromethane. This

reaction failed to produce the desired pyran. The reason may

again be a steric one because there would be an isopropyl

group in the 3-position. This could cause a large degree of

interaction which may explain the failure to prepare the

desired pyran.

III.B.2. REACTIONS OF PYRANS

There are two common and highly useful reactions of

the pyrans:

a) dehydrogenation

b) electrophilic reactions of methylene pyrans

Each of these will now be discussed.

The dehydrogenation of 2H- or 4H-pyrans may occur by

hydride abstraction using a chemical species such as tri-

phenylmethyl perchlorate,[134] or by catalytic reduction.[135]

Pyrans of the type of the one shown (<u>XXXIX</u>), may produce two

a 4H-pyran:
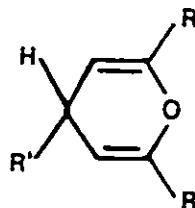
<u>XXXIX</u>

different pyrylium salts: if the group R' is resonance
stabilized, decomposition by acids leads to the initial
reagents; however, a 2,4,6-trisubstituted pyrylium salt and
hydride anion are obtained when R' is alkyl or aryl. The
hydride anion is transferred to an acceptor which may be
methylene blue or indigo.[136] One condition to convert a pyran
into a pyrylium salt is that a removable hydrogen be present.

Two of the more important electrophilic reactions are
protonation,[137] and alkylation or acylation at the exocyclic
methylene carbon atom.[138,139] The alkylation of 2,6-diphenyl-
4-isopropylidene-4H-pyran with refluxing methyl iodide
results in the 2,6-diphenyl-4-t-butyl pyrylium iodide.[139] This
reaction is shown in Scheme 25:
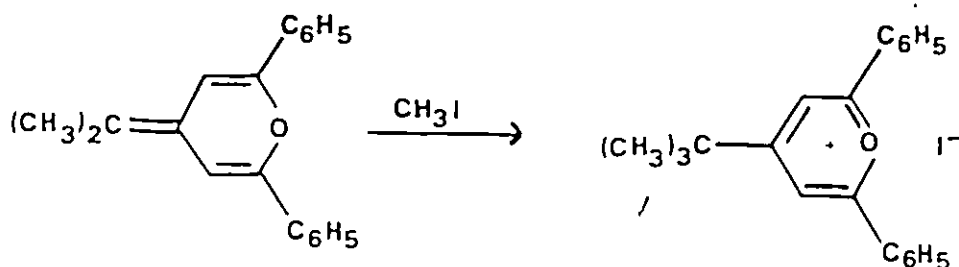
SCHEME 25

Comparing this reaction to protonation, it is obvious that
this alkylation is not reversible.

Attempts to protonate the methyl pyran failed. Per-
chloric and hydrochloric acids, as well as·hydrogen chloride
gas, were used. The procedure involved dissolving the methyl
pyran in methanol or .in chloroform followed by the addition
of the proton source. Based on the above discussions it would
seem reasonable·that a pyrylium salt would be formed
according to the reaction in Scheme 26.

SCHEME 26
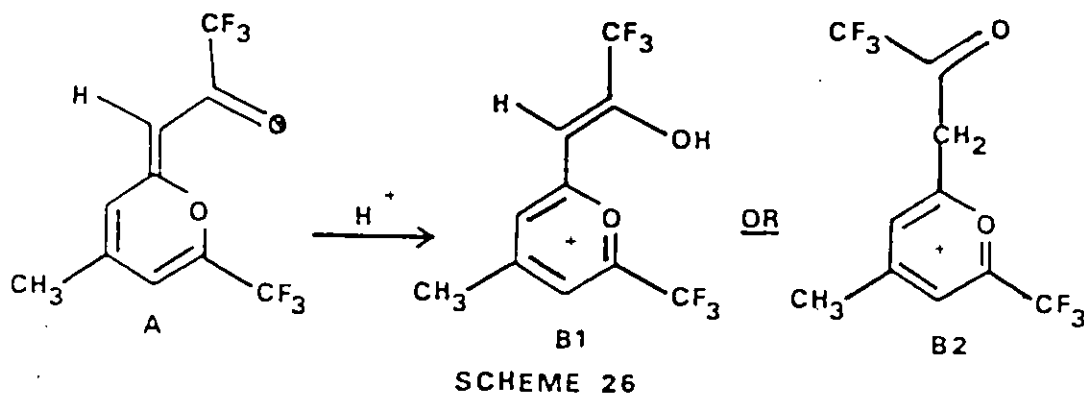
Up to now the position of the methyl and·the per-
fluoromethyl groups, with respect to the ring oxygen, is
unknown. It was hoped that by preparing the pyrylium salt (B)
and recording its infrared and nuclear magnetic resonance
spectra, the position of the alkyl groups might have been
elucidated. However, because the reactions were unsuccessful,
the positions of the alkyl still remain a mystery (but see
Section III.B.4.).

During the course of the protonation reaction, the infrared spectrum was utilized to monitor the reaction in the regions 2600-2300 cm^{-1} and 1700-1500 cm^{-1}. The region 2600-2300 cm^{-1} was used in the hope that structure (B1) would be present, since in the pyrylium chloride, there was a band centred at approximately 2400 cm^{-1}. The second region, 1700-1500 cm^{-1}, was utilized in the case where structure (B2) was formed. Again, as noted in the infrared spectrum of pyrylium chloride, bands in the 1630 cm^{-1} region characterize the presence of a pyrylium salt. The infrared spectra indicated no reaction had taken place.

The trifluoromethyl group has a marked effect on the reactivity, and also on the infrared spectrum, of the pyran under study. The infrared spectrum will be discussed later. Because of the strong electron withdrawal effects of the perfluoroalkyl group that is alpha to a carbonyl group, the addition of HX to the functional group occurs with relative ease,[140] as is seen from reaction Scheme 27:

$$R_F \leftarrow \overset{\overset{R}{|}}{C} = O \quad + \quad HX \quad \rightleftharpoons \quad R_F - \overset{\overset{R}{|}}{\underset{\underset{X}{|}}{C}} - OH$$
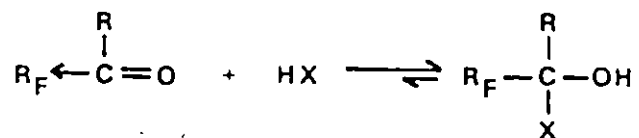
SCHEME 27

Since the carbon atom feels a high positive charge, the equilibrium lies to the right. This case is similar to the

one that was tried in this laboratory (Scheme 26), except
that the reaction does not proceed in our case. Even if the
reaction proceeded as in Scheme 27, the structure shown in
(XL) would give a different infrared spectrum from that of
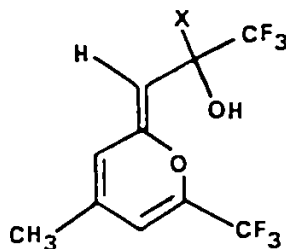
XL

the starting pyran. The difference would lie in the carbonyl
region; there would not be an absorption in that region. It
is difficult at this point to explain why the reaction does
not proceed to give the desired results (products).

III.B.3. CRYSTAL STRUCTURE OF 6-TRIFLUOROMETHYL-4-ETHYL-
3-METHYL-2-TRIFLUOROACETYL-PYRANYLIDENE

A summary of the crystal data and intensity data
collected for the pyran is given in Table 23. The purpose of
obtaining the crystal structure of ethyl pyran was mainly to
determine the relative positions of the alkyl and perfluoro-
alkyl groups on the ring. The two possible structures are
shown in Scheme 28. Infrared spectra failed to determine the
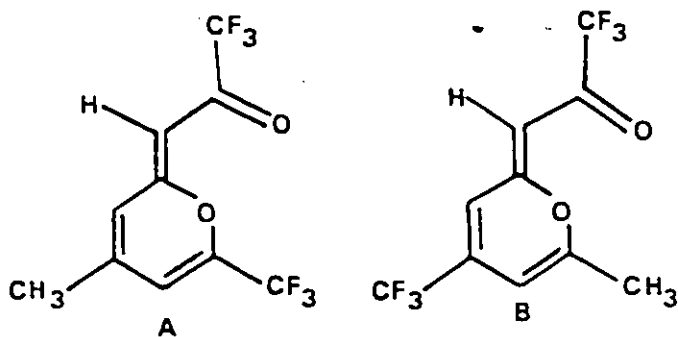
SCHEME 28

positions conclusively. The crystal structure determination
was carried out in hopes of determining the respective
positions of the groups.

The largest peaks (highest electron density) in the
unit cell were determined and organized into fragments of the
structure of the molecule according to symmetry relationships.
A 20% excess of atoms were inputed to this program. Several
attempts to determine unambiguously the position of the ring .
perfluoroalkyl group were unsuccessful.

A Fourier map was prepared in the hope that a
structure indicating the position of the ring perfluoroalkyl
group could be obtained. However, least-squares refinement
of the partial structure resulted in an ambiguous result,
that is, the position of the ring perfluoroalkyl group could
not be determined by this method.

Table 23. Summary of crystal data and intensity data collection for ethyl pyran.

A) <u>Crystal parameters at 18°</u> with Mo K_α = 0.71069 Å

a	9.370 Å
b	9.094 Å
c	16.873 Å
α	90.00°
β	111.60°
γ	90.00°
V	1344.7 Å^3
Space group	P2$_1$/c
Molecular weight	300.20
ρ_{calc}	1.48 for Z = 4

B) <u>Measurement of intensity data</u>

Radiation: Mo K_α = 0.71069 Å

Monochromator: graphite $2\theta_{002}$ = 12.1°

Crystal to detector distance: 25 mm

Detector: scintillation detector and pulse height analyzer set for 100% of Mo K_α peak

Attenuator: Ni foil used for intensities 10^4 cps

Take off angle: 3.0°

Detector aperture: 4 × 4 mm

Table 23, cont'd.

Scan type: coupled $\theta-2\theta$, 1° min^{-1}

Scan length: $\Delta(2\theta) = $ (base width + 0.692 tan θ)

                     starting base width/2 below peak

Rotation axis: b

Reflections measured: $\pm h$, $\pm k$, $\pm l$

Maximum and minimum 2θ: 45.0°, 4.0°

Scan base width: 1.3°.

Number of reflections collected: 1919

Number of reflections with I > $3\sigma(I)$:   1797

III.B.4. NUCLEAR MAGNETIC RESONANCE SPECTRA OF THE PYRANS

A brief review of the nuclear magnetic resonance spectra of pyrylium salts was presented in Section III.A.4. Generally, the three pyrans under study have the same ring structure, and thus, the corresponding protons on the ring in each molecule is expected to have similar chemical shifts (Table 24). The remainder of the molecule is variable, and so the nmr spectra are expected to show variations.

The nuclear magnetic resonance spectrum of methyl pyran is presented in Figure 14. There are two ring protons present in the molecule, located at the 3- and 5-positions. The chemical shifts of these two protons are $\delta 8.16$ and 6.58 ppm, respectively. Determination of these two chemical shifts was obtained by comparing the spectrum of methyl pyran with the spectrum of ethyl pyran. In the nmr spectrum of the ethyl pyran a methyl group is substituted for the proton. Thus, the assignment of the low-field region is complete. A single resonance signal appeared at $\delta 6.00$ ppm, which was assigned as the alkenic proton on the side-chain. There is only one methyl group on this molecule, and it is assigned to the signal found at $\delta 2.29$ ppm. The signal is split into a doublet. One possible explanation for this splitting is the presence of coupling between the methyl protons and the ring protons. Decoupling experiments would prove the presence of coupling between the methyl protons and other protons.

One more point to mention on the nmr spectrum of

Table 24. The proton magnetic resonance chemical shifts of
the pyrans under study in $CDCl_3$.

R^1 (δR^1 ppm)	R^2 (δR^2 ppm)	δH^A (ppm)	δH^B (ppm)
$-CH_3$ (2.29)	$-H$ (8.16)	6.58	6.00
$-C_2H_5$ (1.19 t)	$-CH_3$ (2.06)	6.57	5.77
(2.56 q)			
(J = 7.5 Hz)			
-isopentyl	-isobutyl		
(2.5-0.8)	(2.5-0.8)	6.41	5.72

.methyl pyran is the chemical shift of the proton at the 3-
position. This proton is downfield relative to the proton in
the 5-position on the ring. The orientation of the trifluoro-
acetyl group may be in a trans position to the ring oxygen
(XLI):
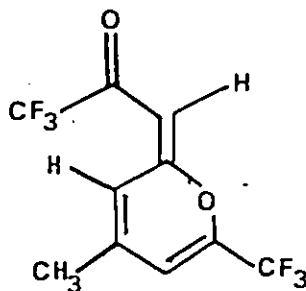
XLI

Figure 14. Nuclear magnetic resonance spectrum of methyl
pyran in CDCl$_3$.
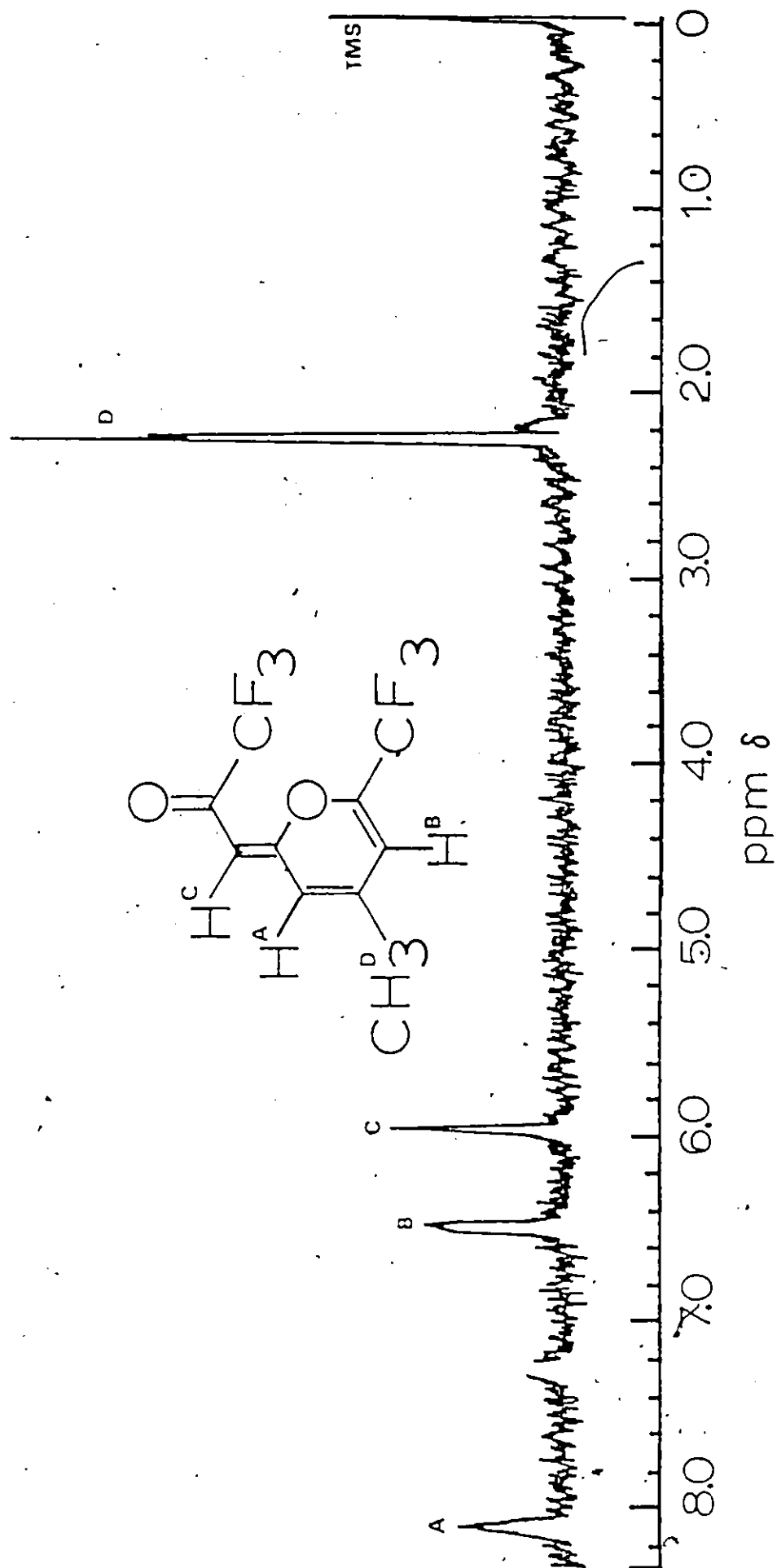
If this were so, there may be an interaction between the fluorine and hydrogen atoms, which causes the position of the signal to shift downfield.

The nuclear magnetic resonance spectrum of ethyl pyran is presented in Figure 15. This molecule has only one ring proton (5-position) which is assigned to the signal at δ 6.57 ppm. The alkenic proton was assigned to the signal at δ 5.77 ppm, since there is only that one proton and only that one signal present in the low-field region. There are two alkyl groups present, an ethyl and a methyl group. The methyl group is in the 3-position and a singlet resonance signal at δ 2.06 ppm is assigned to this methyl group. Ethyl groups produce the characteristic triplet-quadruplet type signals. The triplet (δ 1.19 ppm) is assigned to the methyl group and the quadruplet (δ 2.56 ppm) is assigned to the methylene protons. A coupling constant of 7.5 Hz was observed, consistent with the literature.[119]

The nmr spectrum of the pentyl pyran is presented in Figure 16. Again, the assignment of the ring and alkenic protons is very straightforward. The chemical shift of the aromatic proton is δ 6.41 ppm and that of the alkenic proton is δ 5.72 ppm. There are two alkyl groups present on the ring, an isobutyl group and an isopentyl group. Each of these has a rather complicated splitting pattern and added to this, the chemical shifts are very close to each other; the nuclear magnetic resonance spectrum in the alkyl region is expected to be rather complex. As can be seen from the nmr spectrum,

Figure 15. Nuclear magnetic resonance spectrum of ethyl
pyran in $CDCl_3$.
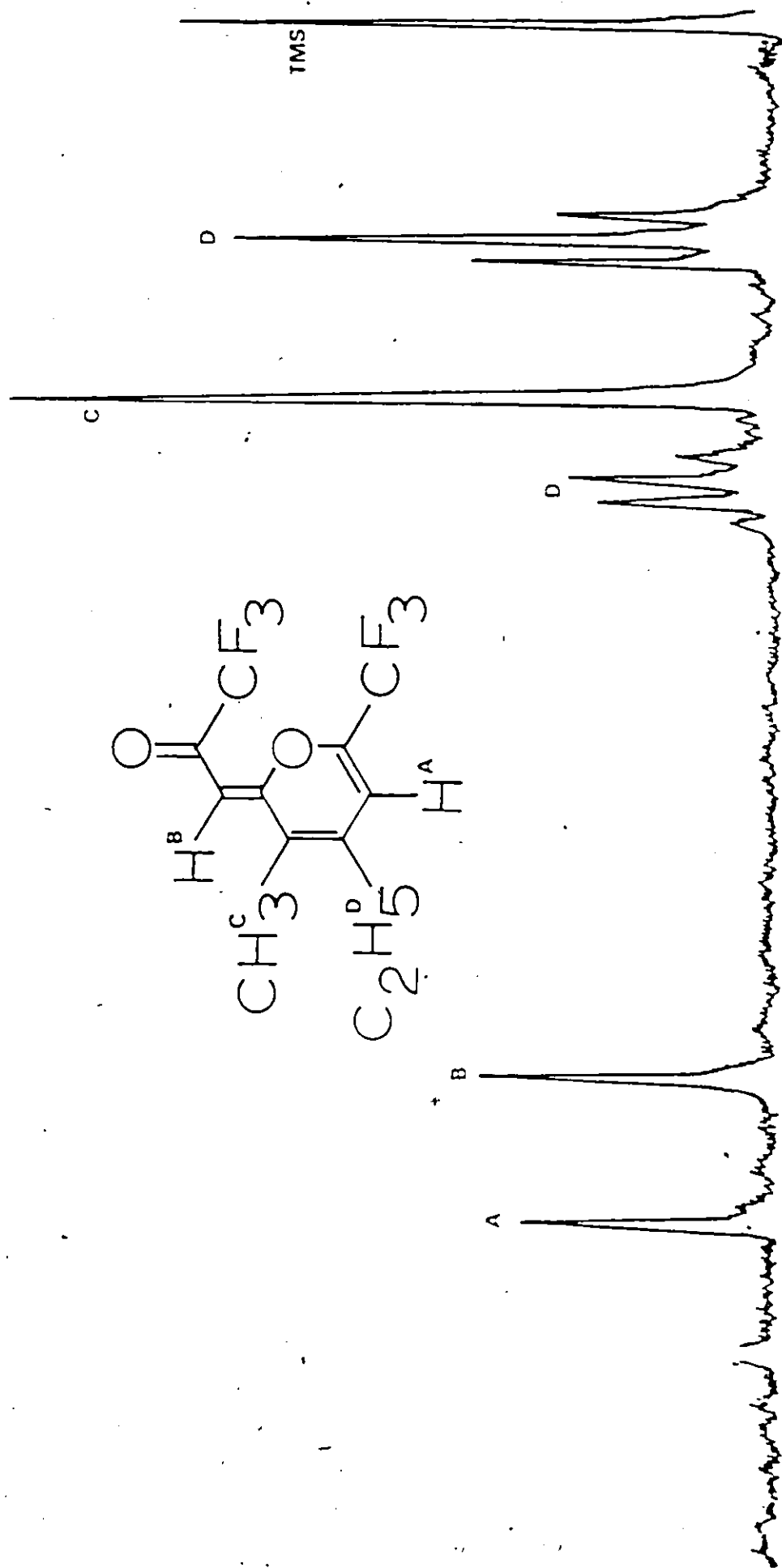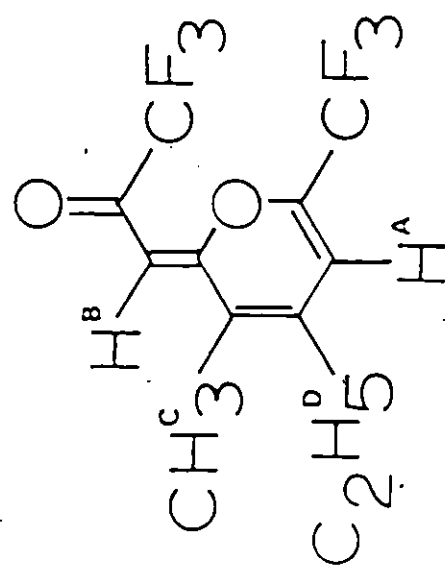
Figure 16. Nuclear magnetic resonance spectrum of pentyl
pyran in $CDCl_3$.
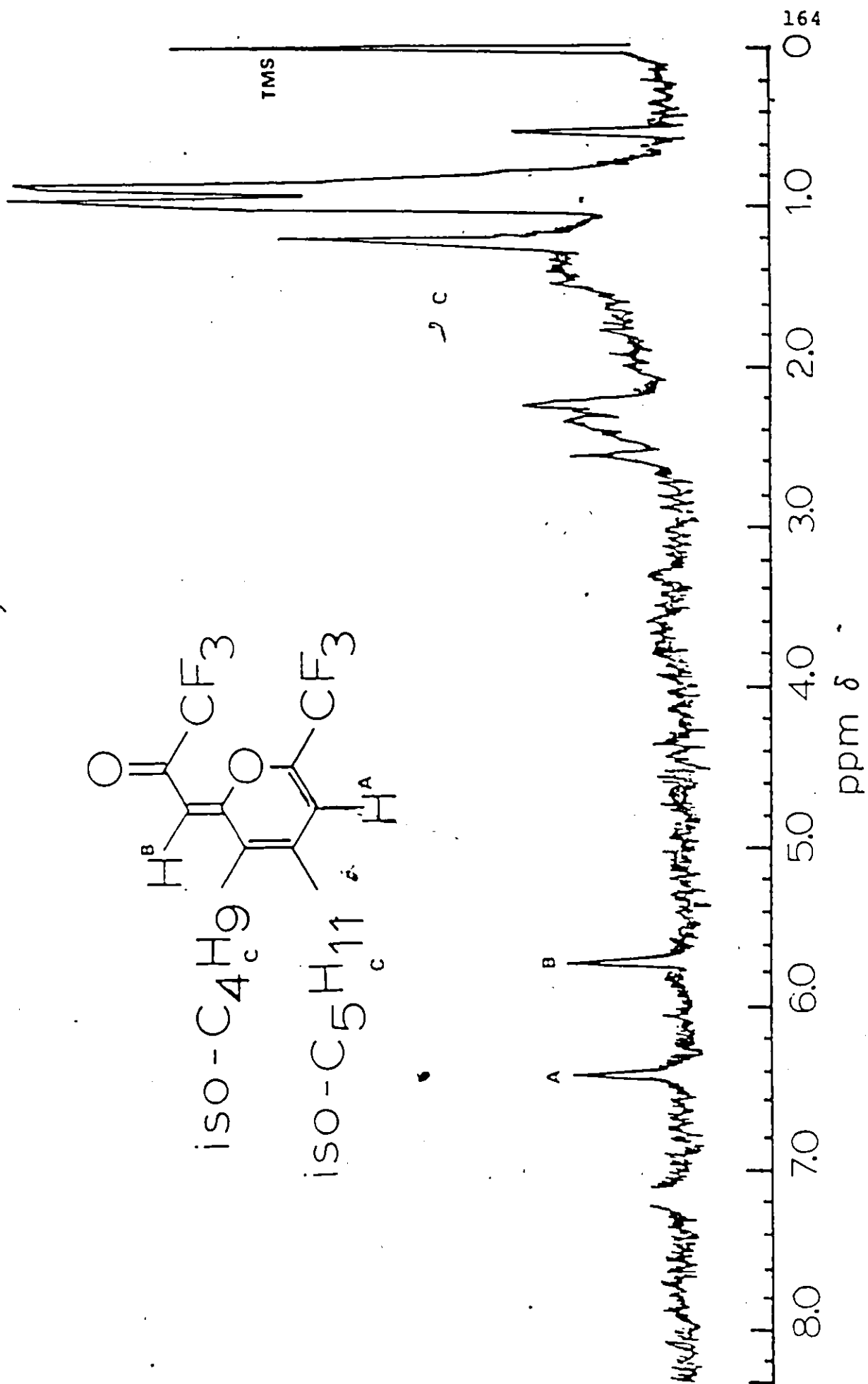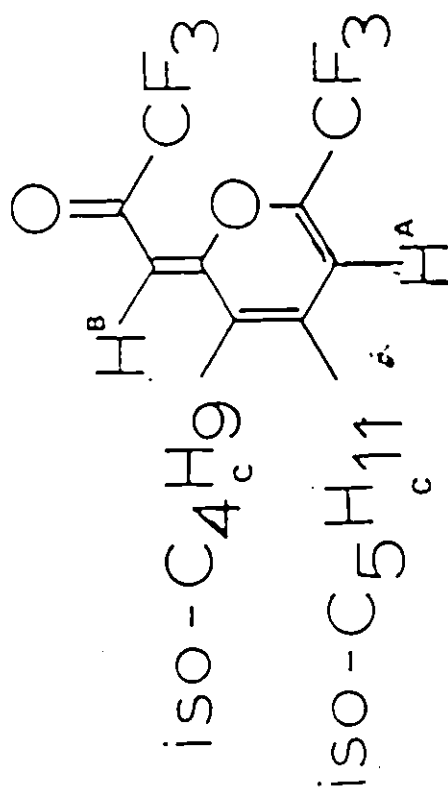
this fact is borne out. This region was assigned on the basis of the integrated area of the peaks. The area integrated to 20 protons which is the number of protons in the alkyl groups. There is an impurity present at about δ 0.5 ppm. This resonance signal is probably due to an organohalosilane impurity.

The position of the perfluoroalkyl group on the pyrans synthesized in this study was determined by the application of several nuclear magnetic resonance techniques. Although the problem appears to be straightforward, the complexity of the proton-proton and proton-fluorine couplings made unambiguous assignment rather difficult. A brief explanation of each technique employed will be presented. More detailed explanations may be found in spectroscopy books.[118,119,141]

Decoupling (or double-resonance) techniques remove the spin-spin couplings between nuclei.[141] A strong radiofrequency field of the resonant frequency of one of the nuclei is applied at the same time as the resonance of the other is being observed. Absorption and emission are induced by the strong radiofrequency field many times per second, and thus the time-average of the coupling between the decoupled nucleus and the other is zero.

Experiments which utilized the decoupling technique, or a slight variation of this method, include:

a) homonuclear decoupling

b) homonuclear triple irradiation which involves the simultaneous decoupling of two protons while

observing the remaining protons.

c) heteronuclear decoupling between the ^{1}H and ^{19}F nuclei (the protons are decoupled and the fluorine resonance signals are observed), and between ^{1}H and ^{13}C nuclei (the selective decoupling of the protons and the observation of the ^{13}C resonance signals).

d) simultaneous homonuclear and heteronuclear decoupling while observing the proton resonance signals.

e) homonuclear and heteronuclear Overhauser effect (NOE) measurements.

The Nuclear Overhauser Effect (NOE) arises when saturation of the resonance of one nucleus can affect the relaxation of another nucleus/nuclei, resulting in intensity changes in the nuclear magnetic resonance spectrum.[119] This NOE phenomenon will occur when the nuclei in question are in close proximity, although spin coupling need not be present between them. Relaxation of the nucleus/nuclei under observation may depend mainly upon spin exchange with the irradiated nucleus, such that the saturation of the irradiated nucleus can give an intensity enhancement of up to 50% when the nuclei are of the same species.

Discussion of the structure determination of methyl pyran will be divided into four parts: (a) ^{1}H-^{1}H decoupling; (b) ^{1}H-^{19}F decoupling; (c) NOE measurement; and (d) ^{1}H-^{13}C decoupling. In some cases, the nmr spectra have lost some fine structure during the photo-reduction process which may affect the understanding of parts of the discussion.

The homonuclear decoupling nmr spectra are presented in Figure 17. The ^{1}H nuclear magnetic resonance spectrum of methyl pyran is pictured in (1) of Figure 17. This spectrum may be assigned to either structure (A) or (B) (Scheme 28). Irradiation of the methyl group (δ 2.3 ppm) affects all of the remaining proton signals, which indicates coupling to the other protons (spectrum 2). Spectrum (3) shows that upon irradiation of the proton signal at δ 8.1 ppm, the methyl protons at δ 2.3 ppm and the proton signal at δ 6.5 ppm and at δ 5.9 ppm are affected. Thus, proton at δ 8.1 ppm is primarily coupled to the methyl group and the proton at δ 6.5 ppm. Irradiation of the methyl proton signal at δ 2.3 ppm (spectrum 4) and looking only at the protons at δ 8.1 and 6.5 ppm, reveals that the methyl group is coupled to these protons. Triple resonance experiments (decoupling protons at δ 5.9 and 2.3 ppm) indicate that the protons at δ 8.1 and 6.5 ppm are coupled (spectrum 5). These data indicate that structure (A) in Scheme 28 could possibly be correct.

In the heteronuclear decoupling experiments, the ^{19}F nuclei were irradiated and the ^{1}H nuclear magnetic resonance spectra were recorded. The ^{1}H nmr spectra of methyl pyran, after decoupling, are presented in Figure 18. Irradiation of the low-field fluorine signal (spectrum 6) removed the coupling from the proton signal at δ 8.1 and 6.5 ppm (compare spectra 1 and 6). Coupling was removed from the proton signal at δ 5.9 ppm (spectrum 7) by irradiating the high-field fluorine signal (compare spectra 1 and 7). Irradiation

Figure 17. Homonuclear decoupled ^{1}H nuclear magnetic resonance spectra of methyl pyran in $CDCl_3$.

(1) ^{1}H nmr

(2) Irradiation of methyl group (δ 2.3 ppm)

(3) Irradiation of proton at δ 8.1 ppm

(4) Irradiation of methyl group (δ 2.3 ppm)

(5) Irradiation of protons at δ 5.9 and 2.3 ppm.
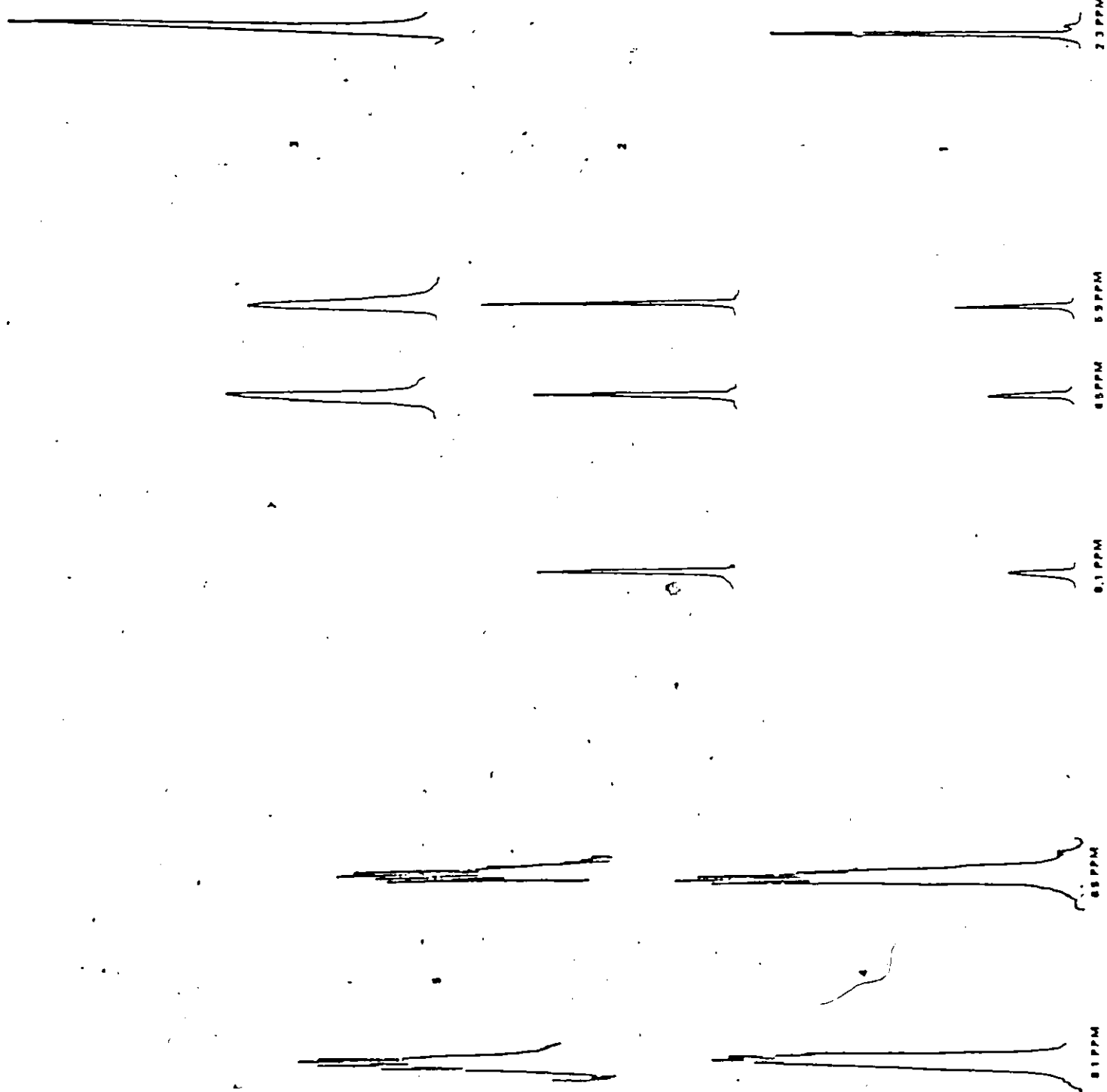
Figure 18. Heteronuclear decoupled (^{19}F) ^{1}H nuclear magnetic
resonance spectra of methyl pyran in CDCl$_3$.

      (6) Irradiation of low-field fluorine signal (72.0 ppm)

      (7) Irradiation of high-field fluorine signal (78.6 ppm)

      (8) Irradiation of low-field fluorine signal and methyl
          proton signal (δ 2.3 ppm)

      (9) Irradiation of low-field fluorine signal and proton
          signal at δ 8.1 ppm

9

8

7

6

8,1   6.5   5.9   PPM   2.3
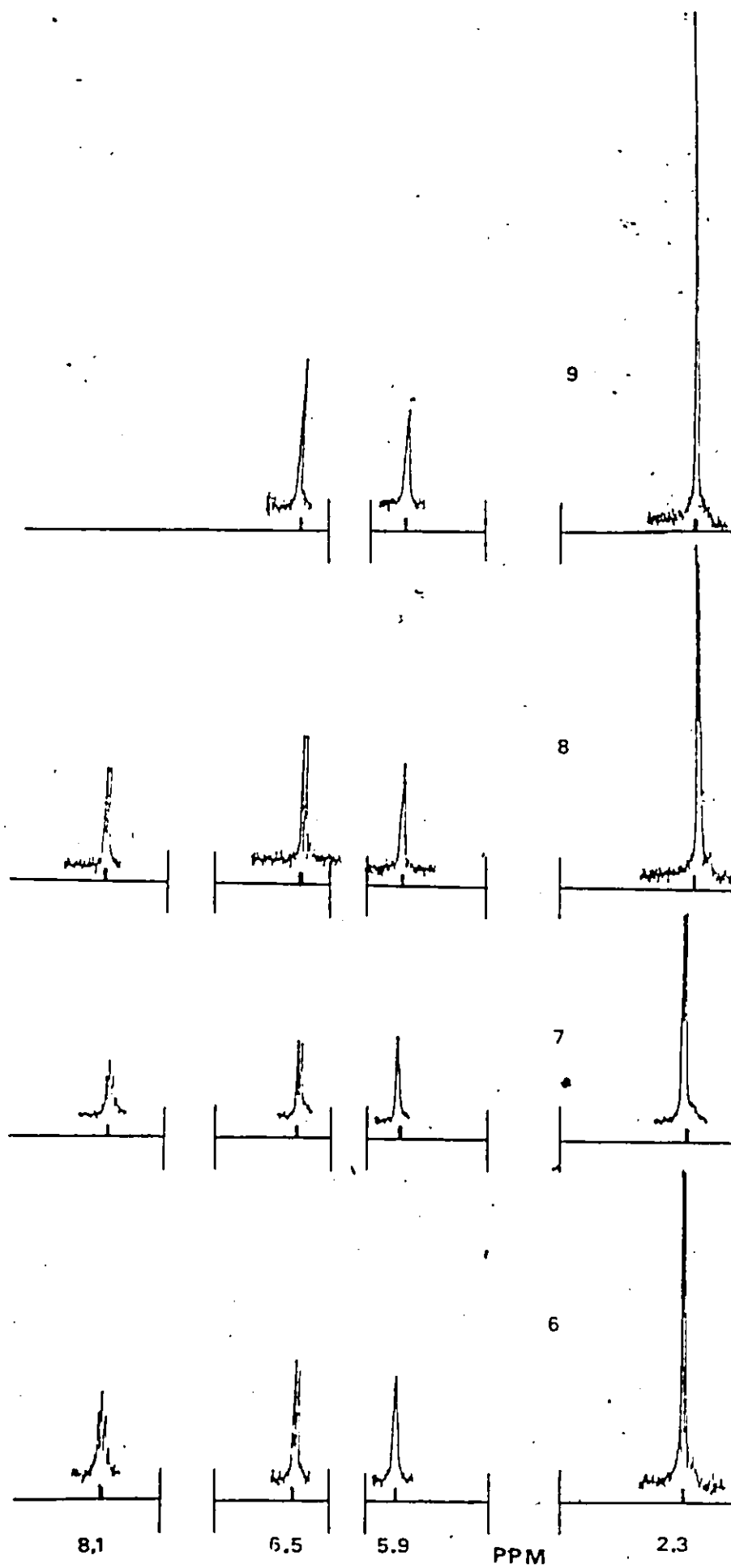
of the low-field fluorine signal and the methyl proton

signals at δ 2.3 ppm indicates that the methyl protons are

coupled to the protons at δ 8.1 ppm in the nmr spectrum (8).

Confirmation that the methyl protons and the proton at δ 8.1

ppm, and that the protons at δ 8.1 and 6.5 ppm, are coupled

was obtained by irradiating the low-field fluorine signal and

the signal at δ 8.1 ppm, simultaneously (spectrum 9).

The ^{19}F nuclear magnetic resonance spectrum of methyl

pyran is presented in Figure 19. Spectrum (10) was recorded

in the absence of the decoupling experiments (spectrum 11

is expanded), whereas spectrum (12) was recorded with the

irradiation of the proton signal at δ 5.9 ppm. The ^{19}F signal

at δ 78.6 ppm (high field) is coupled to the proton at δ 5.9

ppm, and the low-field ^{19}F signal is coupled to the protons

at δ 8.1 and 6.5 ppm. This indicates that the high-field

fluorine signal corresponds to the CF_3 group outside the

ring, that is, on the side chain.

Homonuclear NOE measurements would clearly distinguish

between the two possible structures (Scheme 28). In the case

of structure (A), the protons at δ 8.1 and 6.5 ppm would be

enhanced on irradiation of the methyl proton signal, whereas

in structure (B), only one proton signal would be enhanced on

irradiating the methyl group signal. The results of this

experiment are summarized in Table 25. The proton signals at

δ 8.1 and 6.5 ppm show NOE enhancements of 21% and 14%,

respectively. This confirms structure (A) of Scheme 28 as the

correct configuration of the pyran.

Figure 19. Heteronuclear decoupled (^{1}H) ^{19}F nuclear magnetic
resonance spectra of methyl pyran in $CDCl_3$.

(10) ^{19}F nmr spectrum

(11) ^{19}F nmr spectrum (expanded)

(12) ^{19}F nmr spectrum with irradiation of proton signal
at δ 5.9 ppm
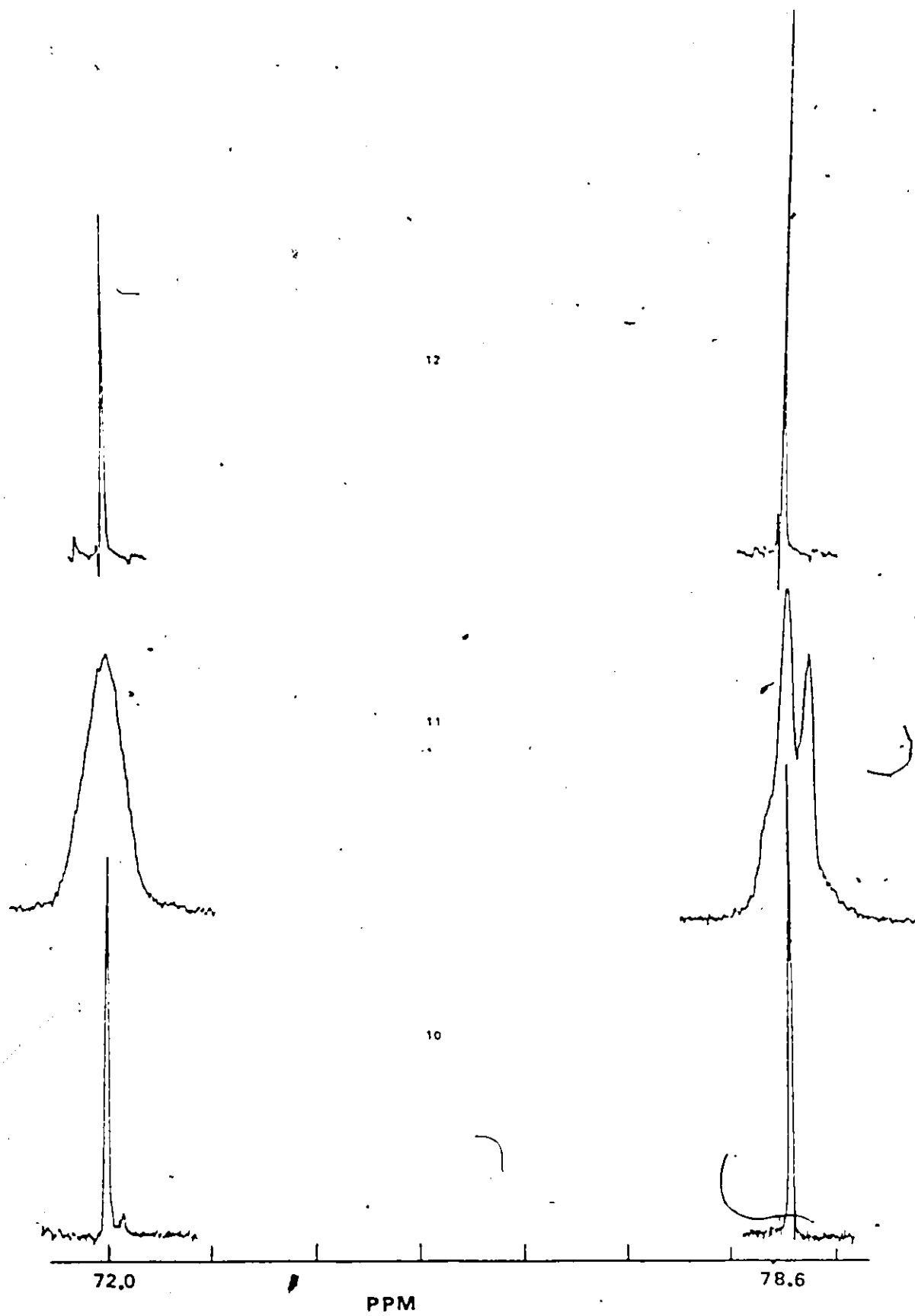
Table 25. Homonuclear NOE measurements on the low-field proton signals of methyl pyran with irradiation of the methyl group signal (δ 2.3 ppm).

Proton signal		Intensity in absence of NOE	Intensity in presence of NOE	Change
δ 8.1 ppm		52	61	
		50	60	
		48	61	
		50	61	
		50	60	
	ave.	50 ± 1	61 ± 0.5	21%
δ 6.5 ppm		56	64	
		55	65	
		57	63	
		56	64	
		56	62	
	ave.	56 ± 1	64 ± 1	14%
δ 5.9 ppm		53	52	
		52	52	
		53	52	
		53	53	
		53	52	
	ave.	53 ± 0.4	52 ± 0.4	≃ 0%

Heteronuclear NOE measurements would allow unambiguous proton assignment and further evidence as to the structure of methyl pyran. The low-field fluorine signal was irradiated and the ^{1}H nmr spectrum indicated the proton signal at δ 6.5 ppm was enhanced in intensity by 19% whereas the irradiation of the high-field fluorine signal enhanced the proton signal at δ 5.9 ppm by 6 %. This is summarized in Table 26. Thus, the position of the perfluoromethyl group on the pyran was located, unequivocally.

. . Carbon-13 nuclear magnetic resonance was utilized to confirm the overall structure of the methyl pyran molecule. Proton decoupling was performed to assign the chemical shifts of carbon atoms obtainable from the ^{13}C nmr spectra. The ^{13}C nmr spectra of methyl pyran are presented in Figure 20 and 21, and the carbon-13 chemical shifts in ppm downfield from TMS are listed in Table 27.

In the fluorine coupled-proton decoupled ^{13}C nuclear magnetic resonance spectrum (Figure 21, A), four quartets are present, two at low field and two at higher field. The low-field quartet (177.7 ppm, J_{CCF} = 33.8 Hz) is assigned to the side-chain carbonyl group adjacent to a trifluoromethyl group. Hence, the other low-field quartet (145.9 ppm, J_{CCF} = 39.5 Hz) is assigned to the ring carbon adjacent to the perfluoromethyl group. The remaining two quartets (118.3 and 117.1 ppm, J_{CF} = 272.1 and 290.8 Hz, respectively) are assigned to the two trifluoromethyl carbons. There is long-range coupling between the fluorine and carbon atoms

Table 26. Heteronuclear NOE measurements on the low-field proton signals of methyl pyran with the low field (72.0 ppm) and high field (78.6 ppm) fluorines irradiated.

Proton Signal	Intensity in absence of NOE	Intensity in presence of NOE		Change	
		Low	High	Low	High
δ8.1 ppm	50	52	57		
	50	51	54		
	48	54	52		
	50	50	52		
	48	50	54		
	50	51	52		
		54	52		
ave.	49 ±1	52 ± 2	53 ± 2	≈6%	≈8%
δ6.5 ppm	54	68	59		
	57	68	54		
	54	63	55		
	55	67	53		
	55	66	52		
		63	54		
		62			
ave.	55 ± 1	65 ± 3	55 ± 2	19%	≈0%
δ5.9 ppm	49	55	52		
	50	53	53		
	50	53	50		
	50	53	49		
	48	52	52		
	49	52	53		
		50			
ave.	49 ± 1	53 ± 2	52 ± 2	≈8%	≈6%

Figure 20. ^{13}C nuclear magnetic resonance spectrum of methyl pyran in CDCl$_3$.
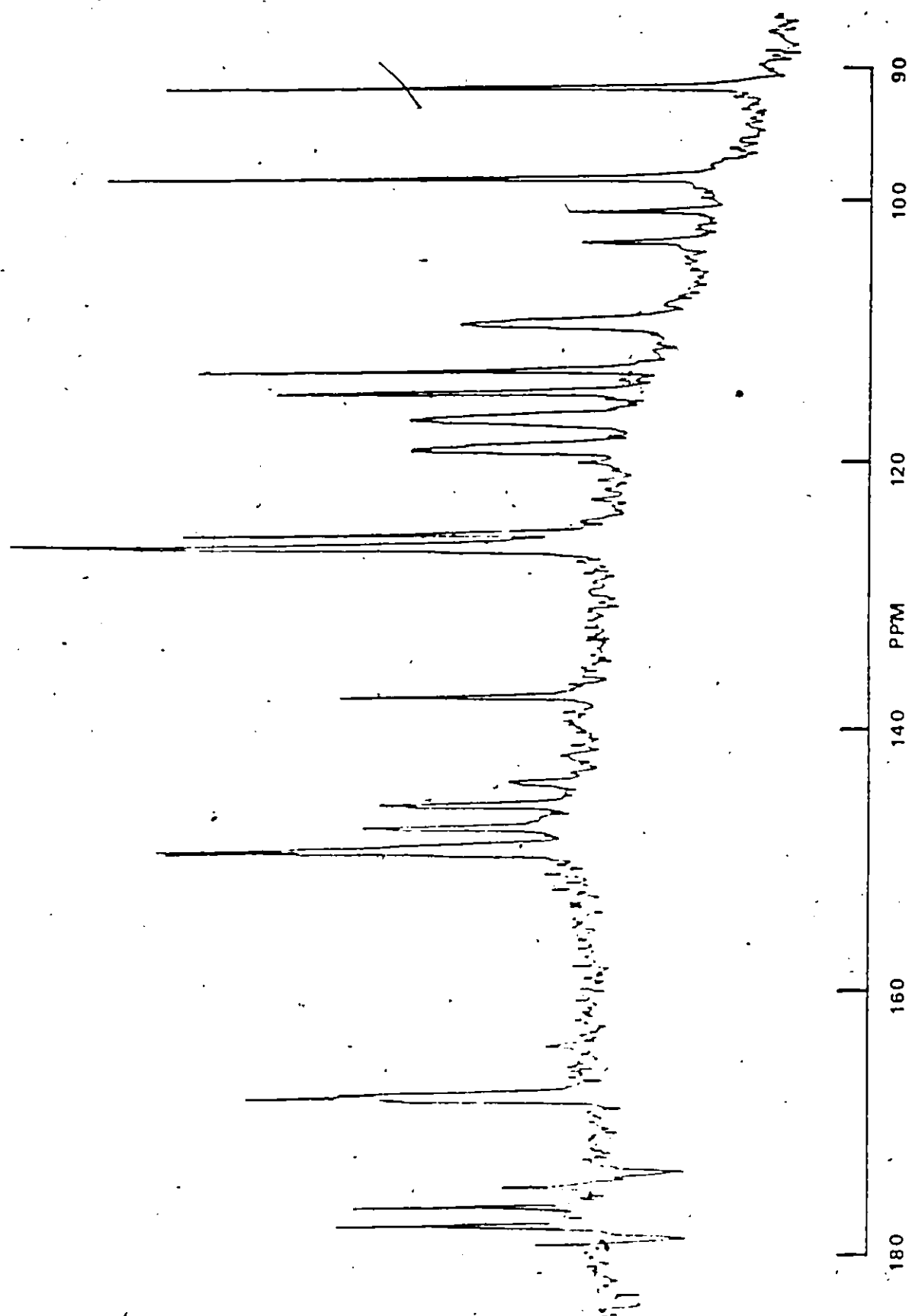
Figure 21. ^{1}H decoupled ^{13}C nuclear magnetic resonance
spectra of methyl pyran in $CDCl_3$.

    (A) Fluorine coupled-proton decoupled ^{13}C nmr spectrum

    (B) Irradiation of methyl group protons

    (C) Decoupling of proton signal at δ 8.1 ppm

    (D) Decoupling of proton signal at δ 6.5 ppm
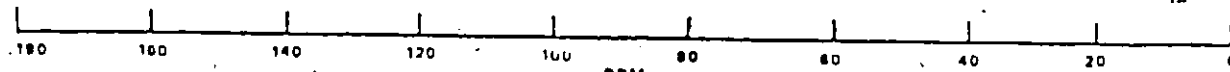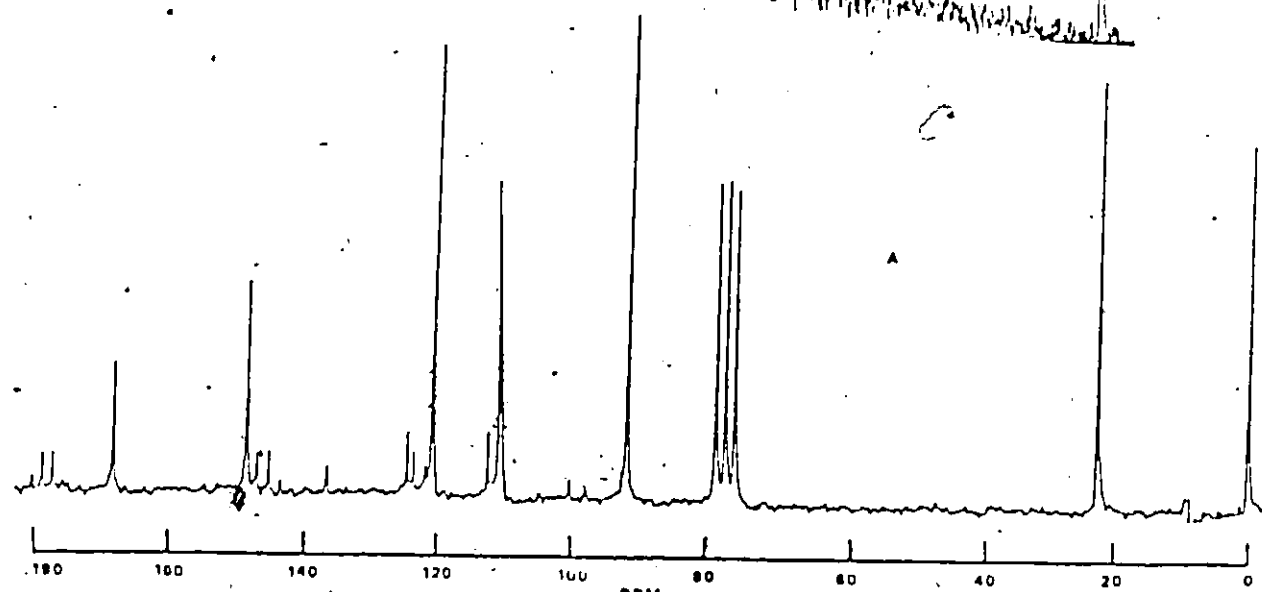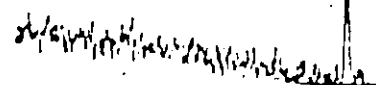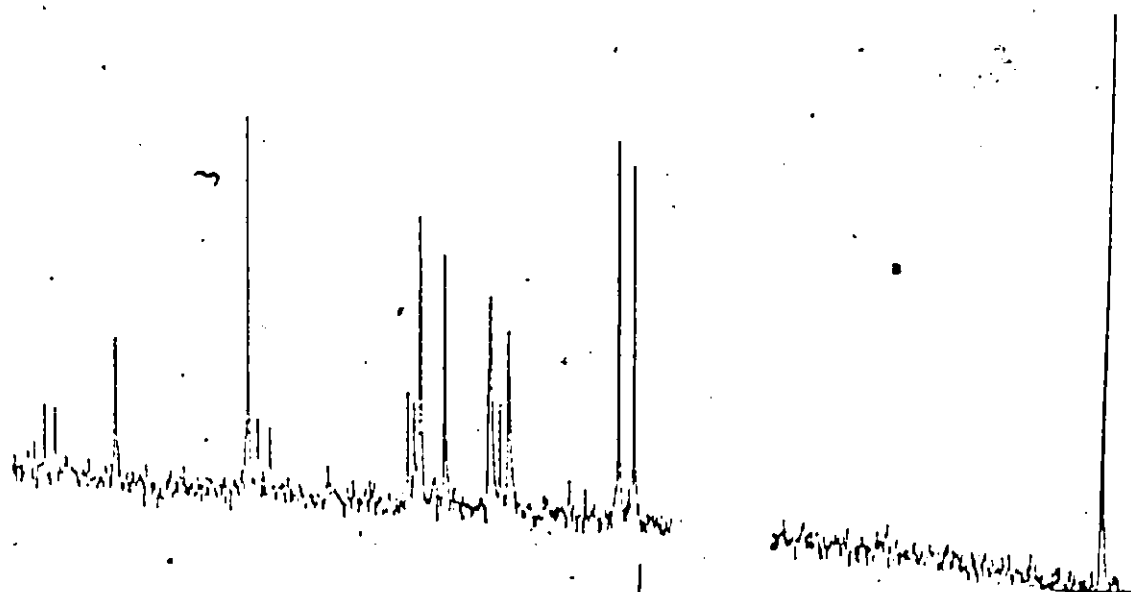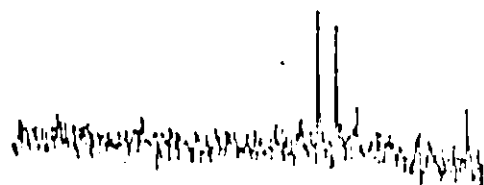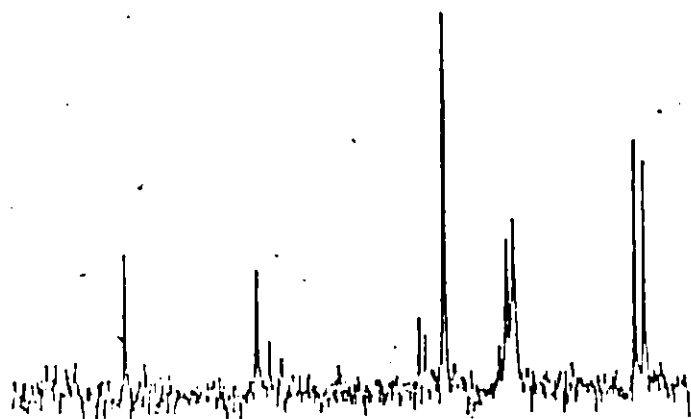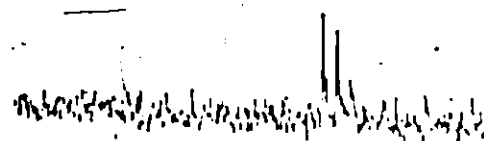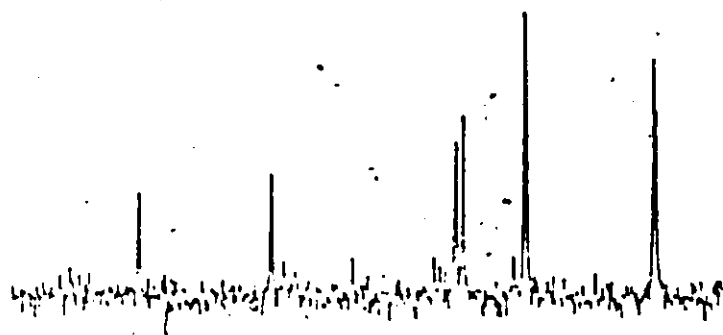
Table 27. Carbon-13 nuclear magnetic resonance chemical shifts in ppm downfield from TMS in $CDCl_3$.

Chemical shift (ppm)	Multiplicity[a]
177.7 (J_{CCF} = 33.8 Hz)	q
168.0	s
148.2	s
145.9 (J_{CCF} = 39.5 Hz)	q
120.7	s
118.3 (J_{CF} = 272.1 Hz)	q
117.1 (J_{CF} = 290.8 Hz)	q
110.5 (J_{CCCF} = 3 Hz)	d
91.6	s
21.9	s

[a] q = quartet; s = singlet; d = doublet.

represented by the signal at 110.5 ppm (J_{CCCF} = 3Hz), as well as proton coupling with the 5-position proton. This was confirmed by decoupling the proton signal at δ 6.5 ppm and observing the effect on the spectrum (Figure 21, D).

Irradiation of the methyl group protons (Figure 21, C) sharpens the signal at 148.2 ppm, which indicates coupling between the two nuclei. The signals centred at 118.3 ppm are enhanced; the irradiation of the methyl protons removes some of the long range coupling from the trifluoromethyl group,

indicating the presence of the perfluoromethyl group on the ring. Decoupling the proton at δ 8.1 ppm (Figure 21, C) results in the enhancement of the signal at 120.7 ppm, thus, assigning this resonance signal to the ring carbon in the 3-position. All of the ring protons were irradiated, but the signal at 168.0 ppm was unaffected. This signal is assigned to the carbon at the 2-position, while the remaining resonance signal at 91.6 ppm (a doublet) must be coupled to the proton at δ 5.9 ppm.

The ^{1}H, ^{13}C and ^{19}F nuclear magnetic resonance spectral data of methyl pyran is summarized in Table 28.

Table 28. The ^{1}H, ^{13}C and ^{19}F chemical shifts of methyl pyran in CDCl$_3$.
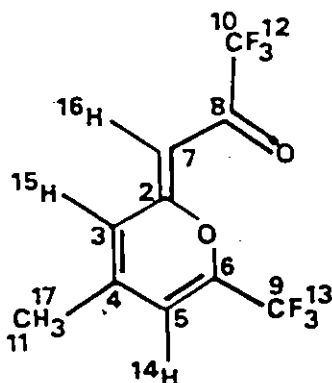
Nucleus	Atom	Chemical shift, ppm (coupling constant, Hz)	Reference (upfield/downfield)
^{13}C	2	168.0	TMS (downfield)
	3	120.7	
	4	148.2	
	5	110.5 (J_{CCCF} = 3)	
	6	145.9 (J_{CCF} = 39.5)	
	7	91.6	
	8	177.7 (J_{CCF} = 33.8)	
	9	118.3 (J_{CF} = 272.1)	
	10	117.1 (J_{CF} = 290.8)	
	11	21.9	
^{19}F	12	78.6 (J_{FCCCH} = 0.8)	CFCl$_3$ (upfield)
	13	72.0	
^{1}H	14	6.5	TMS (downfield)
	15	8.1	
	16	5.9	
	17	2.3	

III.B.5. INFRARED SPECTRA OF THE PYRANS

The infrared spectrum of non-fluorinated pyrans may be analyzed in terms of the well-known functional groups present, namely the ether linkage, and thus needs no introduction. However, the pyrans in this study have per-fluoroalkyl groups which are expected to affect the position of the vibrational peaks. Therefore, the vibrational spectra of fluorinated ethers and carbonyl compounds are briefly discussed.

A pyran is a cyclic ether, and therefore should absorb in the infrared spectrum at 1150-1060 cm^{-1} [142] due mainly to the antisymmetric C-O-C stretching frequency. In vinyl ethers the band is found at higher frequency in the range 1274-1200 cm^{-1}, with a weaker band (the symmetric stretching frequency) found at 1075-1020 cm^{-1}.[142] Use of these absorptions is restricted because of the similar positions of the fluorocarbon absorptions.

Moving on to the next functional group associated with the pyrans under study is the carbonyl region of an infrared spectrum. This region is very sensitive to the substituents attached to it. Normally, the carbonyl stretching frequency is found in the region 1850-1600 cm^{-1}.[142] Changes in the steric and electrical interactions of the substituents with the carbonyl group lead to the positional changes of the carbonyl band.

The introduction of fluorine into a compound

containing a carbonyl group results in an increase in the carbonyl stretching frequency. The position and number of fluorine atoms determine the magnitude of the frequency change.

If the carbonyl group is conjugated with an olefinic or an aromatic system, the frequency of the carbonyl stretching vibration is decreased, because of the reduction in the force constant of the carbonyl bond. The carbonyl stretching frequencies of a representative collection of fluorinated ketones[142] is presented in Table 29. This effect is clearly visible from the stretching frequencies listed in the table. Both aromatic and olefinic systems result in a decrease of the carbonyl stretching frequency.

The infrared spectra of methyl and ethyl pyran were recorded as Nujol mulls and are pictured in Figures 22 and 23. The major vibrations are listed in Tables 30 and 31, along with the postulated assignments.

Inspection of the infrared spectra of the two compounds reveals that the spectra are virtually identical. This is not unexpected as the geometry of the two compounds are very similar, the only difference being an added methyl group in the 3-position. These two spectra may be compared as they were both run in the same solvent.

The two pyrans under study have a side-chain similar to the pure fluorinated diketones. Thus, one would expect the carbonyl stretching frequency to be similar. From Tables 29, 30 and 31, it can be seen that the carbonyl stretching

Table 29. Carbonyl stretching frequencies of fluoroketones.[138]

Compound[a]	Frequency (cm^{-1})	Reference
R_fCOR	1775–1760	143,144
$R_fCOCH_2CH\ CH_2$	1773	145
R_fCOCH_2Ar	1767	143
$R_fCOCH\ CHCH_3$	1730	146
$R_fCOCH_2COCH_3$	1775,1745	147
	1680–1605	148
$CF_3COCH_2COCF_3$	1790,1765	147
	1680	147

[a]R_f is a perfluoroalkyl group; Ar is an aryl group.

frequency is located at 1680-1605 cm^{-1} for trifluoromethyl-2,4-pentanedione,[148] and at 1684 cm^{-1} for methyl pyran and at 1676 cm^{-1} for ethyl pyran.

The other vibrational mode of interest is that concerning the ether linkage. It was stated earlier in this section that the C-O-C antisymmetric stretching frequency is located at 1275-1200 cm^{-1} and at 1075-1020 cm^{-1} for the symmetric stretching frequency for vinyl ethers.[142] For both compounds there are intense bands in these regions. In the methyl pyran, the bands are located at 1206-1276 cm^{-1} and

Figure 22. Infrared spectrum of methyl pyran as a Nujol mull in the region 1800-650 cm^{-1}.
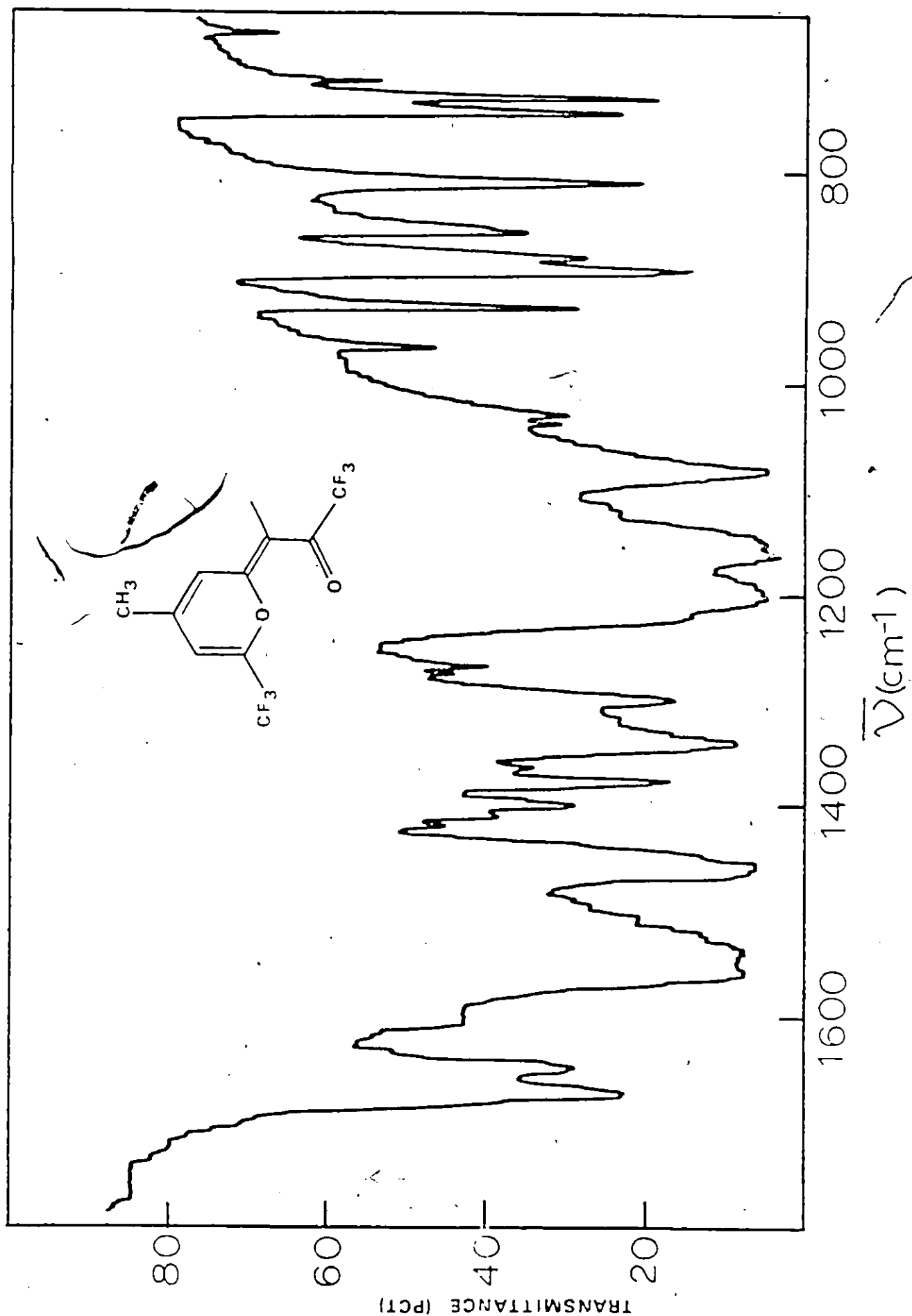
Figure 23. Infrared spectrum of ethyl pyran as a Nujol mull in the region 1800-650 cm^{-1}.
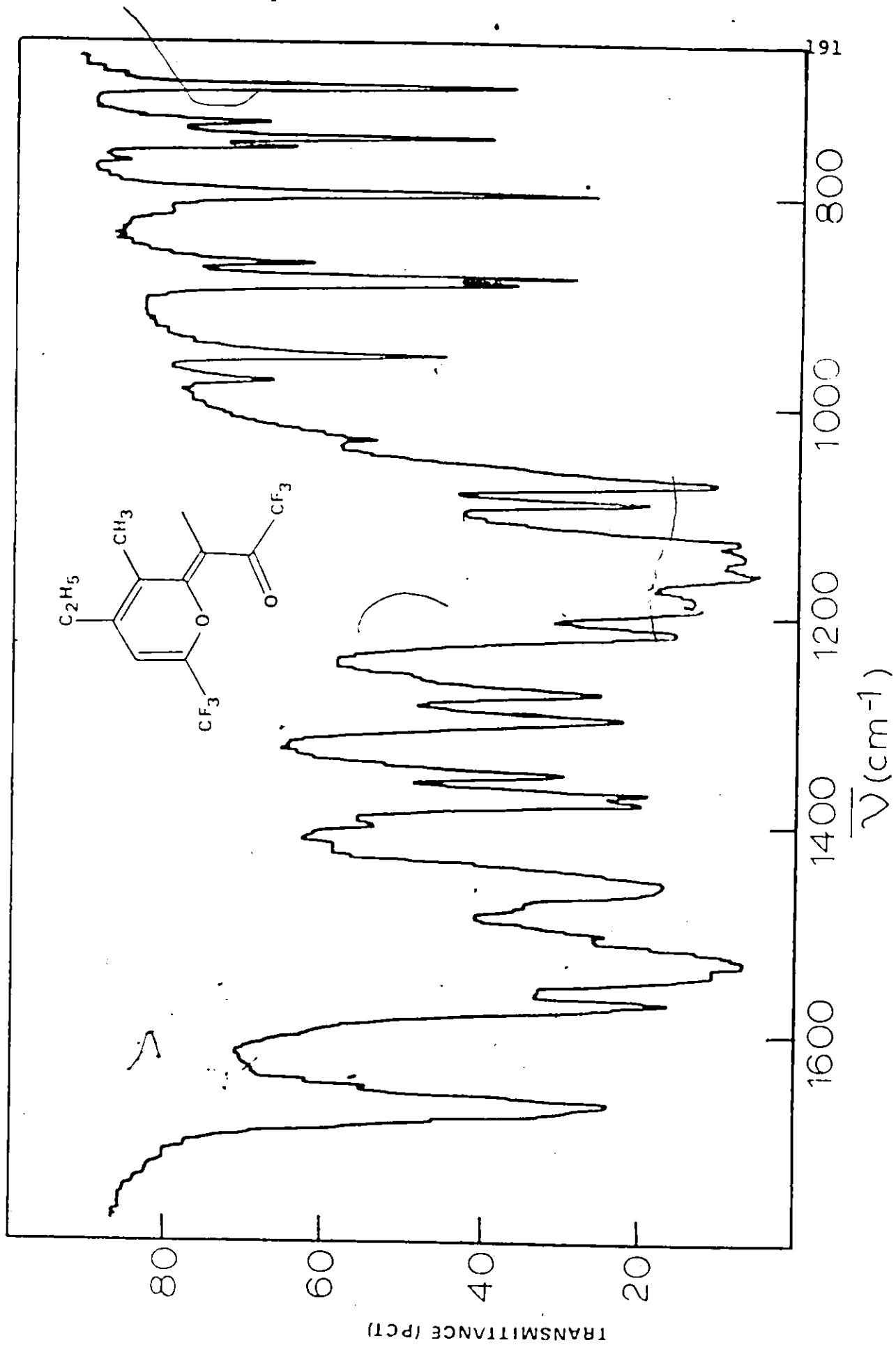
Table 30. The infrared spectral assignments of methyl pyran as a Nujol mull.

$\bar{\nu}$ (cm^{-1})	Intensity[a]	Assignment
1684	s	C≡O
1276	m	C-O-C
1206	vs	C-O-C
1089	vs	C-O-C
1044	m	C-O-C
1035	m	C-O-C

[a] s,strong; m,medium; v,very.

Table 31. The infrared spectral assignments of ethyl pyran as a Nujol mull.

$\bar{\nu}$ (cm^{-1})	Intensity[a]	Assignment
1676	s	C≡O
1282	s	C-O-C
1223	s	C-O-C
1099	s	C-O-C
1081	vs	C-O-C
1038	w	C-O-C

[a] s,strong; w,weak; v,very.

1035-1089 cm^{-1}; in the ethyl pyran, the bands are found at 1223-1282 cm^{-1} and at 1038-1099 cm^{-1}. Both of these sets of bands are in the range found in the literature,[142] and are in agreement with the structure identified via nuclear magnetic resonance spectroscopy in Section III.B.4.

III.B.6. MASS SPECTRA OF THE PYRANS

The mass spectrometry of fluorinated organic compounds is rather complicated. Fluorine compounds undergo rearrangements upon ionization which produce groups of atoms which are not adjacent to each other in the unionized molecule.[149] The trifluoromethyl group is special in the mass spectrum of organofluorine compounds. It can be formed by rearrangement, even though there is no group resembling the trifluoromethyl group, and it is almost always lost from the molecular ion to give the base peak ion in the mass spectrum.

Along the line of formation of the trifluoromethyl group is the rearrangement resulting in the pentafluoroethyl group.[149] This fluorinated alkyl group is less frequently encountered, but it must be kept in mind when discussing the mass spectra of fluorinated organic compounds. Another fragment encountered, often if not always, is that which contains hydrogen, carbon and fluorine. The fragment is found in the mass spectrum at m/e 51, and it corresponds to the

difluoromethyl ion. A rearrangement peak at m/e 33 often appears in the mass spectrum of compounds in which the ratio of fluorine atoms to hydrogen atoms approaches one. This fragment (m/e 33) corresponds to the monofluoromethyl ion (CFH_2^+). The last process to be mentioned which can lead to confusion in the understanding of the mass spectrum of organofluorine compounds is the elimination of difluoromethylene, CF_2. This rearrangement ion is generally observed in the mass spectrum of aromatic compounds at m/e 50.

The mass spectrum of methyl pyran is presented in Figure 24 and the major fragment ions are listed in Table 32. The proposed fragmentation pattern is presented in Scheme 29.

Pyrans are the anhydro bases of pyrylium salts. It was mentioned earlier (cf. Section III.A.6) that in the mass spectrum of pyrylium salts the vaporization of the samples resulted in the abstraction of the hydrogen halide and the anhydro base appears as the molecular ion.[127] It would be expected to be present in these mass spectra (of pyrans) and, indeed, it is. The molecular ion is the ion at the highest m/e value. The loss of a trifluoromethyl radical yields the base peak ion at m/e 203 $(C_9H_6F_3O_2^+)$. There are two fragmentation paths that involve the $C_9H_6F_3O_2^+$ ion (m/e 203). The first begins by the loss of a CO molecule to give the $C_8H_6F_3O^+$ (m/e 175) fragment, with the subsequent loss of the CF_3CO radical (m/e 97), in two stages, to produce $C_6H_6^{+\cdot}$ Loss of a CO molecule results in the formation of a five-membered ring, $C_7H_6F_3^+$ (m/e 147). This ion loses the methyl radical to

Figure 24. Mass spectrum of methyl pyran.
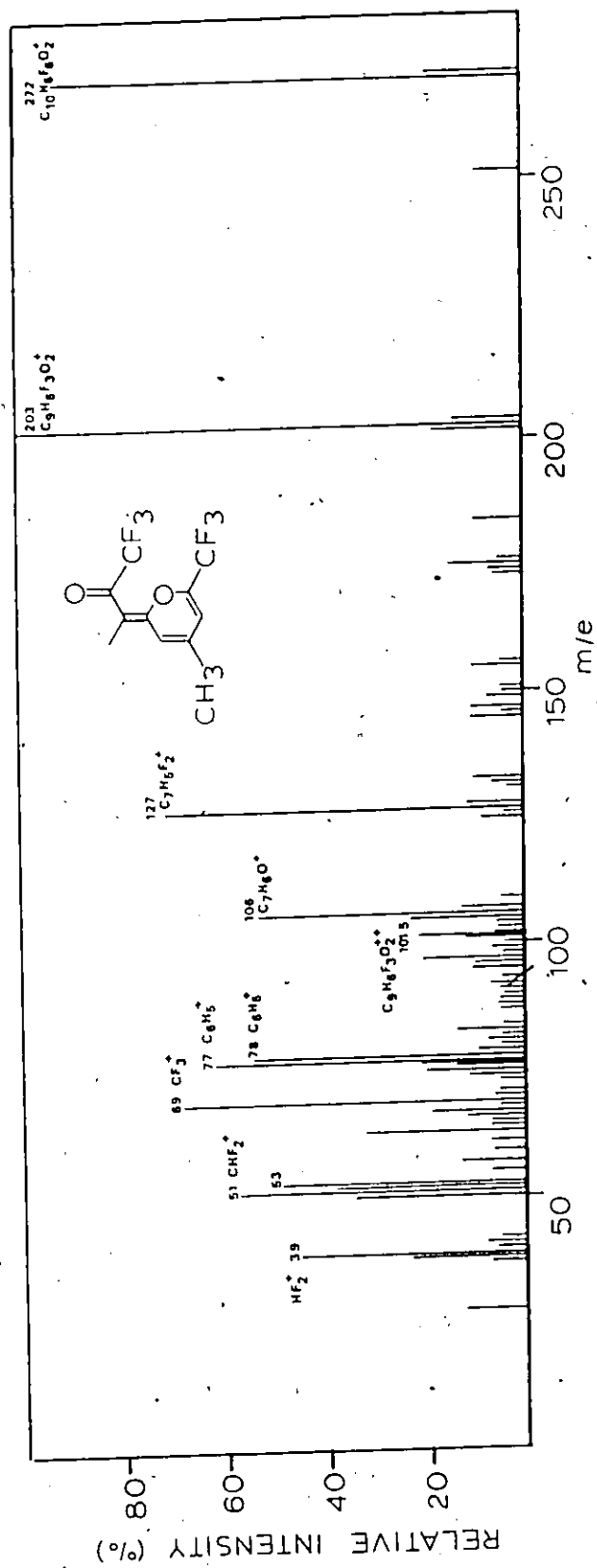
Table 32. The relative intensities of some major fragment ions of methyl pyran.

m/e (amu)	Relative Intensity (%)	Fragment
272	92.6	$C_{10}H_6F_6O_2^{+\cdot}$
203	100.	$C_9H_6F_3O_2^{+}$
127	71.1	$C_7H_5F_2^{+}$
106	52.7	$C_7H_6O^{+\cdot}$
101.5	21.2	$C_9H_6F_3O_2^{++}$
78	53.7	$C_6H_6^{+\cdot}$
77	61.5	$C_6H_5^{+}$
69	67.8	$CF_3\cdot$
50	34.0	$CF_2^{\cdot}$
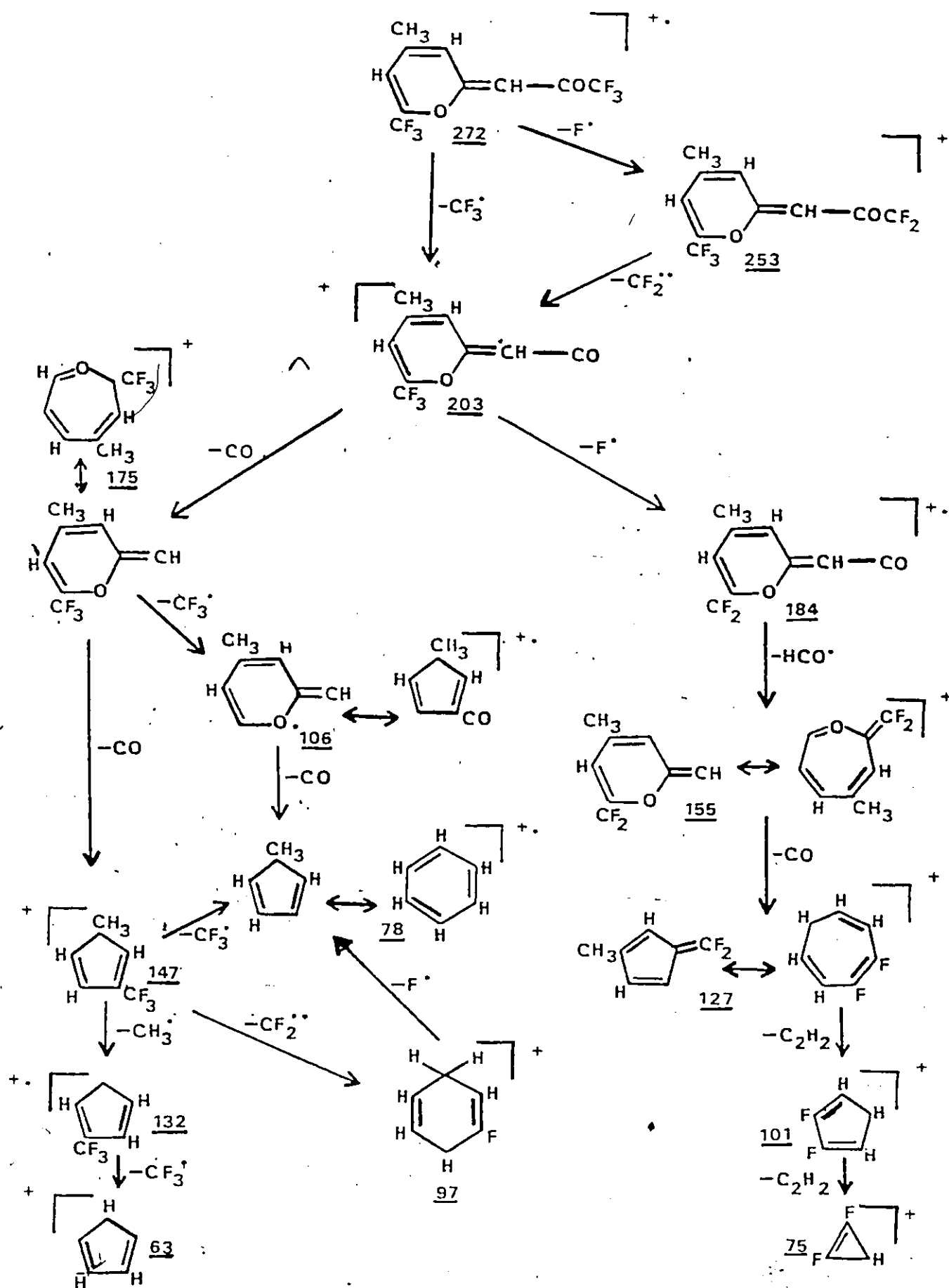
Scheme 29

give $C_6H_3F_3^{\dot{+}}$ (m/e 132) followed by loss of the trifluoromethyl group to produce the five-membered ring, $C_5H_3^+$ (m/e 63).

The second path is initiated by the loss of the fluorine radical to produce the $C_9H_6F_2O_2^{\dot{+}}$ (m/e 184) radical ion. Subsequent loss of the HCO radical followed by the loss of a CO molecule results in the $C_8H_5F_2O^+$ (m/e 155) and $C_7H_5F_2^+$ (m/e 127) ion, respectively. Loss of two C_2H_2 molecules yield the five-membered ring $C_5H_3F_2^+$ (m/e 101) and the three-membered ring, $C_3HF_2^+$ (m/e 75), respectively.

The mass spectrum of ethyl pyran is presented in Figure 25 A and the major fragment ions are listed in Table 33. A fragmentation pattern was postulated and is presented in Scheme 30. On inspection, the scheme is similar to that proposed for methyl pyran. This is expected since the two molecules are very similar. Again, the loss of a trifluoro-methyl group (m/e 69) results in the production of the ion corresponding to the base peak ion ($C_{11}H_{10}F_3O_2^{\dot{+}}$, m/e 231). Two paths are available for the base peak ion to fragment. The first path begins with the loss of a methyl radical followed by the loss of a CO molecule to produce $C_{10}H_7F_3O_2^{\dot{+}}$ (m/e 216) and $C_9H_7F_3O^{\dot{+}}$ (m/e 188), respectively. Loss of a CO molecule from the latter ion results in $C_8H_7F_3^{\dot{+}}$ (m/e 160). Subsequent fragmentation of a trifluoromethyl radical results in the tropylium ion, $C_7H_7^+$ (m/e 91). Successive losses of two C_2H_2 fragments produce the five- and three-membered rings, $C_5H_5^+$ (m/e 65) and $C_3H_3^+$ (m/e 39), respectively. Loss of $CF_3^{\dot{}}$, $CH_3^{\dot{}}$, and CO from $C_9H_7F_3O^{\dot{+}}$ result in the six-membered ring,

Figure 25. Mass spectra of ethyl pyran (A) and pentyl
pyran (B).

Table 33. The relative intensities of some major ions in the
mass spectrum.of ethyl pyran.

m/e (amu)	Relative Intensity (%)	Fragment
300	39.7	$C_{12}H_{10}F_6O_2^{+}$
231	100.	$C_{11}H_{10}F_3O_2^{+}$
149	13.4	$C_9H_9O_2^{+}$
115.5	7.0	$C_{11}H_{10}F_3O_2^{2+}$
91	17.8	$C_6H_3O^{+}$
77	14.2	$C_6H_5^{+}$
69	17.9	$CF_3^{\cdot}$

$C_6H_4^{+\cdot}$ (m/e 76). Fragmentation of a C_2H_2 molecule produces the
four-membered ring, $C_4H_2^{+\cdot}$ (m/e 50). Loss of a methyl radical
and a CO molecule from $C_9H_7F_3O^{+\cdot}$ produces $C_7H_4F_3^{+}$ (m/e 145).
Successive losses of two C_2H_2 molecules result in the five-
and three-membered rings, $C_5H_2F_3^{+}$ (m/e 119) and $C_3F_3^{+}$ (m/e 93),
respectively.

The second fragmentation path originates with the loss
of a CO molecule from $C_{11}H_{10}F_3O_2^{+}$ to produce $C_{10}H_{10}F_3O^{+}$ (m/e
203). Loss of a C_2H_4 molecule results in $C_8H_6F_3O^{+}$ (m/e 175).
Fragmentation of a CO molecule from $C_8H_6F_3O^{+}$ produces $C_7H_6F_3^{+}$
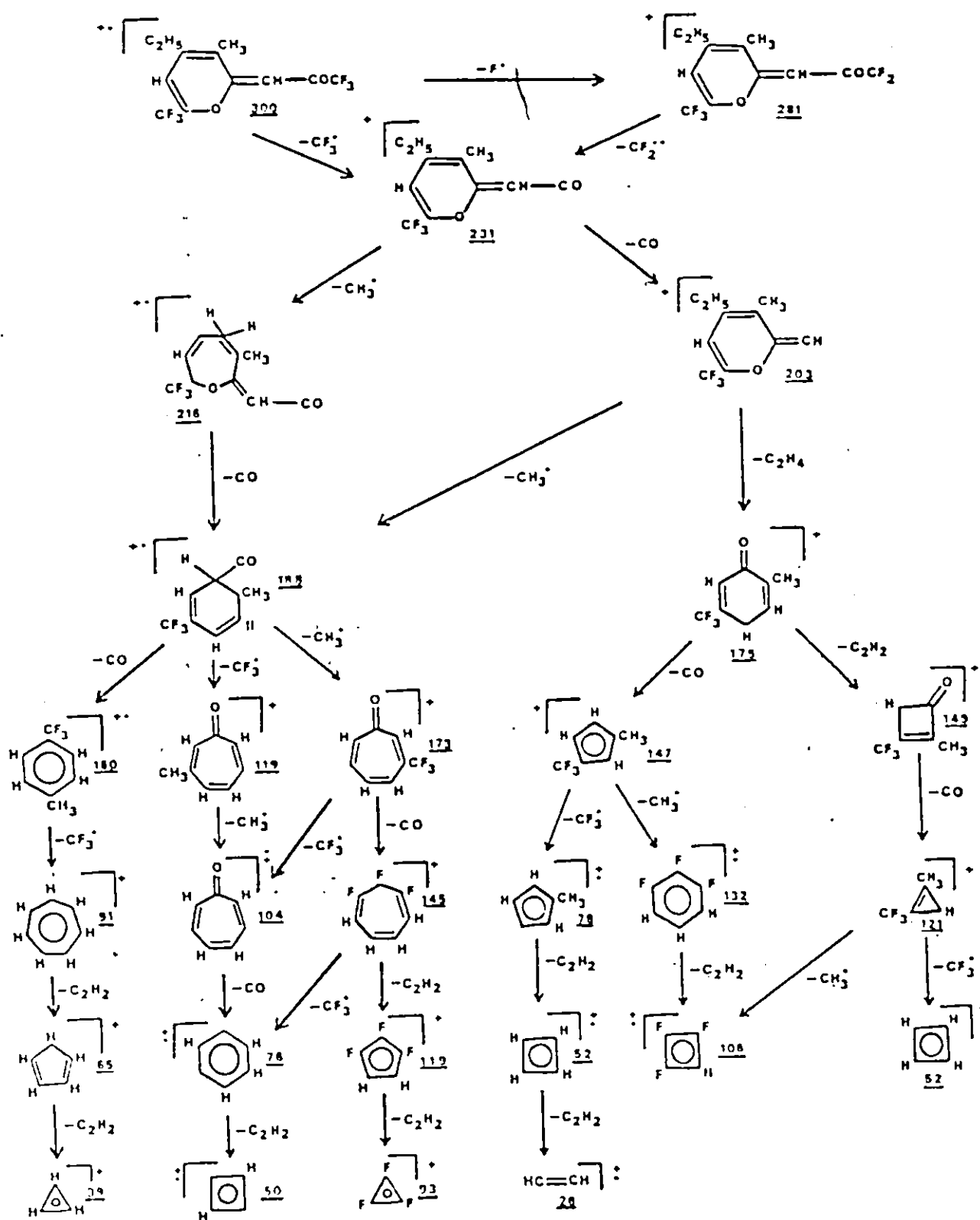
Scheme 30

(m/e 147). Loss of methyl or trifluoromethyl radicals produce $C_6H_3F_3^+$ (m/e 132) and $C_6H_6^+$ (m/e 78), respectively. Subsequent loss of two C_2H_2 molecules from $C_6H_6^+$ results in $C_4H_4^+$ (m/e 52) and $C_2H_2^+$ (m/e 26). Similarly, loss of C_2H_2 molecule from $C_6H_3F_3^+$ produces $C_4HF_3^+$ (m/e 106). Fragmentation of a C_2H_2 molecule from $C_8H_6F_3O^+$ results in $C_6H_4F_3O^+$ (m/e 149). Loss of a CO molecule produces the 3-membered ring, $C_5H_4F_3^+$ (m/e 121). Loss of a CH_3^- or CF_3^- results in the formation of $C_4HF_3^+$ (m/e 106) and $C_4H_4^+$ (m/e 52).

The last mass spectrum to be discussed is that of pentyl pyran and it is presented in Figure 25 B, and the major fragment ions are listed in Table 34. The proposed fragmentation pattern is presented in Scheme 31. The loss of a propyl group ($C_3H_7^-$, m/e 43) results in the formation of the base peak ion. This is not difficult to understand when one considers that the main process in aralkyl compounds is cleavage at the carbon alpha to the ring.[118] The propyl group on the 3-isobutyl side-chain is such a group. A surprising observation is the rather small relative intensity of the CF_3^- fragment ion (m/e 69, 16%) compared to the other pyrans studied.
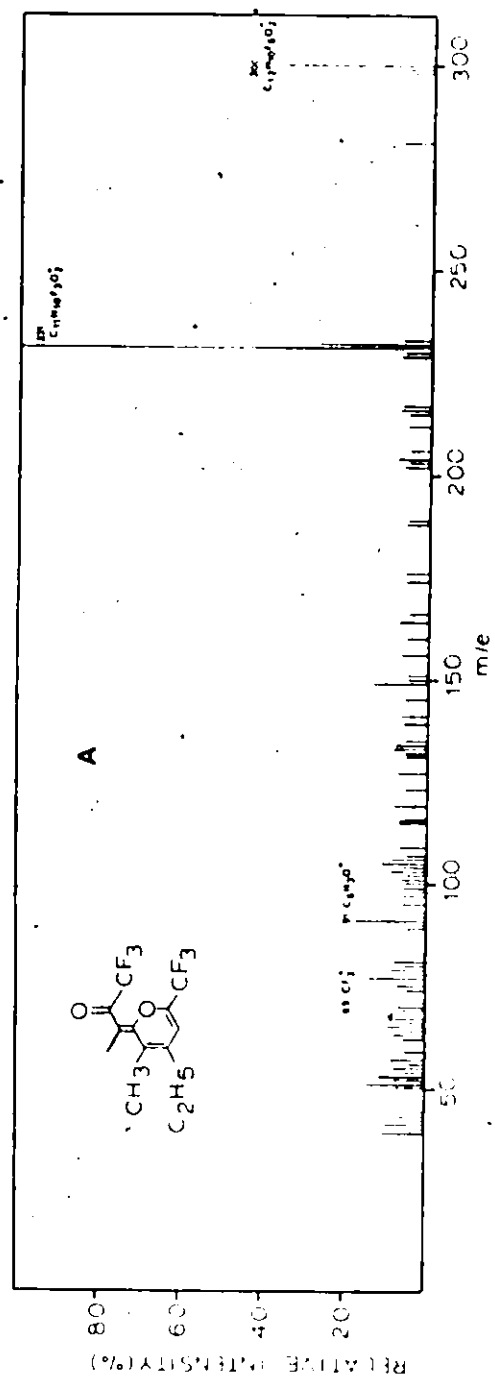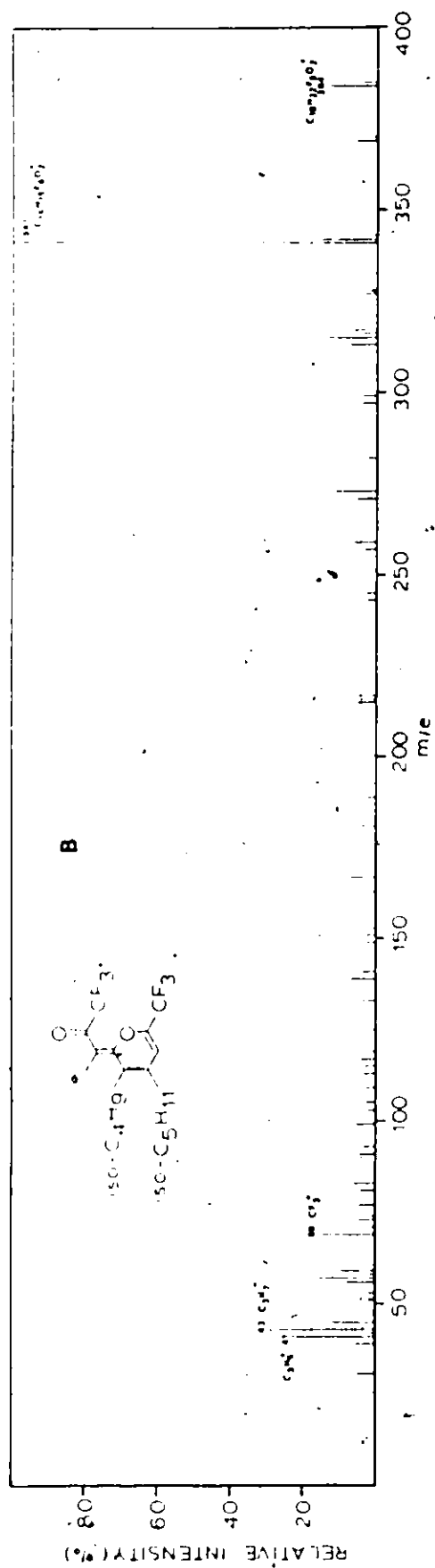
Table 34. The relative intensities of some major fragment ions in the mass spectrum of pentyl pyran.

m/e (amu)	Relative Intensity (%)	Fragment
384	13.7	$C_{18}H_{22}F_6O_2^{+\cdot}$
342	16.5	$C_{15}H_{16}F_6O_2^{+}$
341	100.	$C_{15}H_{15}F_6O_2^{+}$
315	16.4	$C_{17}H_{22}F_3O_2^{+}$
273	11.9	$C_{10}H_7F_6O_2^{+\cdot}$
69	16.3	$CF_3^{\cdot}$
43	30.1	$C_3H_7^{\cdot}$
41	23.6	$C_3H_5^{\cdot}$

III.B.7. ELECTRONIC SPECTRA OF THE PYRANS

The electronic spectra of methyl and ethyl pyran are presented in Figures 26 and 27, respectively, and the corresponding λ_{max} and ϵ_{max} are listed in Tables 35 and 36, respectively. The spectra of both compounds were recorded in methanol and in cyclohexane to assign the transitions.

$$C_{18}H_{22}F_6O_2^{+\cdot}$$

(384)

$$C_{18}H_{22}F_5O_2^+ \quad +F^\cdot$$

(365)   (19)

$$C_{17}H_{22}F_3O_2^+ \quad + CF_3^\cdot$$

(315)   (69)

$$C_{17}H_{22}F_2O_2^{+\cdot} + CF_3^\cdot$$

(296)   (69)

$$C_{16}H_{22}F_3O^+ \quad + CO$$

(287)   (28)

$$C_{16}H_{22}F_2O^{+\cdot} + CO$$

(268)   (28)

$$C_{15}H_{22}O^{+\cdot} \quad + CF_3^\cdot$$

(218)   (69)

$$C_{15}H_{21}F_2^+ \quad + CHO^\cdot$$

(239)   (29)

$-CHO$

(29)

$$C_{14}H_{21}^{+\cdot} \quad + CF_2^\cdot$$

(189)   (50)

$$C_6H_5^+ \quad + 8\ CH_2^\cdot$$

(77)   (14)

Scheme 31

Scheme 31, cont'd.

$$C_{18}H_{22}F_6O_2^{+\cdot}$$

(384)

$COCF_3^{\cdot} + C_{16}H_{22}F_3O^+$

(97)   (287)

$C_{15}H_{20}F_3O^{+\cdot} + CH_2^{\cdot}$

(273)   (14)

$C_{13}H_{20}^+ + CF_3CO^{\cdot}$

(176)   (97)

$C_{15}H_{15}F_6O_2^+ + C_3H_7^{\cdot}$

(341)   (43)

$C_{15}H_{15}F_5O_2^{+\cdot} + F^{\cdot}$

(322)   (19)

$C_{14}H_{15}F_2O_2^+ + CF_3^{\cdot}$

(253)   (69)

$C_{13}H_{15}F_2O^+ + CO$

(225)   (28)

$C_{12}H_{14}F_2^{+\cdot} + CHO^{\cdot}$

(196)   (29)

$CF_2^{\cdot} + C_{11}H_{14}^+$

(50)   (146)
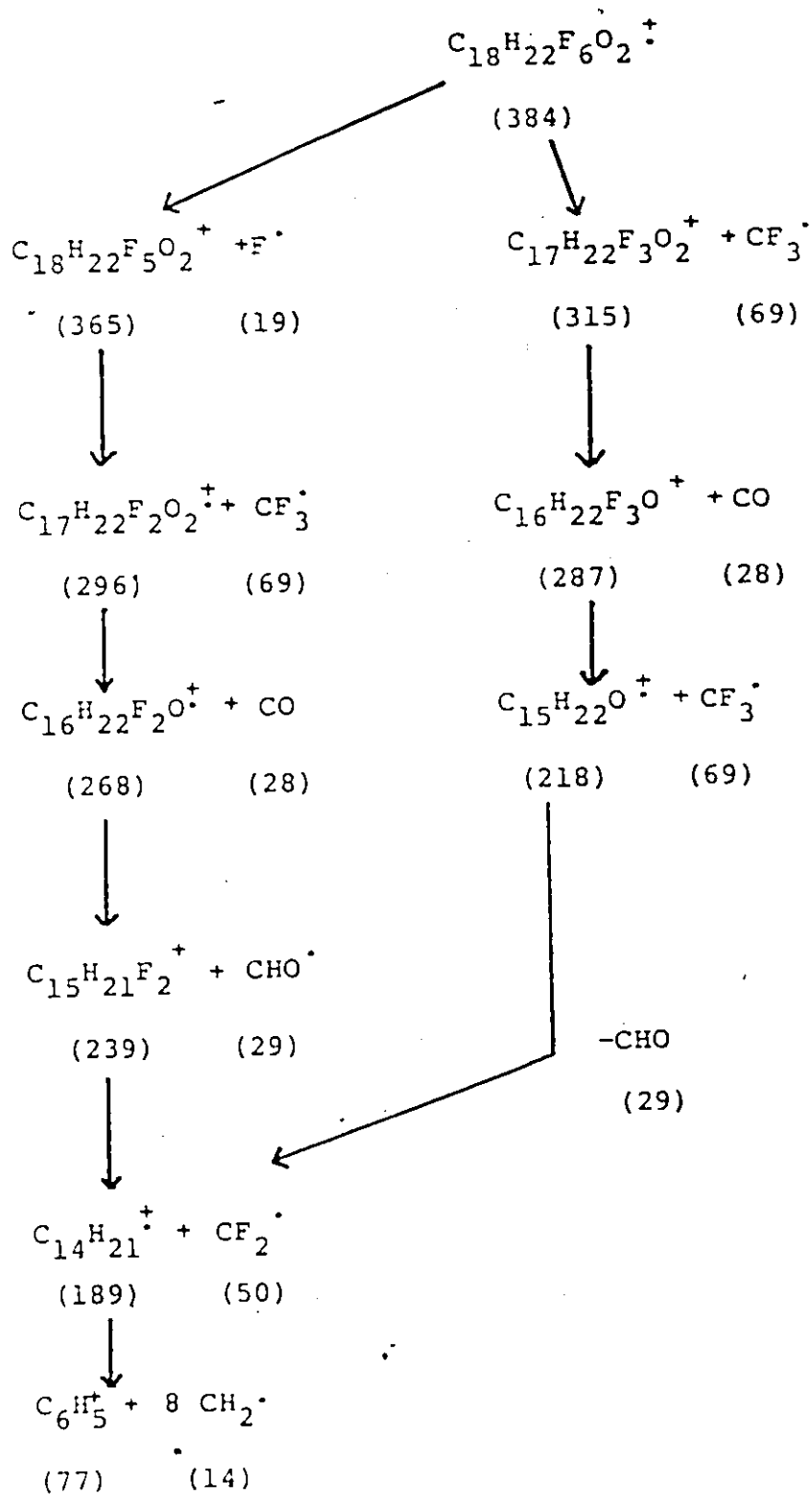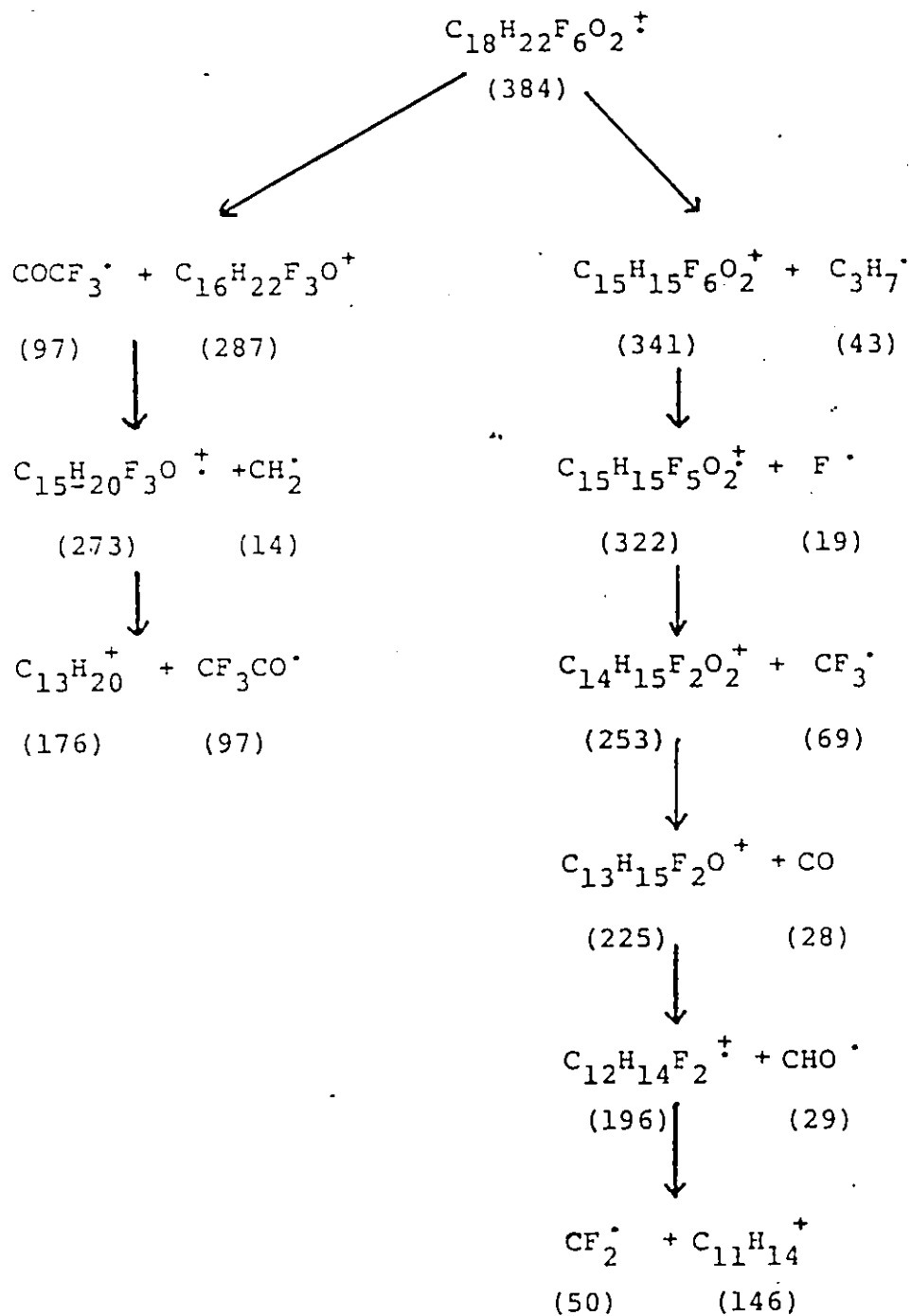
Figure 26. Absorption spectra of methyl pyran in methanol
and in cyclohexane.

209

210
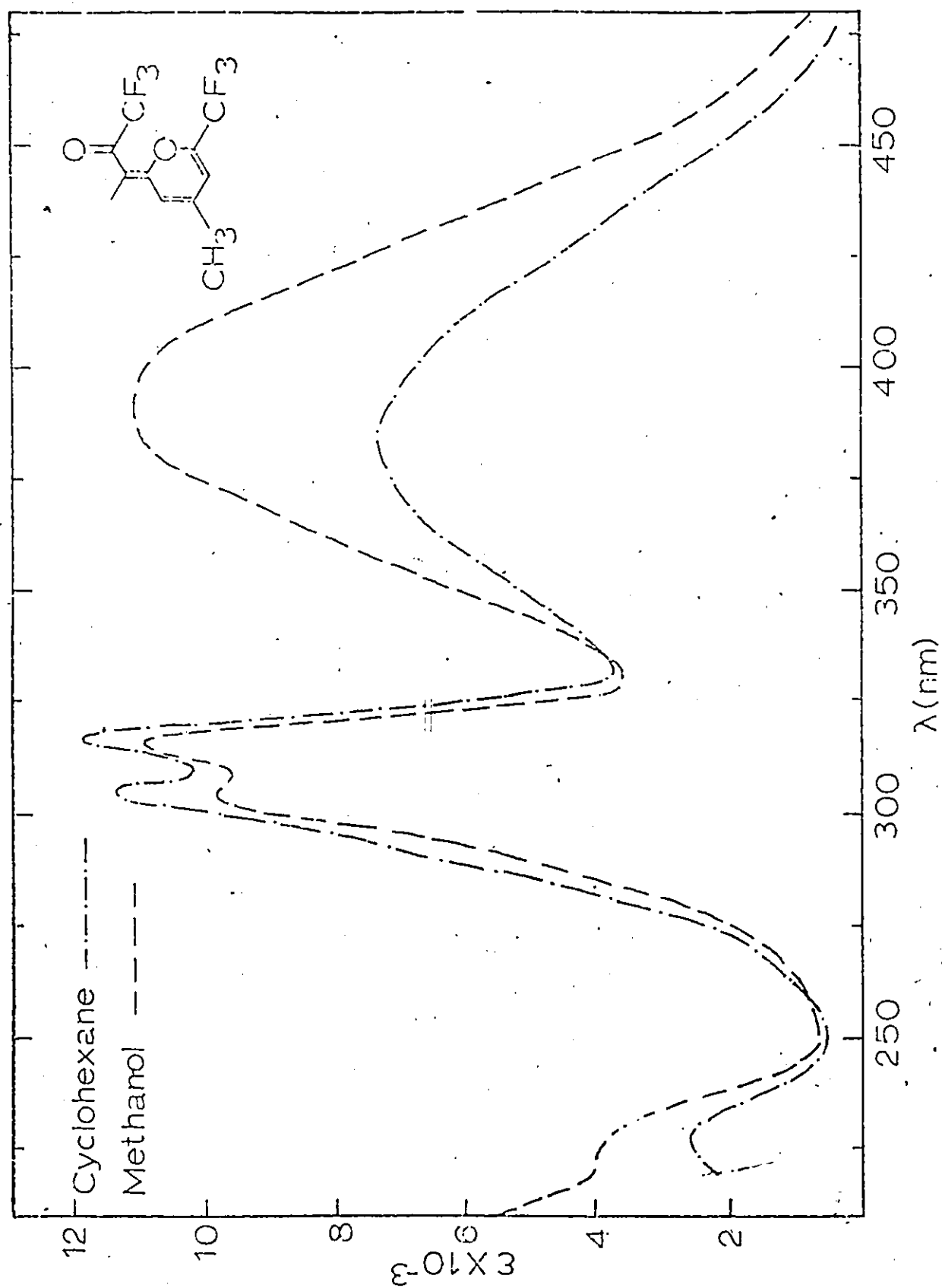
Figure 27. Absorption spectra of ethyl pyran in methanol and in cyclohexane.
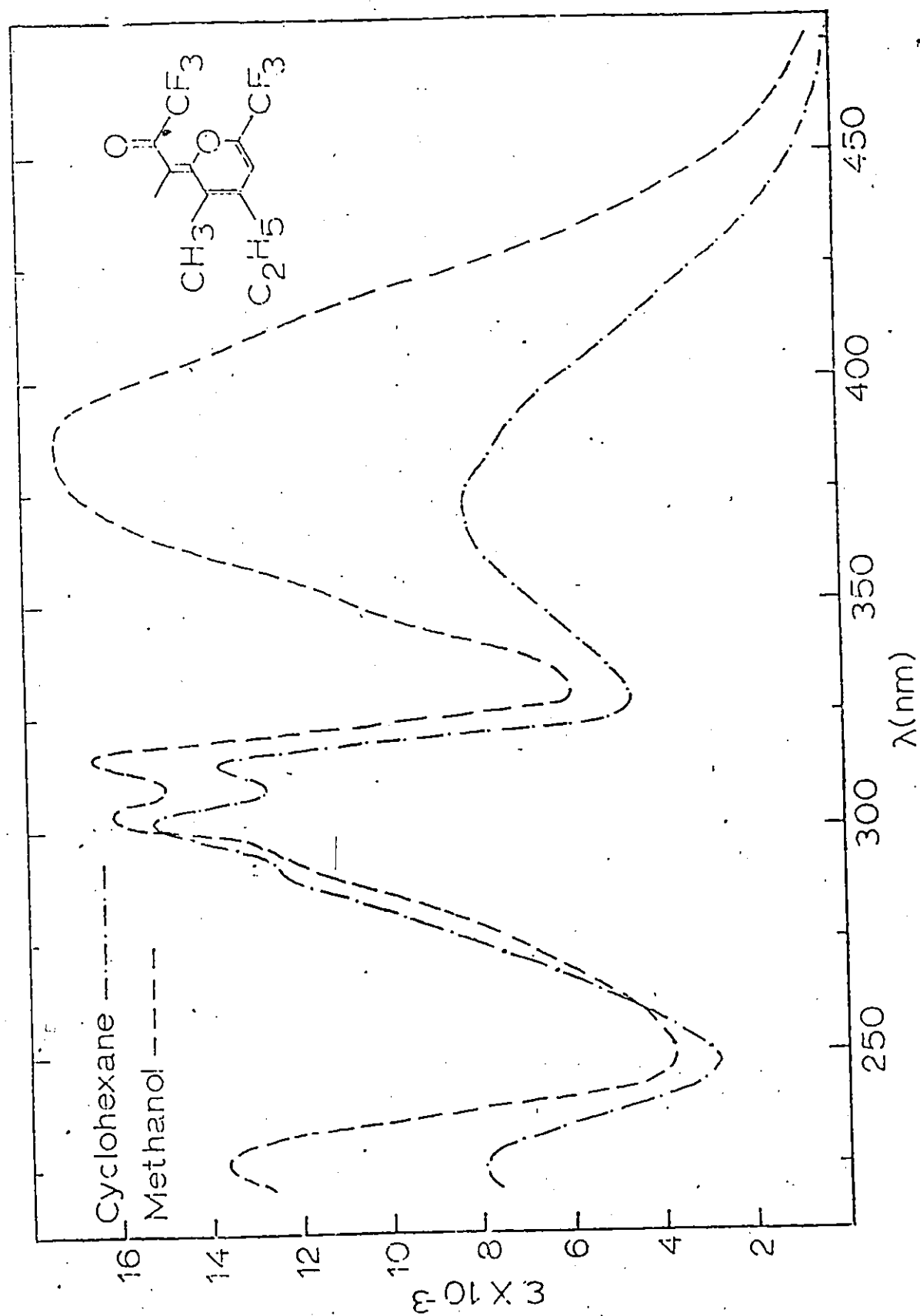
Table 35. Absorption spectra of methyl pyran in methanol and in cyclohexane.

Solvent (Concentration, $\underline{M}$)	λ_{max} (nm)	$\epsilon_{max} \times 10^{-4}$ ($M^{-1}cm^{-1}$)
Methanol (1.179×10^{-4})	221.0	0.41
	304.0	0.98
	316.0	1.10
	391	1.11
Cyclohexane (6.98×10^{-5})	227.0	0.26
	≈294 (sh)	0.77
	305.0	1.14
	317.0	1.19
	384.0	0.73
	≈411 (sh)	0.61
	≈441 (sh)	0.32

In the methyl pyran spectra, the high energy transition (221-227 nm) is shifted by 6 nm to shorter wavelength on going from cyclohexane to methanol, and this would indicate an n-π* transition. The next two bands in the ultraviolet region (305 and 317 nm) are unaffected by changes in the solvent polarity and this would indicate the bands are the

Table 36. Absorption spectra of ethyl pyran in methanol and in cyclohexane.

Solvent (Concentration, $\underline{M}$)	λ_{max} (nm)	$\varepsilon_{max} \times 10^{-4}$ ($M^{-1}cm^{-1}$)
Methanol	226.0	1.36
(5.995×10^{-5}).	≈ 290 (sh)	1.14
	304.0	1.61
	315.0	1.66
	≈ 350 (sh)	1.07
	390.0	1.72
	≈ 421 (sh)	1.01
Cyclohexane	224.0	0.79
(6.33×10^{-5})	≈ 292 (sh)	1.25
	303.0	1.52
	316.0	1.33
	≈ 346 (sh)	0.57
	370.0	0.82
	≈ 386 (sh)	0.76
	≈ 414 (sh)	0.44

result of $\pi-\pi^*$ transitions. A shift to longer wavelength is observed in the visible region band on going from cyclohexane to methanol (384 and 391 nm, respectively). This is indicative of $\pi-\pi^*$ transition.

A similar argument was used to assign the transitions of ethyl pyran. Thus, the bands in the ultraviolet region (224-316 nm) undergo a red shift or no observable shift on going from cyclohexane to methanol solvents, and thus these bands are assigned to $\pi-\pi^*$ transitions. The absorption bands in the visible region (<u>ca</u>. 350-420 nm) appear to consist of several bands, superimposed. Thus, assignment of this region is difficult.

In comparing the intensity of the bands in the spectra of the two pyrans in methanol and in cyclohexane, the largest difference lies in the bands at the high (<u>ca</u>. 225 nm) and the low energy (<u>ca</u>. 410 nm) end of the spectrum. Solvent stabilization of the excited state (n-π^*) of the pyran results in the greater intensity of the high energy band (<u>ca</u>. 225 nm) in the polar solvent, methanol. Thus, the large intensity increase in the low energy band (<u>ca</u>. 410 nm) would indicate the presence of n-π^* transition.

III.C. REACTION PATH FOR THE FORMATION OF THE PYRANS AND

    THE PYRYLIUM SALTS

    The reaction path proposed for the formation of the

pyrylium salts is presented in Scheme 32. Nucleophilic

displacement of the halide from the silicon atom by 2,4-

pentanedione (or 2,4-pentanedionato) to yield the tetravalent

silane containing two unidentate 2,4-pentanedionato ligands

is a well known reaction.[70] A proton from the terminal methyl

group is abstracted by the 2,4-pentanedionato anion to give

the resonance-stabilized anion (III). Abstraction from the

other less acidic and unstabilizable methyl group is highly

improbable. An Aldol condensation[123] between the terminal

methylene anion and carbonyl group produces the ten-membered

hetero-ring (IV). Subsequent attack by the $-O^-$ on the

organohalosilane (R_2SiCl_2) generates the siloxy group, which

is a good leaving group.[150] Abstraction of a proton from the

most acidic site to generate an enolizable carbanion results

in the expulsion of the siloxide group[150] (VII). A nucleo-

philic attack at Si by Y (where Y is 2,4-pentanedionato or

R_2SiX-O^-) with migration of $-O^-$ to the carbonyl carbon, to

bring about cyclization to the desired ring. Attack by $-O^-$

on Si to displace $-O^-$, followed by the subsequent loss of

the siloxide, produces the pyran (X). Protonation by HX

produces the desired pyrylium salts.

    The pyran, synthesized by reacting trifluoromethyl-

2,4-pentanedione with $SiCl_4$, would follow the same reaction

path (CF$_3$ groups replace the circled CH$_3$ groups), with the exception of step (X) to (XI). Protonation would be inhibited because of the large electron withdrawing power of the tri-fluoromethyl group.[140] This effect would remove electron density from the carbonyl oxygen producing a more acidic centre.
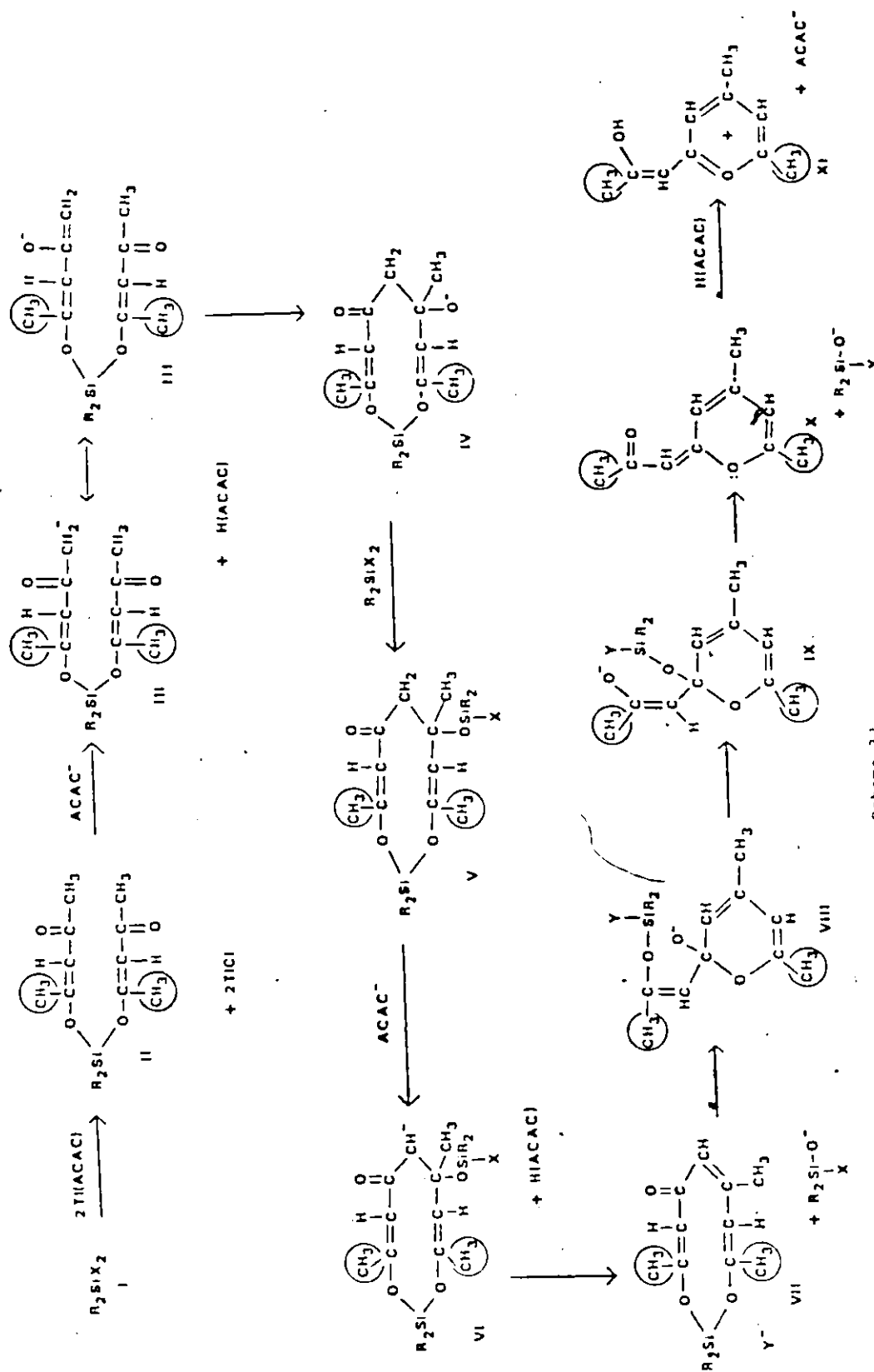
Scheme 12

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V. APPENDICES

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V.A. pH TITRATION CURVES OF PYRYLIUM CHLORIDE AND SODIUM HYDROXIDE

A summary of the data required for the determination of the pK_a of pyrylium chloride _via_ the titration method is presented in Table 37.

Table 37. pH titration data for the determination of the pK_a of pyrylium chloride.

Curve	HA ($\underline{M}$)	NaOH ($\underline{N}$)	Equivalence Volume (ml)	Equivalence Point pH	pK_a
1	0.0984	0.1113	22.20	7.64	2.80
2	0.0984	0.1113	22.58	7.84	3.15
3	0.0516	0.1064	24.63	7.90	3.24
4	0.0526	0.1064	25.07	8.98	5.39
	0.0489	0:1064	23.40	9.27	5.99

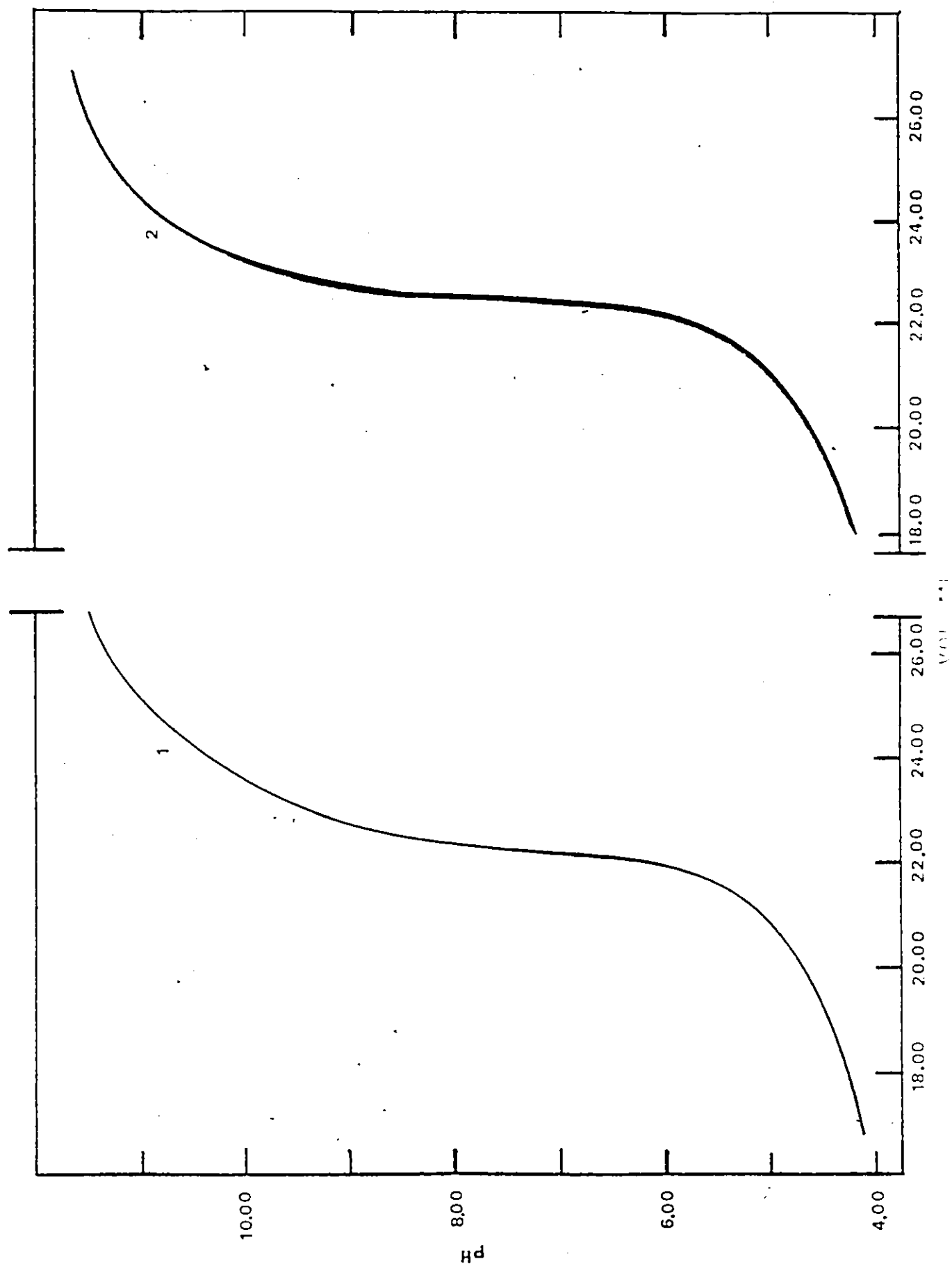Figure 28. pH titration curves (1) and (2) of pyrylium chloride and sodium hydroxide.
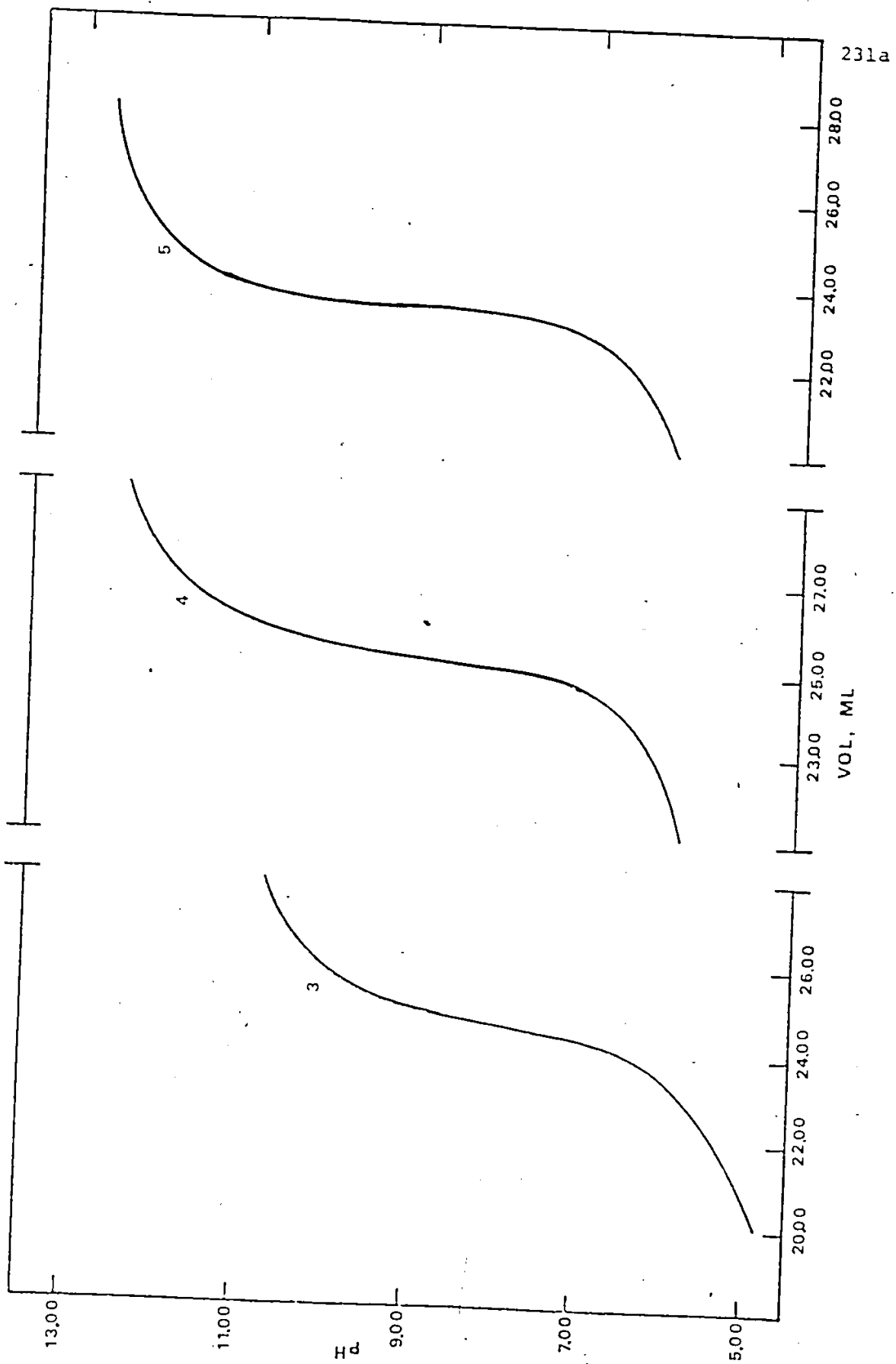
Figure 29. pH titration curves (3), (4) and (5) of pyrylium
chloride and sodium hydroxide.

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V.B. ABBREVIATIONS OF CHEMICALS USED IN THIS WORK

acac	2,4-pentanedionate anion
Hacac	2,4-pentanedione
pyrylium chloride	2,4-dimethyl-6-(2'-hydroxy-1'-propenyl) pyrylium chloride
methyl pyran	6-trifluoromethyl-4-methyl-2-trifluoro-acetyl-pyranylidene
ethyl pyran	6-trifluoromethyl-4-ethyl-3-methyl-2-trifluoroacetyl-pyranylidene
pentyl pyran	6-trifluoromethyl-4-isopentyl-3-isobutyl-2-trifluoroacetyl-pyranylidene
bzac	benzoylacetonate anion
Hbzac	benzoylacetone