Photochemical and Thermal
Interconversions of Protonated
Phenols and Bicyclo[3.1.0]hexenones.

By

© Baha Edward George, M.Sc.

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Doctor of Philosopy

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PROTONATED PHENOL/BICYCLO[3.1.0]
HEXENONE INTERCONVERSIONS

This Thesis is Dedicated To

Elham

Who, by her example and the encouragement
of a loving wife gave me the direction
and to my daughters
Nadine and Noor
who didn't request it,
but for whom it was written.

DOCTOR OF PHILOSOPY

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ABSTRACT

The work described in this thesis involves a quantitative study of the photoisomerizations of a series of protonated phenols and the reverse, thermally induced ring opening reactions of protonated bicyclo[3.1.0]hexenones. In the first chapter the importance of these reactions is established in terms of their potential use in photochemical latent heat solar energy storage systems.

The second and third chapters consist of the results and discussion of this present work. In the first place the protonation of polymethyl and chlorophenols in CF_3SO_3H (room temperature) and FSO_3H (low temperature) have been investigated using ^1H NMR and UV spectroscopy. Apart from 2,3,4,5-tetramethylphenol protonation at C_4 was observed for all methylphenols in CF_3SO_3H. In the case of 2,3,4,5-tetramethylphenol, both C_4 (95%) and C_6 (5%) protonation was observed. With 2-chloro- and 3,5-dichlorophenols <u>85</u> and <u>87</u> in FSO_3H O- and C_4-protonation was observed.

One difference in this work to that previously reported is the use of CF_3SO_3H as a strong acid medium. Overall, the same cations were produced in CF_3SO_3H as in FSO_3H. However, in certain cases there were some differences noted in the ^1H NMR spectra of these ions as compared to those obtained at low temperature in FSO_3H. These differences are

discussed in terms of an exchange of the ring protons of some of these protonated phenols with CF_3SO_3H.

The photochemical reactions of the C_4 protonated phenols in strong acid media (i.e. CF_3SO_3H and FSO_3H) have been examined. Most of these protonated phenols were found to undergo clean photoisomerizations to give protonated bicyclo[3.1.0]hexenones. Neutralization of the irradiated acid solutions gave substituted bicyclo[3.1.0]hexenones.

The quantum yields for the photoisomerizations of a number of protonated phenols to the bicyclo[3.1.0]hexenones were measured in CF_3SO_3H. It was found that substituents have a profound influence upon the efficiency of these reactions. Methyl groups in the two ortho positions were found to increase the efficiency of the reaction, while methyl substituents in the meta position were found to reduce the efficiency dramatically. This substituent effect can be understood in terms of a two step mechanism with the initially formed intermediate undergoes competitive thermal reactions. The relative rate of these two processes would seem to depend on the positioning of the methyl substituents.

A quantitative investigation of the ground state isomerizations of a series of methyl substitued bicyclo[3.1.0]hexenones in CF_3SO_3H was also undertaken. In every case the protonated bicyclo[3.1.0]hexenones isomerized to give a protonated phenol. The activation energies for these processes were sufficiently high in several instances to necessitate heating the solutions to 100°C for several hours in order for

the reaction to be completed. An analysis of the products of these reactions showed that the ring opening could take place by three different mechanisms. The factors which determine the preferred isomerization route are discussed in the thesis.

In the concluding part of the thesis the quantitative results found in this work for the protonated methyl substituted phenol/bicyclo[3.1.0]hexenone interconversion are discussed in terms of their use for solar energy storage.

CHAPTER 1

INTRODUCTION

Photochemical Conversion and Storage of Solar Energy

Recently, and especially since the "energy crisis" of the mid 1970's, efforts have been made to decrease the dependence of the Western World on the more conventional sources of energy. With the realization that our reserves of nonrenewable fossil fuels could run out within the next 100 years,[1] alternative and preferably renewable energy sources must be found. Solar energy is one such source and the use of solar energy has been receiving very serious attention by many industrialized nations.

Solar energy is an immense energy resource. Each year the earth receives about 3×10^{24} J from the sun. In contrast, the estimated proven reserves of oil, natural gas, coal, and uranium represent only about 2.5×10^{22} J, or about 1/2 week of the total solar input.[2]

While the sun is an immense energy source, solar energy has two major drawbacks - it is intermittent and diffuse. The first limitation requires some form of a storage system to be provided so that the energy can be made available when it is needed. The second draw back means that collecting devices must cover very large areas. Both of these factors place severe but not impossible economic constraints on solar energy systems.

Nature has solved both of these problems and stores solar energy through photosynthesis. It is estimated that each year about 5×10^{10} tonnes of carbon are fixed through photosynthesis.[3] This, while large, represents a storage of only 0.04% of the world's annual solar input and there is considerable scope for other ways of capturing the sun's energy.

A variety of non biological methods of storing solar energy have been suggested.[4] One such system, which provided the motivation for this work, involves the use of sunlight to induce photochemical reactions to generate storable products of high energy content that are reconvertible at will to the original material with the release of this stored energy.

Such a photochemical energy storage cycle is shown schematically in Figure 1. The absorption of a photon of energy E_{ex} excites a reactant R to the photoreactive state R^*, which then is converted to product P. If the overall free energy change associated with this process is ΔG, then $\Delta G/E_{ex}$ represents that fraction of the incident photon which is converted to and stored as the increased chemical potential energy of P as compared to R. Reversion of the system to the initial material occurs with the release of this stored energy, generally in the form of heat. The reverse step must be slow at ambient temperature, requiring the presence of a kinetic barrier, $\Delta G^{\dagger}$, which must be surmounted in reaching the transition state, T. This feature ensures that energy can be stored indefinitely and is released only at elevated temperatures or upon the addition of an appropriate catalyst. Overall the changes can be summarized as shown in equations 1 and 2.

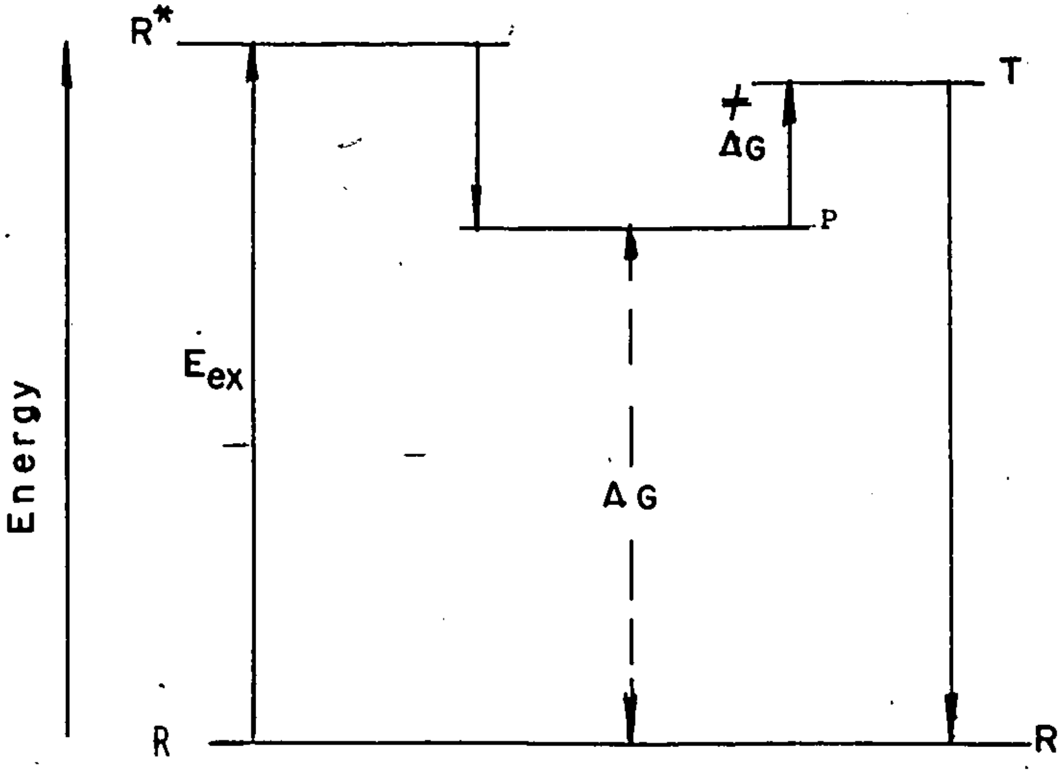


Figure 1. Schematic Photochemical Latent Heat Energy Storage Cycle

Energy storage $$R \xrightarrow{h\nu} R^{*} \longrightarrow P \tag{1}$$

Energy release $$P \xrightarrow[\text{catalyst}]{\Delta} R + \text{heat} \tag{2}$$

The net effect of cycling the energy storage-energy release steps is to convert sunlight to a storable and thus usable form without consuming nonrenewable resources.

General Requirements for an Efficient Energy Storage System

Many authors have considered the general requirements for useful photochemical solar conversion and storage reactions.[5-10] In summary they are:

1. The photochemical reaction must be endothermic.
2. The process must be cyclic.
3. Side reactions leading to the irreversible degradation of the photochemical reactants must be totally absent.
4. The starting material but not product must be able to absorb visible light.
5. The quantum yield for the photochemical reaction must be high.
6. The back reaction must be extremely slow under ambient conditions to permit long-term storage, but should proceed rapidly under specially controlled catalytic conditions or at elevated temperatures.
7. The product(s) of the photochemical reaction should be easy to store and transport.
8. The system must be as cheap as possible.

At present the only photochemical storage system that meets most of the above requirements is photosynthesis. In addition, there are several possible systems that have the potential to satisfy most of the requirements. These are considered in detail in the next section.[11-16]

Examples of Thermally Reversible Endothermic Photoreactions

An example of an inorganic system which has been studied in terms of the storage of solar energy is shown in equation 3.[11]

$$NOCl \xrightarrow[\Delta]{h\nu} NO + 1/2Cl_2 \qquad (3)$$

Nitrosyl chloride is highly colored and is photochemically active over much of the visible region of the solar spectrum. The quantum yield for decomposition in solution is high ($\phi = 0.7 - 1.1$). The storage enthalpy (i.e., the difference in the molar standard enthalpies of the ground states of reactants and products) is relatively low ($-\Delta H = 9.0$ kcal/mole).

The major drawback of this system is the ease of the back reaction. The colorless nitric oxide and chlorine products readily combine to reform NOCl and to this point no suitable means of separating the photoproducts prior to their recombination exists. The ease of this reverse reaction prohibits the use of NOCl in a photochemical/latent heat storage system.

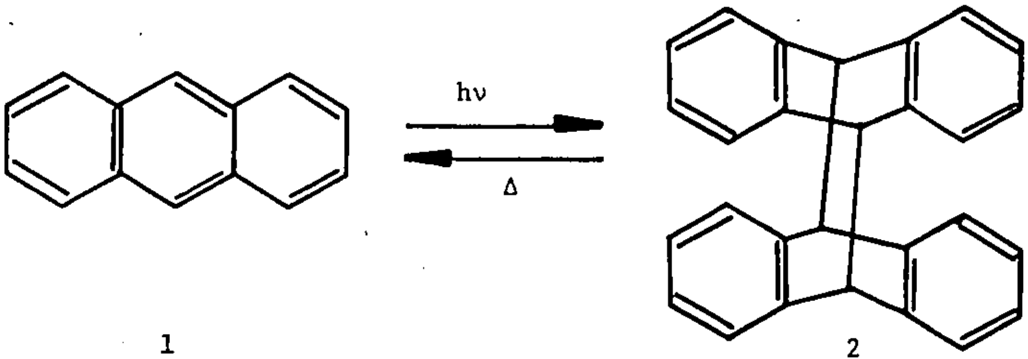
Another reaction that has been examined for its use in solar energy storage is shown in equation 4.[12]

$$FeBr^{2+} \longrightarrow Fe^{2+} + 1/2Br_2 \tag{4}$$

Ferric bromide again absorbs in the visible region and in this case the reaction has the advantage that the Br_2 can be easily removed from solution in a stream of nitrogen. It suffers, however, from a very low quantum yield (ϕ = 0.01 - 0.02).

Some of the most promising candidates for this type of reversible solar energy storage are the isomerizations of organic molecules. A blend of factors enables organic materials to store electronic excitation energy efficiently. The energy storage feature of these reactions often arises from excessive "strain" or loss of resonance energy in the product molecule.[17,18] In addition, orbital topology or symmetry constraints[19] often result in substantial kinetic barriers to the thermal reversion of the photoproducts to the starting material. The energy rich photoproducts can then withstand a substantial thermodynamic driving force for the back reactions.

Although no organic photochemical/latent heat storage system which makes efficient use of solar energy is yet known, a number of prototypes have been examined. For example, the photodimerization of anthracene, equation 5, is one such case.[20] Anthracene and its



(5)

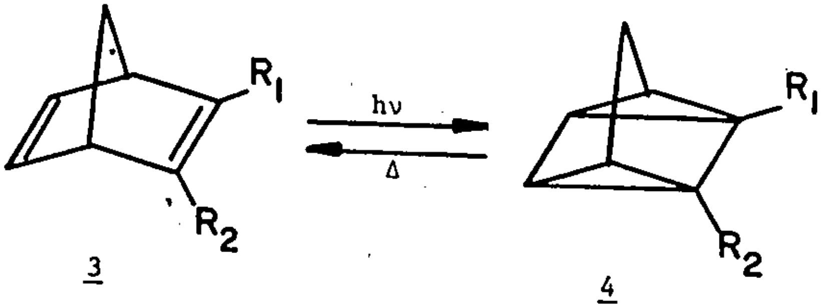
1

2

derivatives dimerize on irradiation with light of wavelengths up to 400 nm. The quantum efficiency for photodimerization is concentration dependent, approaching 0.3 at high anthracene concentrations.[21-23] The dimer 2 reverts to 1 on heating to 220 - 250°C. The difference in energy between 1 and 2 ($-\Delta H$ = 15.6 kcal/mole)[24] is caused not only by the loss of resonance energy[25] in 2 but also by repulsive interactions between the eclipsed benzene rings.[26]

Overall this photodimerization is not being seriously considered for use as a photo latent heat storage system for two reasons. First, the high temperature required for the photodimer to revert thermally to monomer anthracene and second, the relatively low storage potential of this reaction make it impractical.

The photoisomerization of norbornadiene 3 ($R_1 = R_2 = H$) to quadricyclane 4 is a further potentially attractive system which has received a great deal of attention.[13,27] Since norbornadiene itself 3



(6)

($R_1 = R_2 = H$), does not absorb solar radiation (> 300 nm) the use of either an appropriate sensitizer or the introduction of substituents is required to realize a facile isomerization in sunlight. High quantum efficiencies for direct[28] and sensitized[27,29] photoisomerizations of norbornadiene derivatives have been reported. The energy rich products are thermally stable at ca. 150°C,[30] and the reverse isomerizations can be catalysed using a variety of metal catalysts over a range of temperatures.[31]

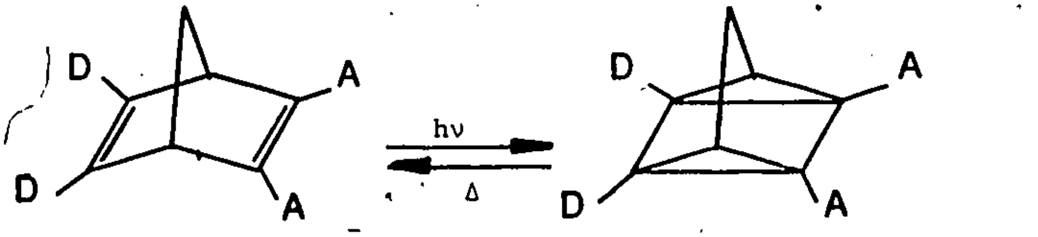
Several different substituted norbornadienes and a variety of sensitizers have been examined. Some of these are summarized in Table 1.1.

TABLE 1.1. Isomerization of Norbornadienes

Substituent	Sensitizing Agent	Absorption Edge (nm)	Φ	$-\Delta H$ (kcal/mole)	Ref.
3 → 4 [R_1=R_2=H]	PhCOPh	420	0.70^a	26.7	32
	$[CuCl]_2$	330	0.40^b		
	$Cu(PPH_3)_2BH_4$	330	0.20^b		
3 → 4 [R_1=R_2=CO_2Me]	c	320	0.50^b	18.5	28b,33
3 → 4 [R_1=C_6H_5,R_2=CO_2Me]	d	360	0.60	23	28b,5a

a) Measured at 400 nm.
b) Measured at 313 nm.
c) Direct irradiation.
d) Direct irradiation at 334 nm.

Recently Z. Yoshida et al. have suggested that norbornadienes with donor-acceptor (DA) substituents are good candidates for molecular energy storage systems,[34-37] equation 7. The absorption spectra of a DA



(7)

norbornadiene can be shifted to longer wavelengths by increasing the electron donating nature of the donor (D) part and the electron-withdrawing nature of the acceptor (A) part, as is shown in Table 1.2.

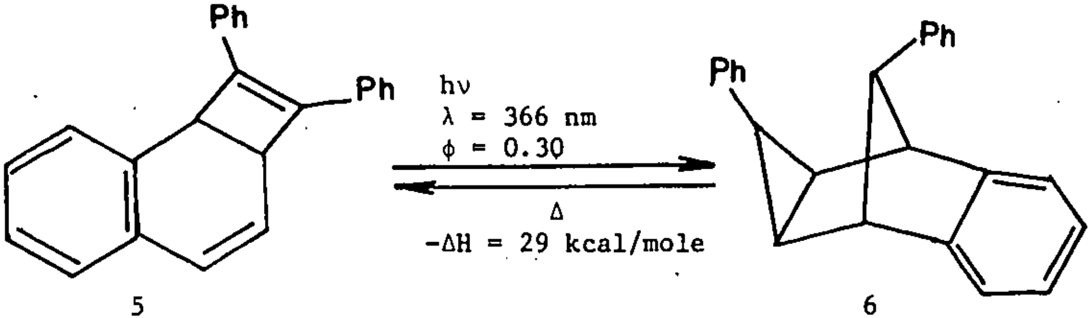
TABLE 1.2. Isomerization of DA Norbornadienes

Substituent	λ nm	Φ^a	$-\Delta H$ kcal/mole
D = H, A = CN	300	0.59	
D = Me, A = CO_2Me	300	0.87	19.0
D = Me, A = CN	350	0.96	21.0
D = P-$MeOC_6H_4$, A = CO_2Me	380		
D = P-$MeOC_6H_4$, A = CN	450		

a = direct irradiation at 313 nm.

This new approach of using DA norbornadienes would seem to be attractive in terms of developing a reversible photolatent heat storage system. One major drawback is the relatively high molecular weight of the materials as this will inevitably result in a system with low storage capacity on a weight basis.

A variety of other organic materials have been examined in terms of solar energy storage. Some examples are shown in the following three equations.



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Ref.

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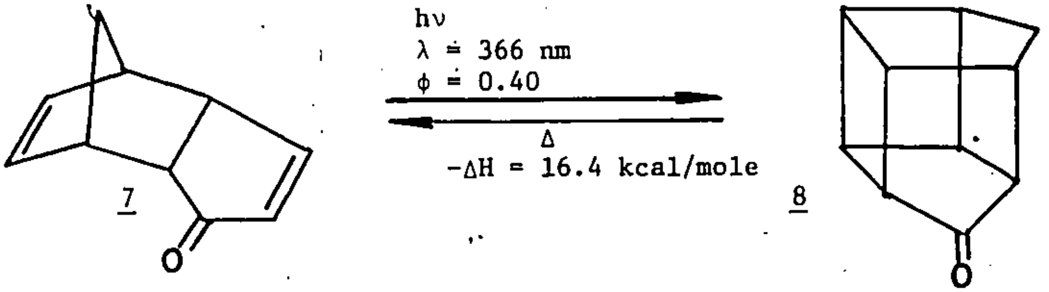

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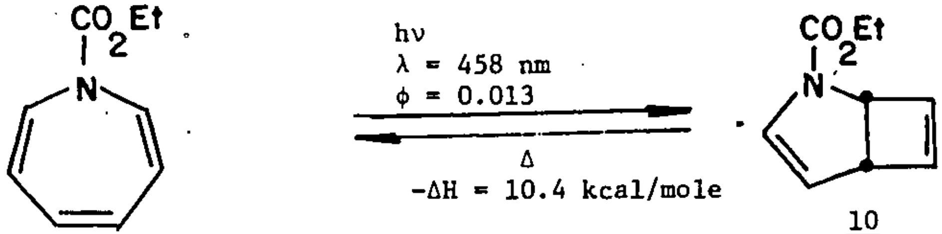


9 10

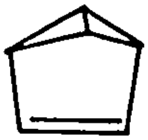
40 (10)

The Potential Use of Benzenoid Compounds as Storage Systems

None of the above mentioned candidates for a photochemical/latent heat storage system is ideal or indeed can be used in a practical storage device, and thus there is still a need to investigate different systems. Aromatic compounds offer some attractive possibilities in as much as the simple hydrocarbons are cheap and readily available, they can be converted to their valence isomers on irradiation and, these valence isomers are much less stable than the starting aromatic compounds.

The irradiation of benzene and its derivatives leads to the formation of the valence isomers, Dewar benzene 11, benzvalene 12, prismane 13, and fulvene 14.[41] These valence isomers are not always detected directly as they can revert to the arenes, however they are suspected because of the transposition of the ring carbons of the aromatic ring.[42] The effect of phase, wave- length, temperature, and substitution on the formation of the various isomers has been examined[43,44] and will be summarized here.

11



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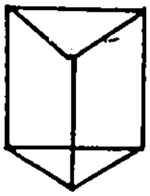

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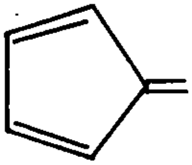


14

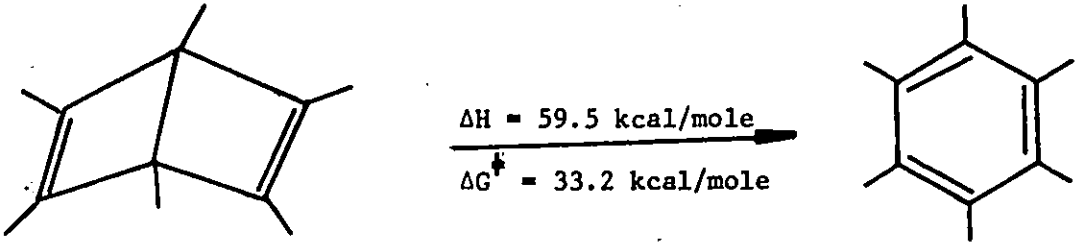
Irradiation of benzene as a liquid with light of 254 nm results in a mixture of fulvene 14[45,46] and benzvalene 12[47,48] but no Dewar-benzene. The quantum yields for these conversions are in the range 0.01 - 0.03. The formation of both 12 and 14 from benzene is promoted by an increase of temperature, and between 50 and 60°C, limiting concentrations of each isomer are obtained. This temperature dependence of the formation of both 12 and 14 in the liquid phase suggests the need for thermal activation of a thermal reaction following photoexcitation.[47,49]

Irradiation of liquid benzene at shorter wavelengths (165-200 nm) gives Dewarbenzene 11, benzvalene 12, and fulvene 14, in the ratio 1:2:5.[50] While substituted prismanes have been produced by the irradiation[50] of benzene derivatives, the light-induced formation of 13 has not as yet been reported. As 13 has not yet been prepared by any route, its lack of formation upon irradiation of benzene may simply be due to its thermal instability.[51]

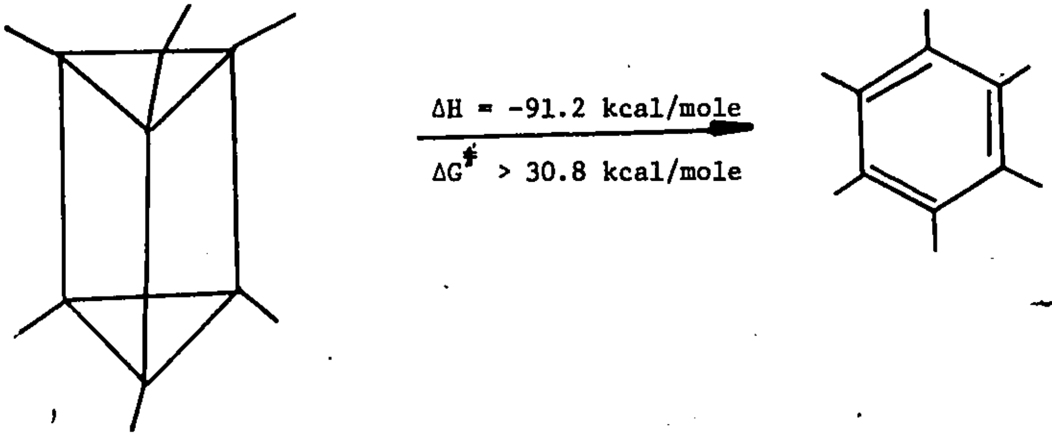
The photoisomerization reactions of benzene are complicated by the high reactivities of the products. The three valence isomers, 11, 12 and 14 are kinetically stable at room temperature but their reversion to benzene can be easily achieved with a variety of catalysts or photochemically.[52]

The tri-t-butylbenzenes are the most studied examples of the photoisomerization of substituted benzene derivatives. Prismane, benzvalene and Dewar isomers are formed.[53] The t-butyl groups render the photoproducts more stable kinetically than the unsubstituted materials, and this has enabled the interconversions to be studied in some detail.

The reversion of the various benzene valence isomers produced in these photochemical reactions to the parent hydrocarbon are symmetry forbidden in the ground state.[54,55] However, many of these reactions can occur thermally as is shown in equations 11 and 12.[56-58]



(11)



(12)

The surprisingly low barriers to these thermal reactions are due in no small measure to the very large exothermicities of the reactions. The valence isomers are highly strained and lack the aromatic resonance energy of the benzenoid products.

There have been no direct measurements of the heats of isomerization of the parent isomers 11, 12 and 14 to benzene, however, Stein et al. have esimated these.[59] (See Figure 2). It is clear from the magnitudies of the energy differences between the various valence isomers and the parent benzenoid systems that in principle these photoisomerizations represent a potentially attractive photochemical/latent heat storage system.

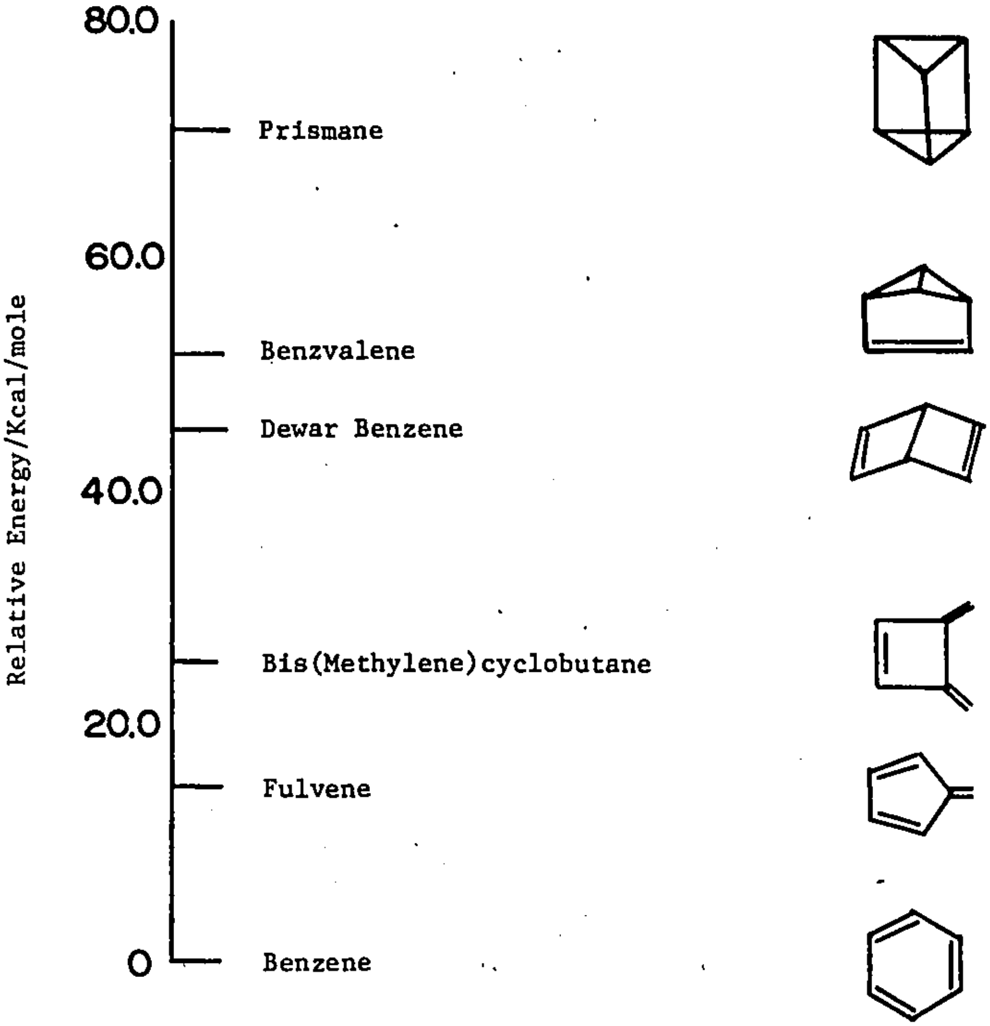
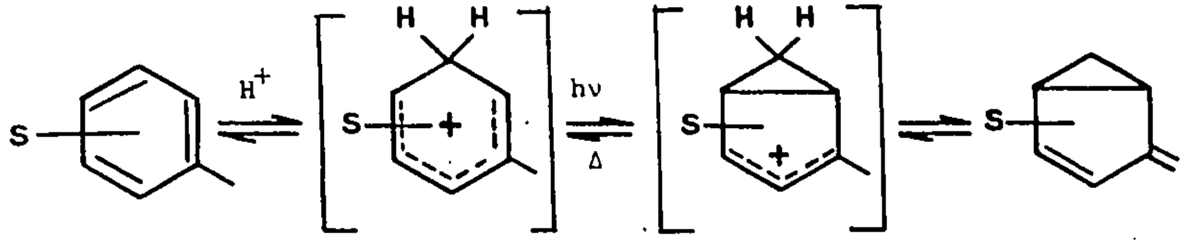


Figure 2. Relative energies of benzene valence isomers.

Despite their attraction in terms of their potential storage capacity, the photovalence isomerizations of benzene and substituted benzenes have not been used in any practical schemes for the efficient utilization of solar energy. In large part this deficiency is caused by two factors: first, the mismatching of the absorption spectra of most benzenoid compounds with the solar spectrum. Most simple benzenoid chromophores absorb at wavelengths less than 300 nm. The broad solar spectrum is most intense in the visible and IR regions (~400 - 1000 nm) and simple benzenoid compounds do not absorb light at these wavelengths. The second drawback is the relative inefficiencies (low quantum yields) of the photo-reactions of benzenoids. In addition it seems that the more highly substituted benzenes are photochemically less reactive than simple benzenoid compounds.[41d,60]

Benzenium Cation Storage Systems

Recently, R.F. Childs and co-workers[61] suggested the possibility of using acids to catalyse the photoisomerization of substituted benzenes. The basis behind this suggestion is the observation that polymethyl-benzenium cations undergo efficient photoisomerization to give bicyclohexenyl cations, equation 13. Linking this photoreaction with the protonation and deprotonation steps of equation 13, it should be possible to convert a methyl substituted benzene to homofulvene. The big advantage of this proposal is that benzenium ions 16 absorb at much longer wavelengths than the neutral benzenoid hydrocarbons.



15 16 17 18

S = Substituent(s).

In principle, it is possible to store energy by converting a methyl substituted benzene, 15, into its valence isomer, 18, by this acid catalysed photoreaction. The retro process 18 → 15 is known to proceed either on direct heating or with acid catalysts.[63-65] In order to evaluate this approach it is necessary to examine the individual steps involved in equation 13 using polymethyl substituted benzenes.

Arenium Ions

Introduction

Arenium ions represent a large class of carbenium ions that have been intensively studied.[66] These ions have long been of interest as they were proposed as intermediates in many important reactions of aromatic compounds. These reactions include the electrophilic substitutions,[67-69] as well as the isomerization reactions.[70]

Arenium ions can be generated by the protonation of benzenoid compounds in strong or super-acid media. The formation of arenium ions is not confined to hydrocarbon systems. Many aromatic compounds that carry hydroxy, alkoxy, or even amino substituents have been found to be susceptible to protonation at one of the ring carbons.

With the wide application of modern physical methods in recent years much evidence has been accumulated on the structure and reactivity of arenium ions under "long life" conditions.[71,72]

In view of the extensive reviews of this material discussion here is confined to the protonation of some polymethyl substituted benzenoid compounds and their photochemistry in strong acid solutions.[66]

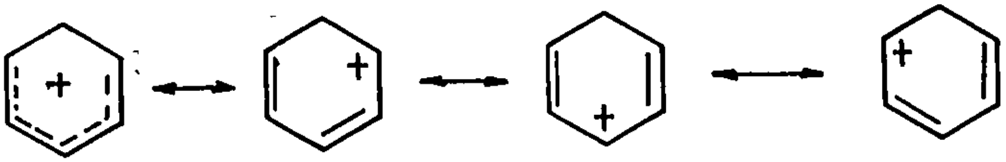
Protonation of Polymethyl Substituted Benzenes

It has long been known that protonation of benzenes in a variety of strong acids and superacids give the corresponding benzenium ions. Many studies have appeared in the literature dealing with different aspects such as their methods of formation, their electronic and, nuclear magnetic resonance spectra, their stability, quantum mechanical calculations and their reactions.[66]

Substituted benzenes normally contain several non-equivalent ring carbon atom, and in general protonation leads to the formation of an equilibrium mixture of isomeric benzenium ions.

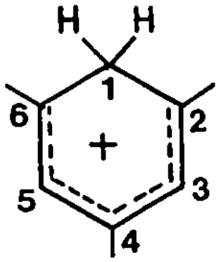
As is shown by molecular-orbital calculations,[73-75] and an analysis of ^{13}C NMR chemical shifts,[76-78] the positive charge in a benzenium ion is largely centered at C_2, C_4 and C_6. This is readily seen in the various resonance forms which can be written for these ions.

One result of this charge density distribution in benzenium ions is that the more stable ions have electron donating substituents located at C_2, C_4 and C_6.



19 20 21

Thus for example, in protonating mesitylene, of the two possible isomers 22 and 23 only 2,4,6-trimethylbenzenium ion 22 is detected by ^1H NMR.[79]



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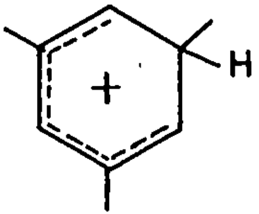


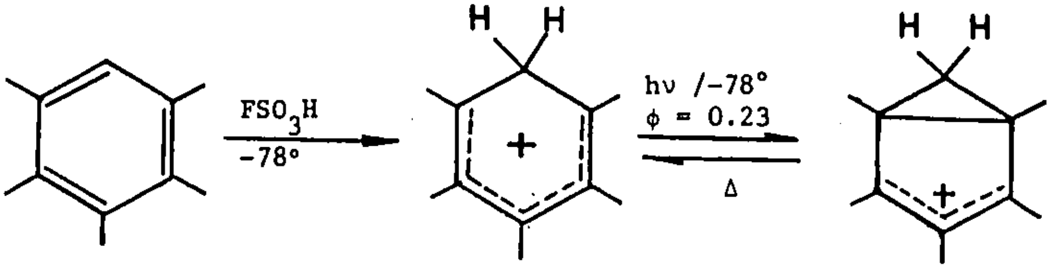
23

As a rule, protonation of methyl substituted benzenes occurs to give the cation which has the largest number of methyl substituents at positions ortho and para to the point of proton attachment.[74,80-84]

Photochemistry of Polymethylbenzenium Cations

Interest in the photoisomerization of protonated arenes dates back to observations by Childs and Winstein, some eighteen years ago.[85] It was reported then that methyl substituted benzenium ions undergo valence isomerization reactions when irradiated in strong acid solutions.

Thus irradiation of pentamethylbenzenium ion 24 at -78°C gave 25 in 80% yield.

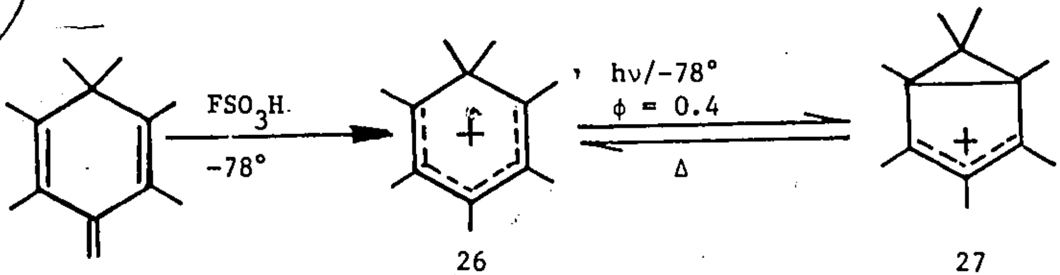


(14)

24 25

λ_{max} = 379 nm

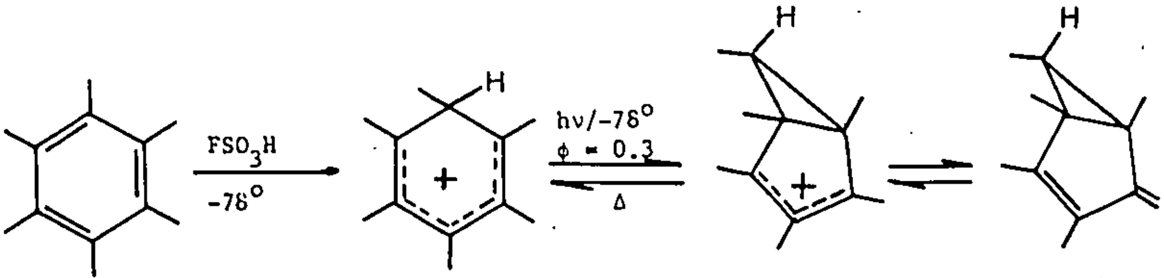
Similarly, irradiation of heptamethyl- and hexamethylbenzium ions 26 and 28, under the same conditions gave the corresponding bicyclo [3.1.0] products, 27 and 29.[63] Of the two conceivable stereoisomers which can arise from 28 only one was observed. This was identified as the endo isomer, i.e., the one in which the C_6 methyl group is inside.[86-89]



(15)

26 27

λ_{max} = ·400 nm



(16)

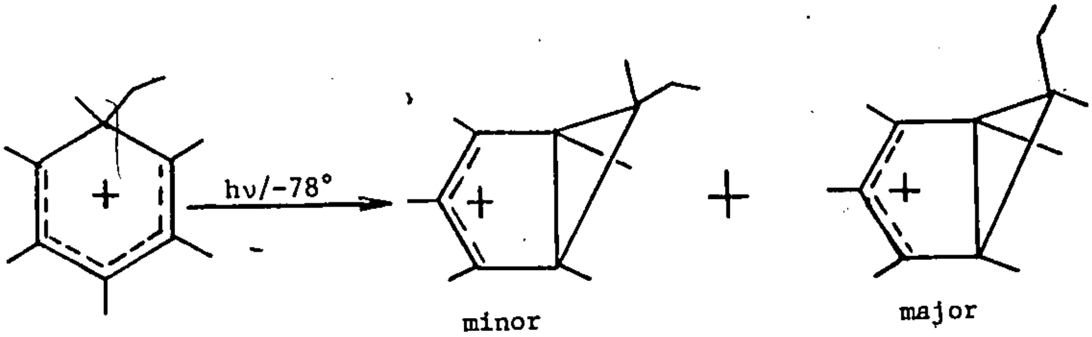
28 29 30

λ_{max} = 395 nm

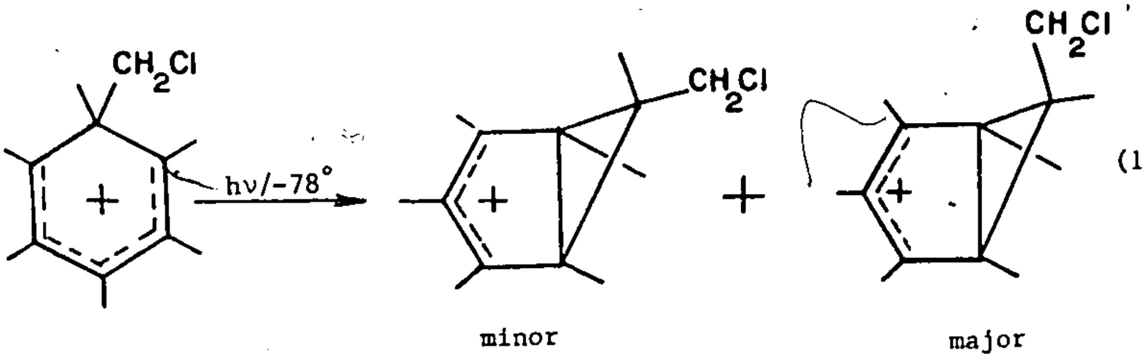
It is clear from these results that the photoisomerizations of these benzenium ions are clean, relatively efficient reactions as compared to the neutral hydrocarbons themselves.

Recently, Childs and Gibala,[90] extended the above photoisomerizations by using Lewis acids and heterogeneous acids as catalysts. Their results showed that Lewis acid catalysed photoinduced isomerizations of benzenoid compounds tend to be very complex compared to the protic acid catalysed reactions.

Other examples of phototransformations of benzenium ions were reported by Koptyug and co-workers,[87] equations 17 and 18.



(17)

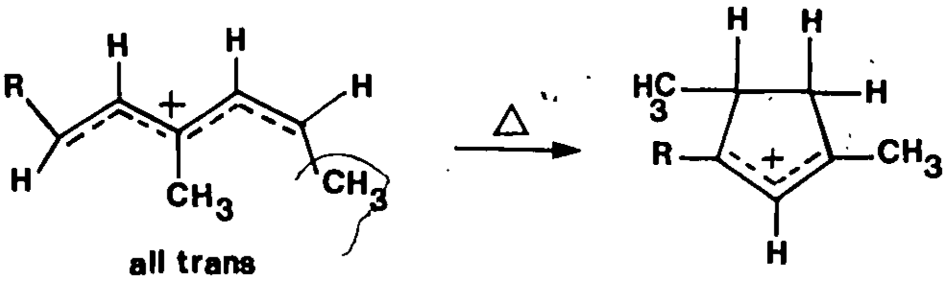


(18)

The preferred formation of bicyclo[3.1.0]hexenyl cations with the less bulky substituent located in the exo position is explained by smaller steric hindrance to its passage between the two CH_3-groups as the ring sp^3-hybridized carbon leaves the plane of the rest of the ring carbons.[87-89]

Mechanism of the Photochemical Ring Closure

The conversion of a benzenium cation to a bicyclo[3.1.0]hexenyl cation can be regarded as an electrocyclic reaction. Methyl substituted pentadienyl cations undergo thermal rearrangement upon heating to give the corresponding cyclopentenyl cations. The suggestion by Woodward and Hoffman[91a] that this electrocyclic ring closure would proceed in a conrotatory manner was confirmed experimentally by Sorenson.[92]



(19)

Conrotatory ring closure of benzenium cations to bicyclo[3.1.0] hexenyl cations can not occur in the ground state. Such a motion will result in a product which has a trans fused cyclopropyl ring, and this, even if formed, would open to give the starting material.

However, in the first excited state disrotatory photochemical ring closure of benzenium cations is allowed and this would give a cation with cis fused rings.

The exact nature of the excited state involved in the photoisomerizations of these benzenium ions has not been established. However, the lack of any difference in the rate of isomerization of carefully degassed or oxygen-saturated FSO$_3$H solutions of benzenium ions would suggest that the reactions proceed via singlet or very short lived triplet states.

Of the possible mechanisms for this photoisomerization, a symmetry allowed photochemical disrotatory ring closure of the benzenium cation was considered to be likely.[93] However, a $[\sigma 2a + \pi 2a]$ cycloaddition reaction is an alternative process, which has been postulated to account for many of the photoreactions of cyclohexadienones and cyclohexenones.[91b] This alternative mechanism usually involves antarafacial addition at the double bond and inversion at the migrating saturated carbon as shown in Figure 3.

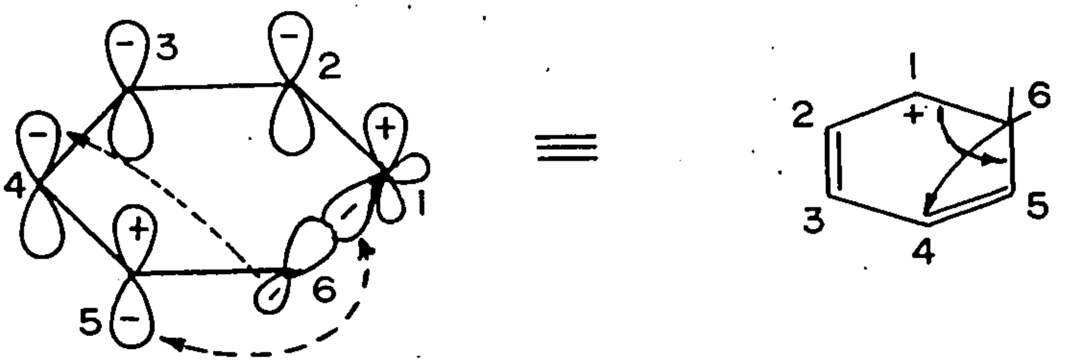
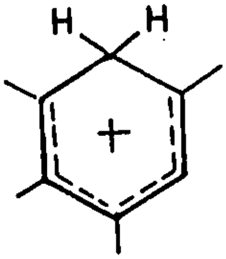
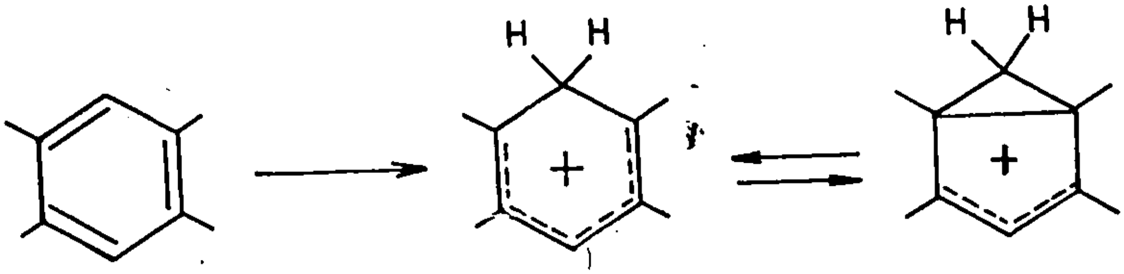


Figure 3. Huckel $[\sigma_{2a} + \pi_{2a}]$ cycloaddition of benzenium cation in its excited state.

In order to make a distinction a ring label is necessary. For this purpose the photochemistry of 31 and 32 was examined.[93] Since protonated durene 32 yields the 1,2,4,5-tetramethyl bicyclo[3.1.0]hexenyl cation 33 and not the 1,2,3,5-isomer,[93,94] the photochemical conversion must be a disrotatory electrocyclic process rather than a result of the [$\sigma 2a + \pi 2a$]-cycloaddition.



31



(32) (33)

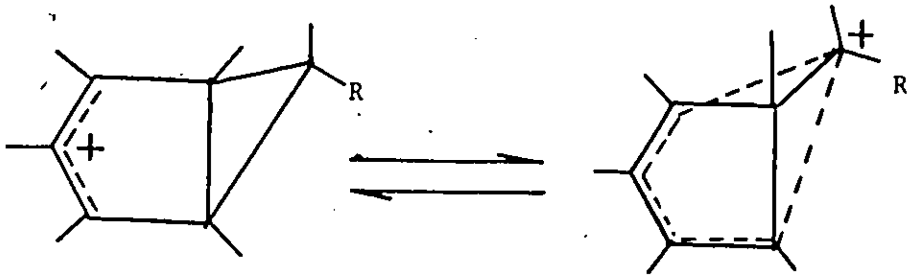
(20)

Thermal Chemistry of Bicyclo[3.1.0]hexenyl Cations

The bicyclo[3.1.0]hexenyl cations are particularly interesting in that they undergo two different thermal rearrangments. The first of these is a "degenerate" rearrangement in which the cyclopropyl ring migrates around the five membered ring. The second is an irreversible electroyclic reversion into the corresponding benzenium ion.

The cation 23, obtained by irradiation of 22 in FSO_3H/SO_2ClF, provide a good example of both types of rearrangement.[95] The ^1H NMR spectrum of 23 was found to exhibit a reversible temperature dependence. At temperatures above -90oC only three signals were observed, in the ratio 15:3:3, whereas below -90oC, the original five-line spectrum was restored. It was evident that a process was occurring that had the effect of moving the cyclopropane group around the five-membered ring. This circumambulatory migration was suggested to take place by successive concerted 1,4-sigmatropic shifts, Scheme 1. Such a migration in these systems is bound to be suprafacial and thus when thermally induced must involve inversion of configuration at the migrating carbon. Many other comparable cyclopropyl migrations have been described.[96,97]

The ease of migration of the cyclopropyl ring around the five-membered ring was shown to depend on the nature of the substituents at C_6. The rate of the rearrangement is greater when C_6 bears charge-stabilizing groups, indicating that an increased fraction of the positive charge is located on this carbon in the transition state for the rearrangement as compared to the ground state, equation 21.[86,87,95,98]

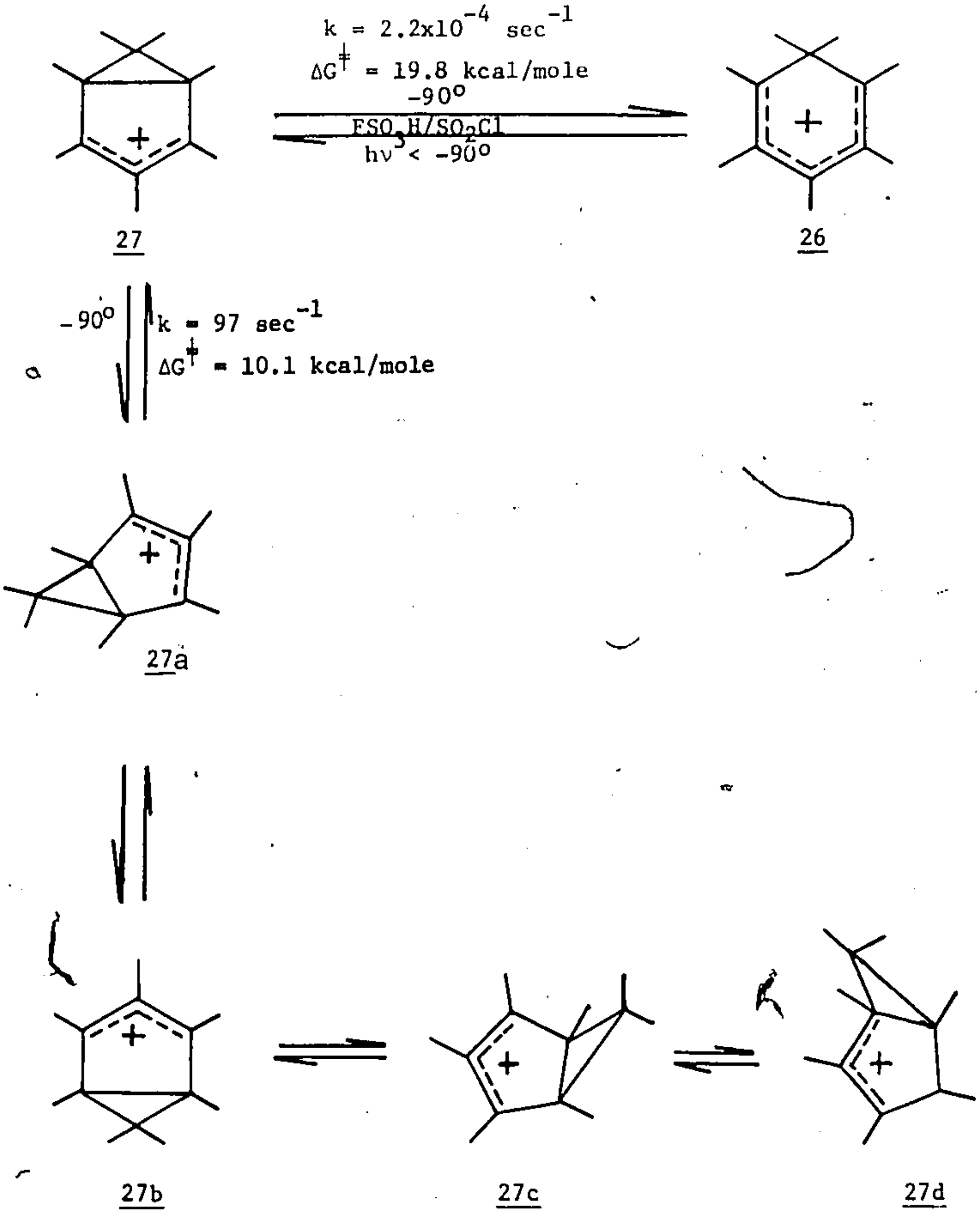


(21)

27, R = Me

29, R = H

Scheme 1


$k = 2.2 \times 10^{-4}\ sec^{-1}$
$\Delta G^{\ddagger} = 19.8$ kcal/mole
-90°
FSO_3H/SO_2Cl
hν < -90°
27
26
-90°
$k = 97\ sec^{-1}$
$\Delta G^{\ddagger} = 10.1$ kcal/mole
27a
27b
27c
27d

On heating, all known bicyclo[3.1.0]hexenyl cations undergo an irreversible electrocyclic ring opening leading to the cyclohexadienyl cations.[85-87,93-95] Thus the dynamic NMR methods can only be applied to study circumambulatory rearrangements when these reactions proceed much faster than ring opening. Only the hepta- and hexamethyl cations 27 and 29 fulfill this requirement.[85,87,94] Experimental evidence for walk rearrangements in the other systems shown in Table 1.3 was obtained by the use of specifically labelled starting materials.

TABLE 1.3. Energy Barriers of the Competing Process in Bicyclo[3.1.0]hexenyl Cations[94]

Cation	Walk Rearrangement $\Delta G^\dagger$ (kcal/mole)	Ring Opening $\Delta G^\dagger$ (kcal/mole)
27	10.1	19.8
29	17.5	17.4
25	not observed > 13	17.6
33	not observed > 18.6	17.1

The rather high energy barrier for the ring opening reaction is not surprising since the disrotatory electrocyclic reactions that break the C_1-C_5 cyclopropane bond are "forbidden" in the ground state.[91]

Conclusions Regarding Use of Benzenium Cations in Solar Energy

It is evident that there are several advantages to the use of acid catalysed photoreactions to store energy in benzenoid materials. First, protonation of benzenoid compounds has enabled the use of visible wavelength light (400 nm) to drive the reaction. Second, the protonation of benzenoid compounds has permitted very clean, relatively efficient ($\Phi = 0.2 - 0.4$) photoisomerizations as compared to those of the neutral hydrocarbons themselves. In addition the storage potential of these reactions is very high. For example, in the case of hexamethylbenzenium ion system shown in Figure 3, some 42.8 kcal/mole can in principle be stored.

However, there are some difficulties with the particular systems studied. First, the temperature of the acid solution has to be kept below -60°C during the irradiation in order to prevent the thermal reversion of the bicyclic cations to the starrting benzenium ions at room temperature. Second, catalytic photoisomerizations of these cations tend to be unsuccessful. Third, the activation barriers for the back reaction <u>17</u> → <u>16</u>, equation 13, are considerably smaller than that of the endothermic deprotonation of <u>17</u>, and hence formation of the homofulvene will not compete with the reverse isomerization of <u>17</u> to <u>16</u>. In the case of hexamethylbenzenium ion system shown in Figure 3, the barrier to the reverse isomerization of <u>29</u> → <u>28</u> ($\Delta H^{\neq} = 20.1$ kcal/mole) is substantially less than that of the endothermic deprotonation of <u>29</u> → <u>30</u> ($\Delta H^{\neq} > 35.6$ kcal/mole).

There are ways to overcome these problems. Modification of the activation barrier to the reverse isomerization can be achieved by

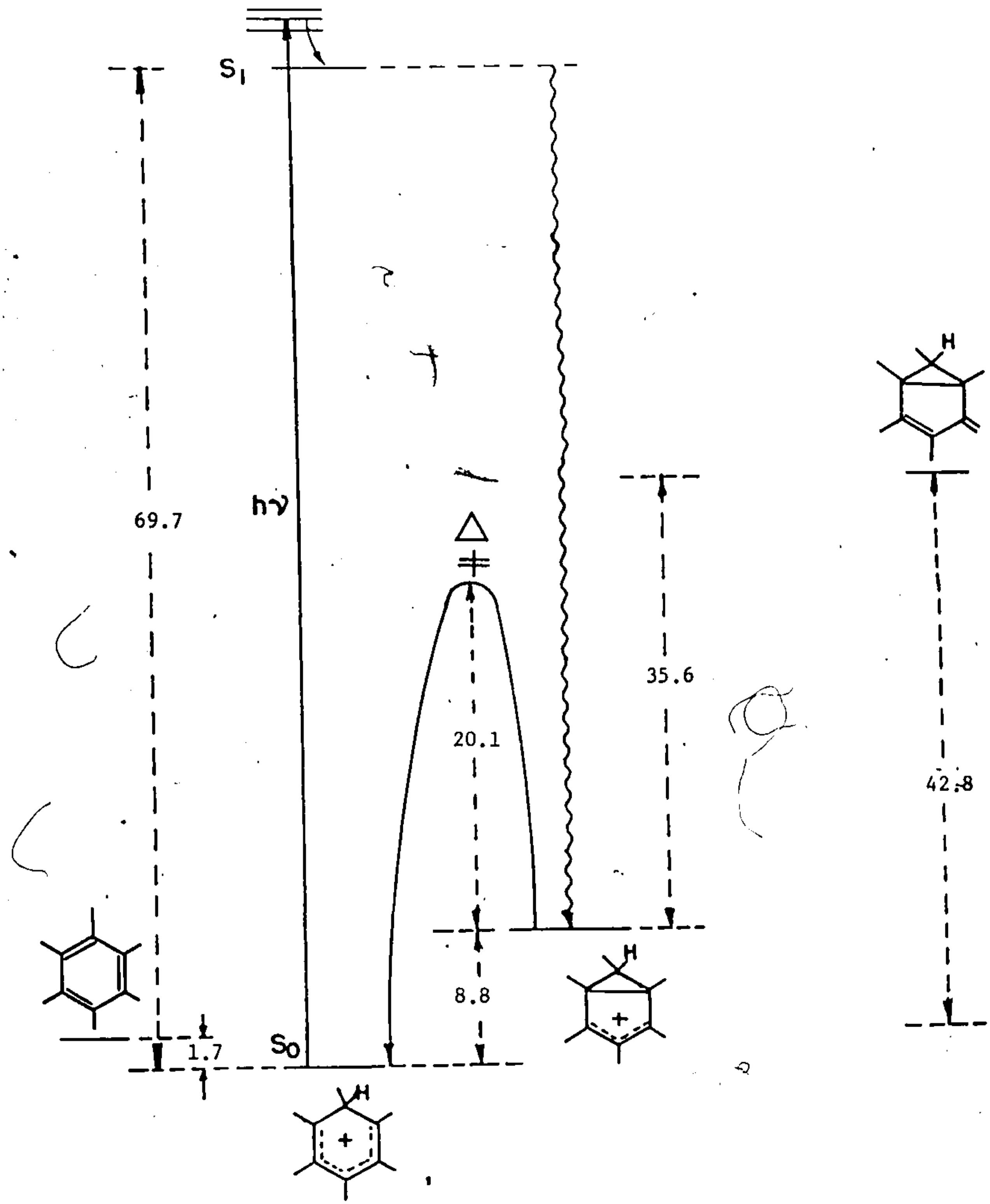
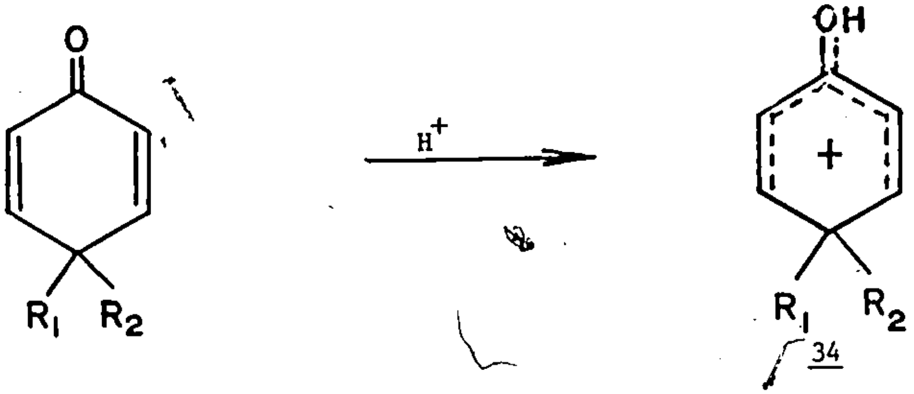


Figure 3. Summary of enthalpy differences (kcal/mole) for the hexamethyl series 28, 29, and 30. Taken from reference 61.

varying the substituents on the benzene ring. In addition, variation of the acid considerably modifies the relative energies of the protonation/deprotonation steps. Examples of the effect of substituents on these isomerization can be found with the hydroxy-substituted system.

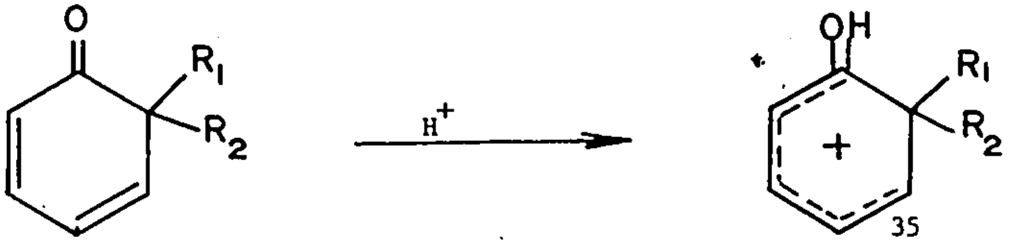
Protonation of Cyclohexadienones

Hydroxybenzenium ions with structures 34 and 35 can be obtained by protonation of the corresponding 2,4- and 2,5-cyclohexadienones.[99-101]



34

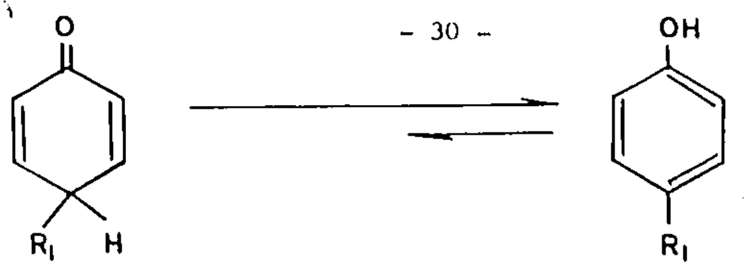
(22)



35

(23)

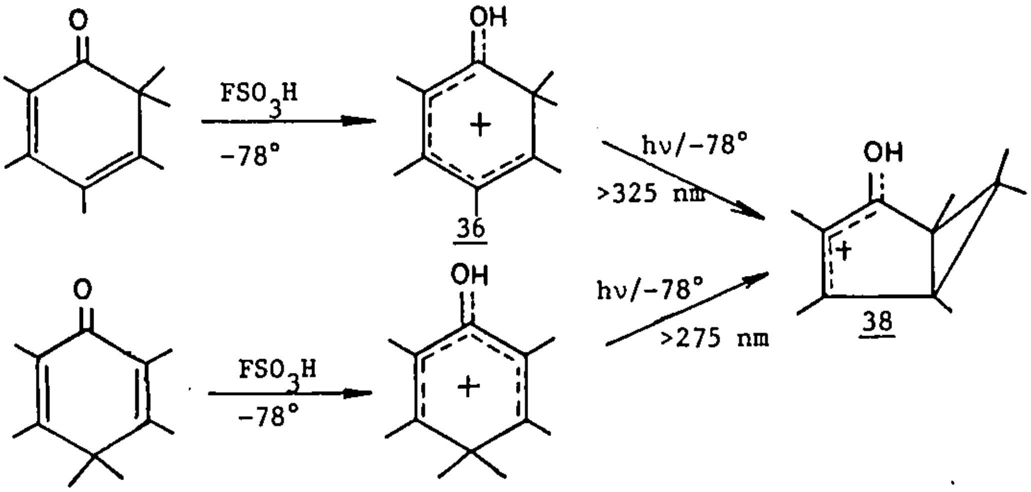
Cyclohexadienones in which R_1 or R_2 is H are kinetically unstable and they revert to more stable phenol tautomers. Thus, starting with a cyclohexadienone it is not possible to generate hydroxybenzenium ion which have only a single substituent at the sp^3 hybridized ring carbon, equation 24.


(24)

Photochemistry of Protonated Cyclohexadienones

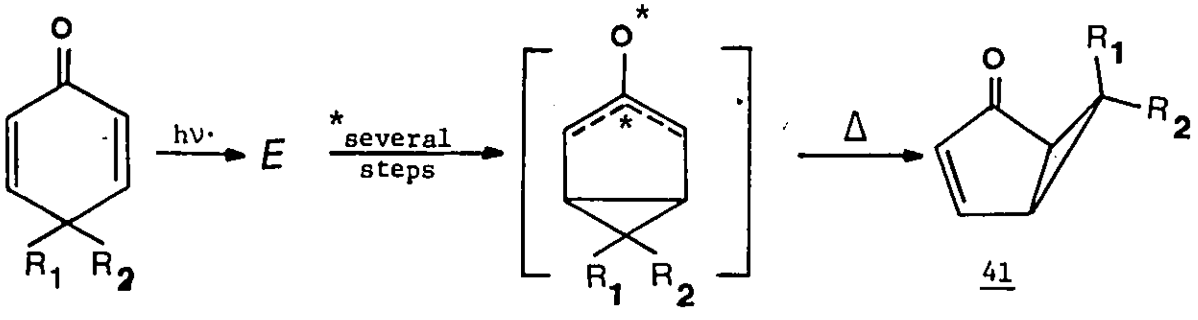
Hydroxy substituted benzenium cations undergo light-induced valence isomerization reactions in strong acids to yield 2-hydroxybicyclo[3.1.0]hexenyl cations.[102-104] For example, irradiation of the hexamethyl cations 36 and 37 has been shown in each case to result in the formation of 38, Scheme 2.

Scheme 2



The mechanism of cyclohexadienone photoisomerizations have been extensively investigated, however little has been reported on the mechanism of the photoreactions of the protonated cyclohexadienones.

Almost 25 years ago Zimmerman and co-workers[105] advanced mechanistic suggestions to account for what they term a type A rearrangement for the photoisomerization of 4,4-disubstituted 2,5-cyclohexadienones 39 to 6,6-disubstituted bicyclo[3.1.0]hexenones 41. It is now generally accepted that this rearrangement takes place via 3,5-bonding in the excited state to form, depending on reaction conditions, either a zwitterionic or radical-like intermediate 40. This then can undergo rearrangement to give the bicyclo[3.1.0]hexenone 41, equation 25.[96,106-110] A similar rearrangement is known to occur with conjugated 2,4-dienones.[111]



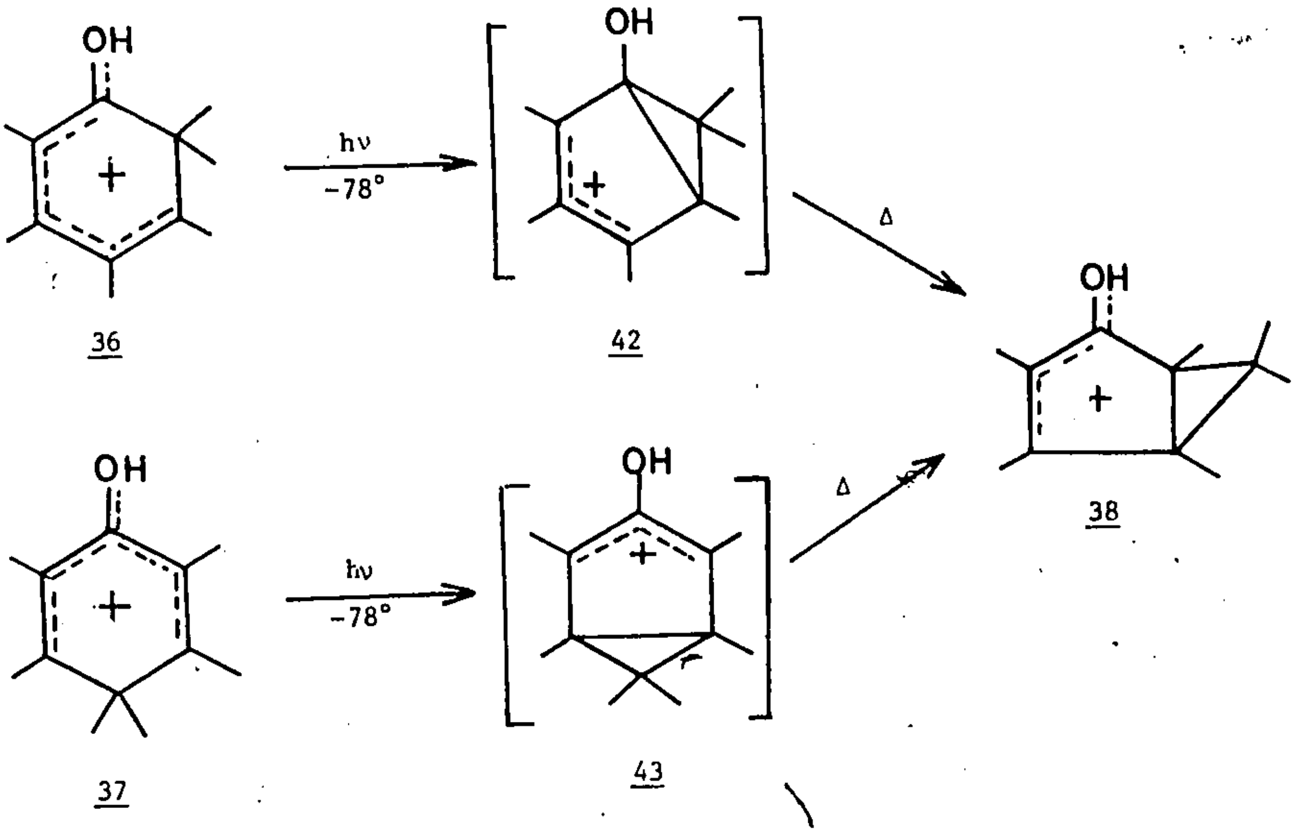
(25)

39 40

* = radical or zwitterion

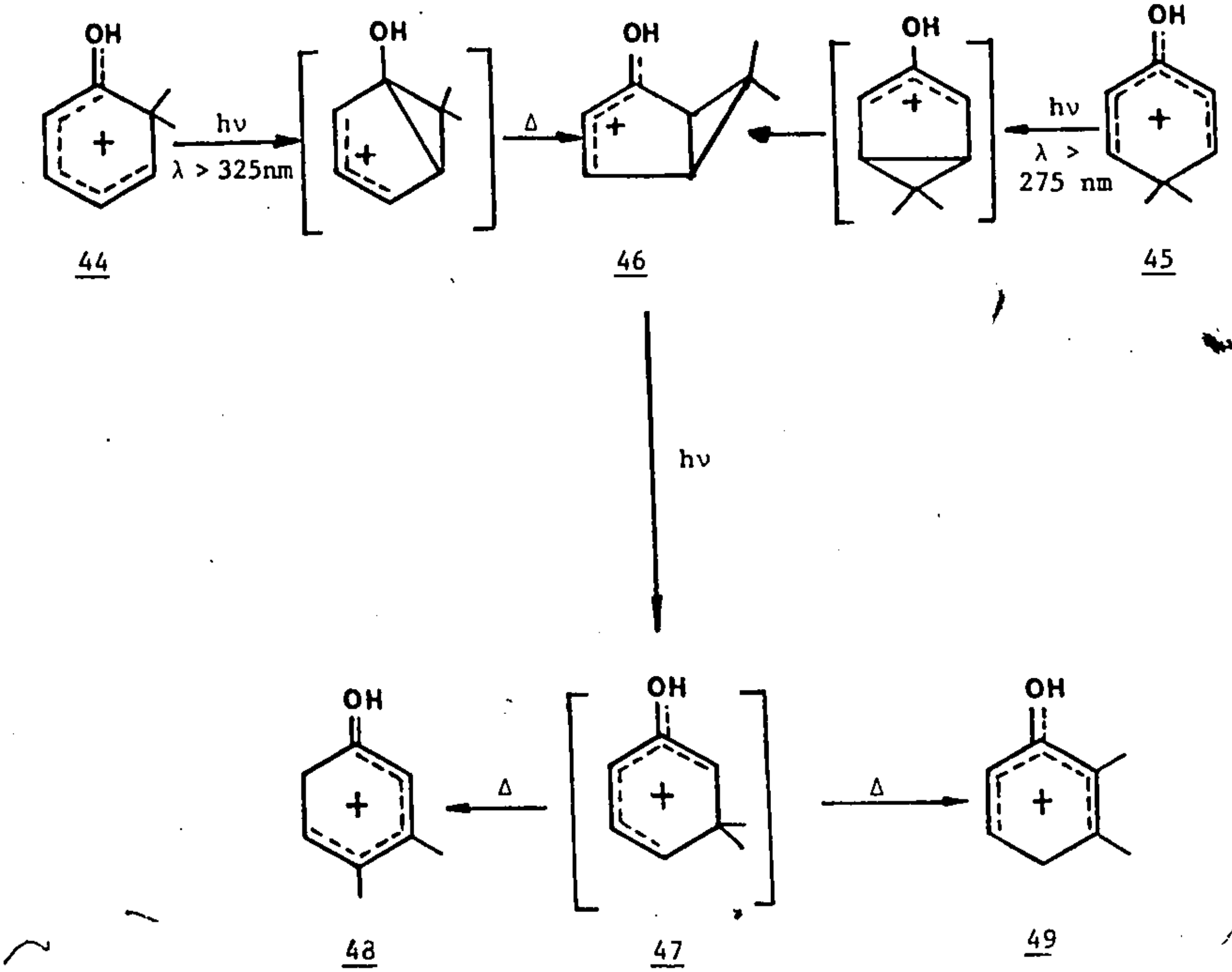
It would seem likely that the photoisomerization of protonated cyclo- hexadienones would involve similar steps, Scheme 3. Any mechanism involving an initial thermal rearrangement can be ruled out, as at -60° the cations 36, 37 and 38 are all thermally stable.

Scheme 3



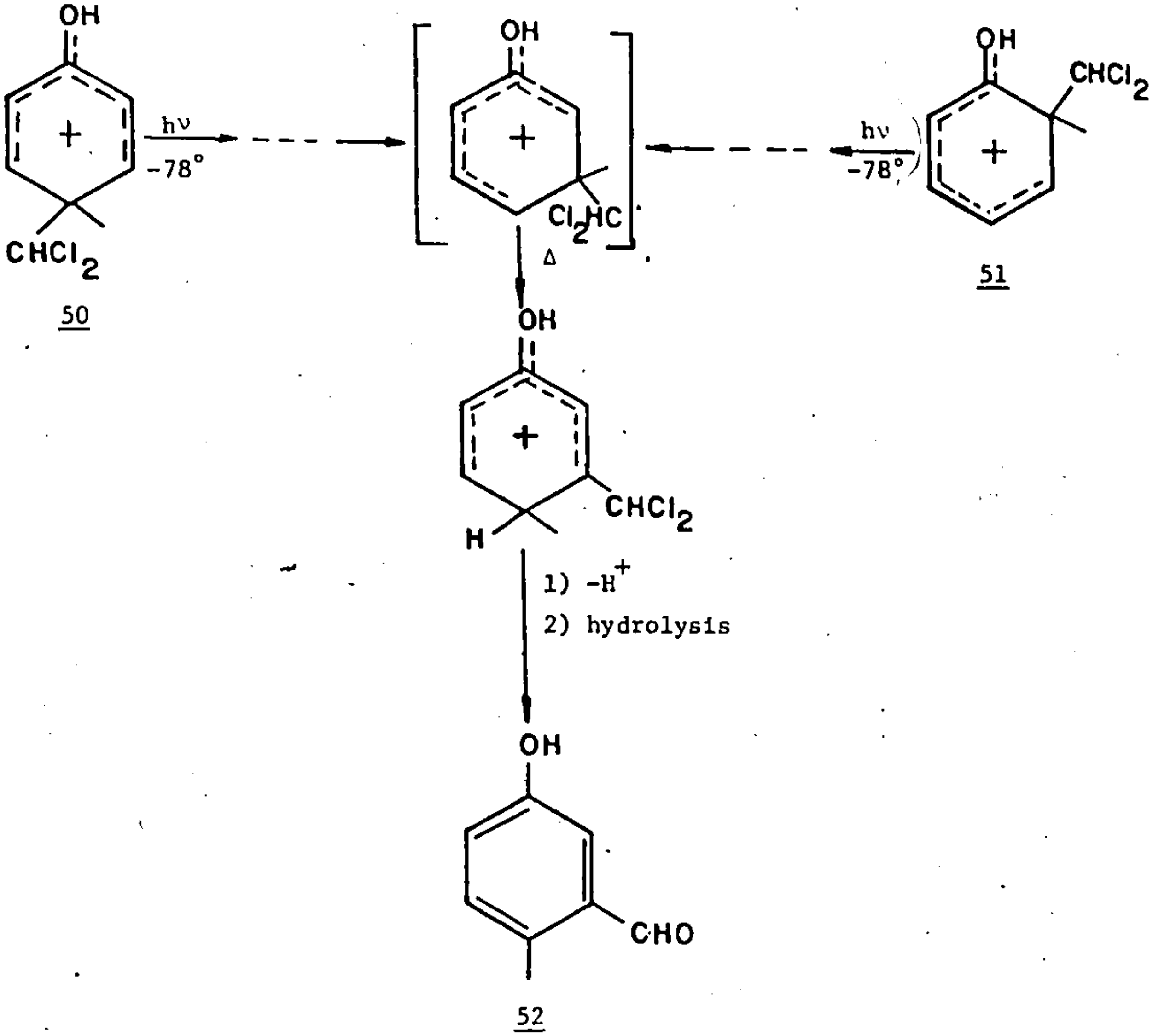
The 2,2-dimethyl-1-hydroxy- and 4,4-dimethyl-1-hydroxy- benzenium ions 44 and 45 (λ_{max} 363 and 298 nm) are photochemically isomerized first to 46 and subsequently to the C-protonated 3,4- and 2,3-dimethyl phenols, Scheme 4.[102]

Scheme 4



In a similar manner protonated 4-methyl-4-dichloromethylcyclohexa-2,5-dienone 50 and 6-methyl-6-dichloromethylcyclohexa-2,4-dienone 51 are converted into 5-hydroxy-2-methylbenzaldehyde 52, Scheme 5.

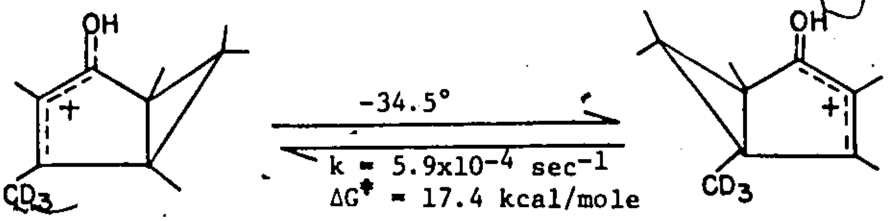
Scheme 5



Overall it is clear that photoisomerizations of protonated dienones are more complex than those of simple benzenium ions.

Thermal Chemistry of Hydroxy Substituted Bicyclo[3.1.0]hexenyl Cations

The results obtained from the thermal isomerization of hydroxy substituted bicyclic cations are analogous to the thermal conversions of methyl substituted bicyclo[3.1.0]hexenyl cations. For example, a walk rearrangement of hydroxybicyclohexenyl cation 38 is involved in the acid catalyzed isomerization of bicyclohexenone 53 to protonated cyclohexadienone 36.[95,97,112] The reversible nature of this walk rearrangement has been demonstrated by the equilibration 38-4-CD_3 ⇄ 38-5-CD_3,[95,97] equation 26, which precedes the ring-opening to the protonated cyclohexadienone derivative,[95] Scheme 6.

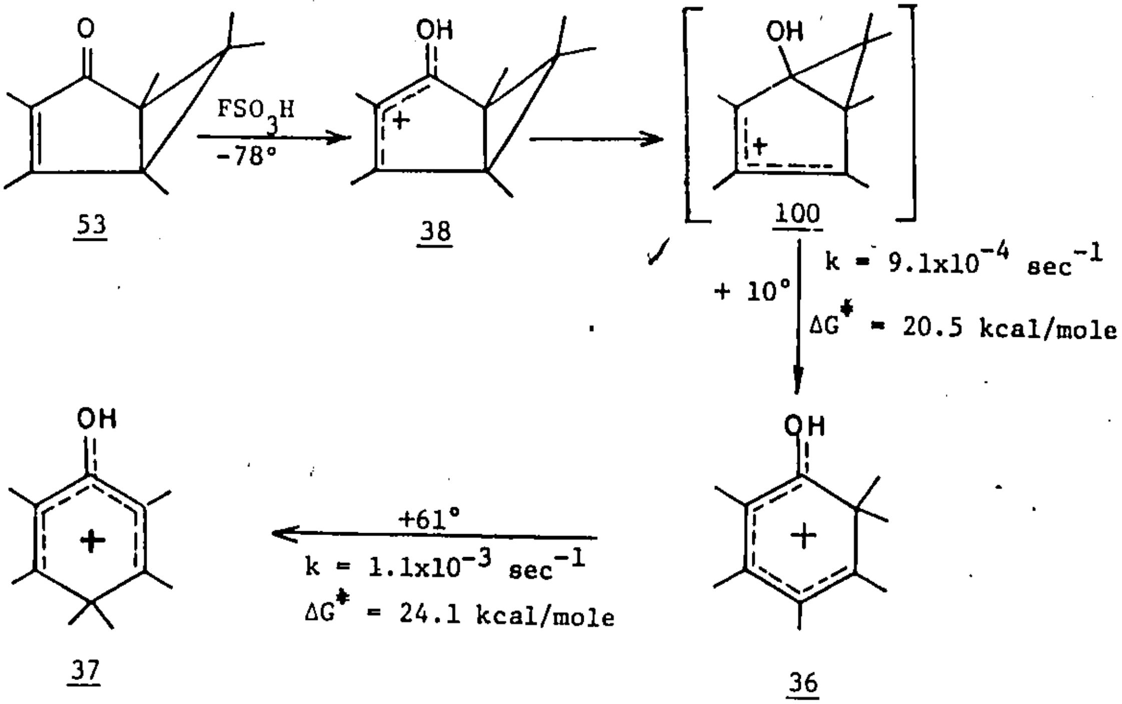


38-4-CD_3

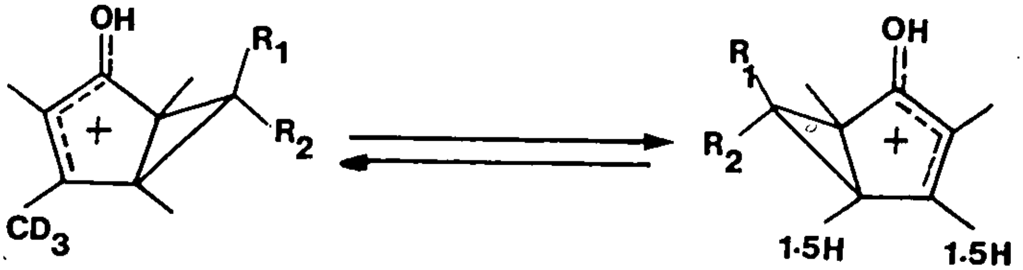
38-5-CD_3

(26)

Scheme 6



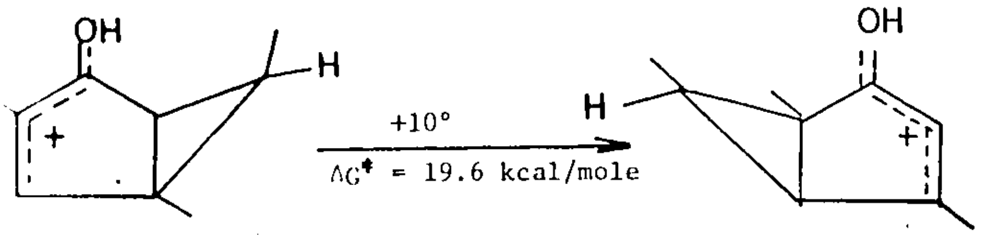
As in the case of bicyclohexenyl cations, in these cases where it has been examined, the circumambulation rearrangements in the hydroxy substituted bicyclohexenyl cations are highly stereoselective, equation 27.[112]



(27)

$R_1 = CH_3$, R_2 = n-propyl

A good example of the stereoselectivity is provided by the recent work of Childs and co-workers on the interconversion of 54 into 55 equation 28.[113]

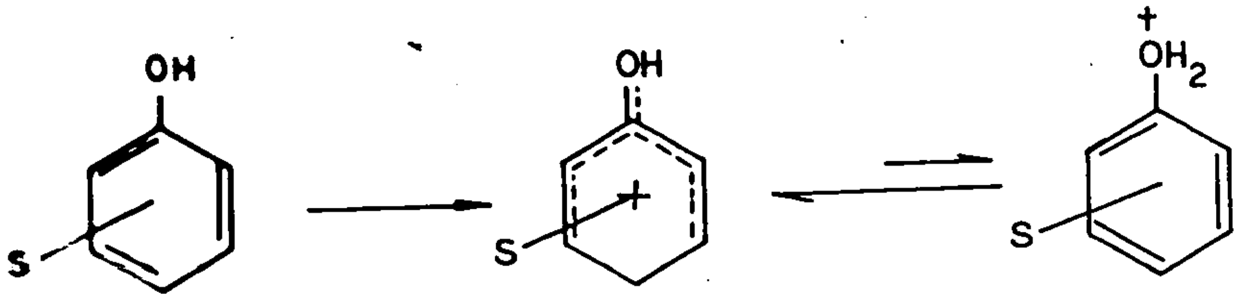


54 55 (28)

It is clear from the above results that the activation barriers for the ring opening of the hydroxy bicyclic cations to the protonated dienones are higher than those of the corresponding bicyclic cations lacking a hydroxy group.

Protonation of Phenols in Superacids

While studies on the photoisomerization of neutral 2,5-cyclohexadienones have been restricted to molecules bearing two substituents at C_4 this restriction is relaxed with protonated systems. Thus ring protonation of phenols by strong acids yields the equivalent of protonated cyclohexadienones, equation 29.



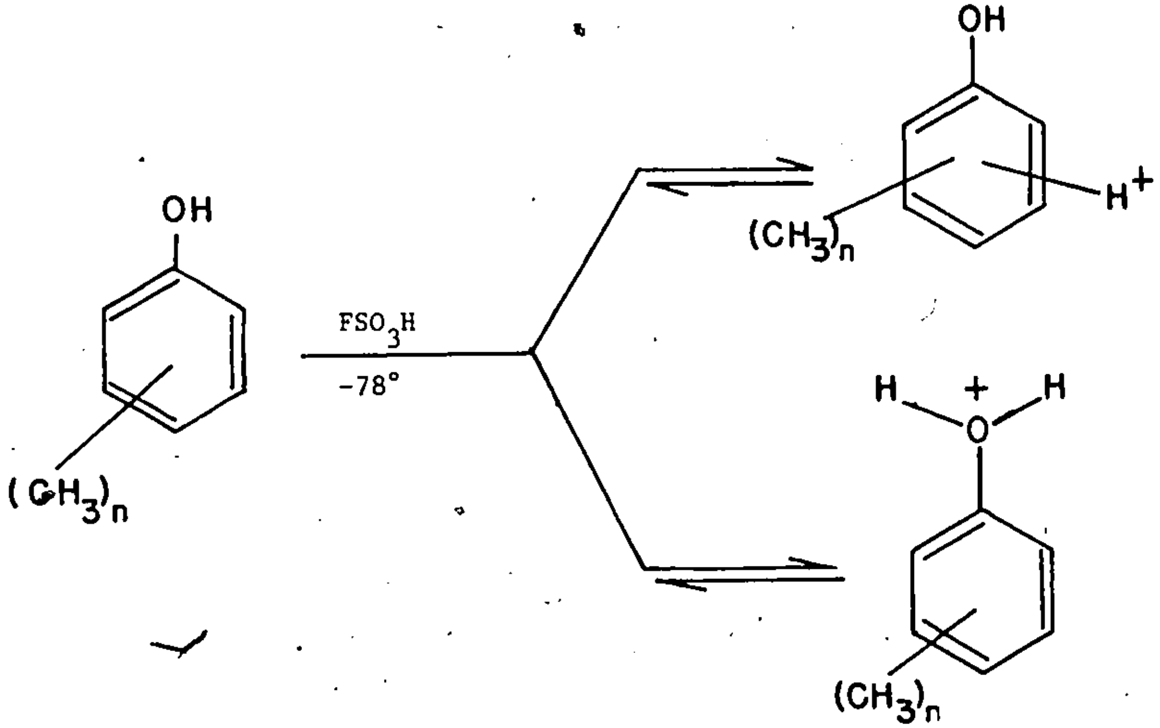
(29)

S = substituent(s)

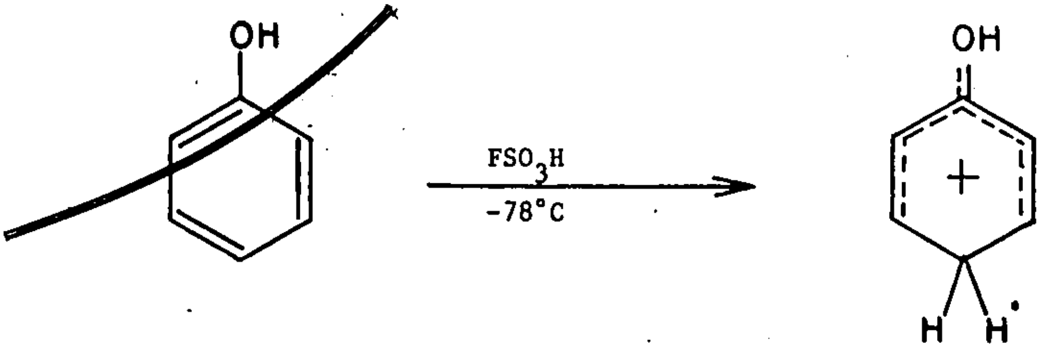
In principle therefore, it should be possible by using strong acids as a protonating medium to extend the range of 2,5-cyclohexadienone photoisomerizations to systems lacking substituent at C_4.

The protonation of phenols in a variety of strong acids and super-acid media has been extensively studied,[114-119] and the factors which can affect the preferred site of protonation have been discussed.[120-123] Proton attachment can take place either on oxygen to form an oxonium ion or on one of the ring carbons to give a protonated ketone structure, Scheme 7. The preferred site of protonation depends both on the nature of the acid medium used and on the substituents on the phenol.

Scheme 7

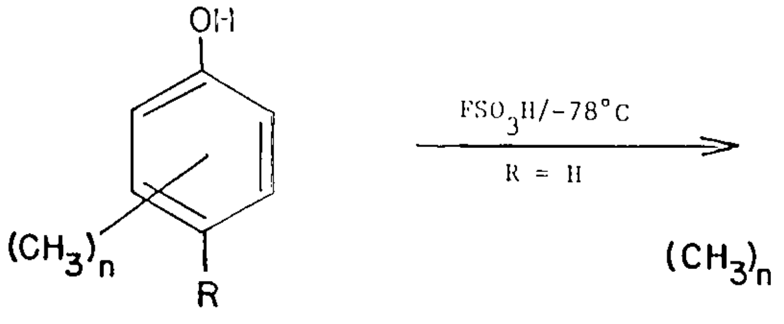


It is generally agreed that, when phenol is protonated in FSO_3H, only one ion corresponding to the attachment of the proton at the para position is observed,[66a,115,124,125] equation 30. This observation indicates that the strong electron-releasing properties of the hydroxy group enhances the basicity of the benzene ring in phenol to such an extent that C_4 can compete with the oxygen atom for the acid proton.



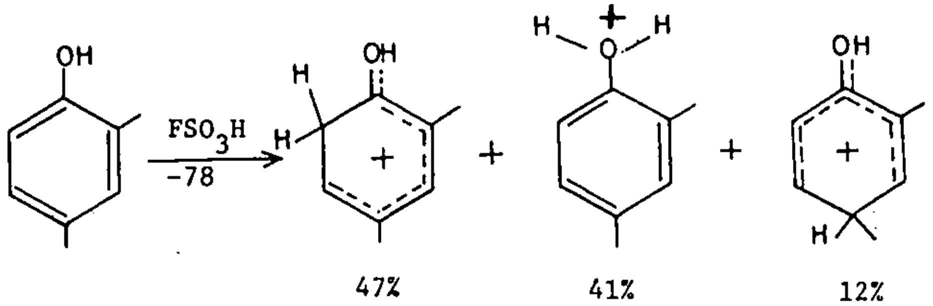
(30)

Methyl substituents on the six membered ring, or indeed oxygen atom can play an important role in determining the site of protonation of a phenol. For example, when phenols with no methyl substituent at C_4 are protonated in FSO_3H only one cation resulting from protonation para to the oxygen is observed,[118,124,125] equation 31. This indicates that for such compounds C_4 is clearly the most basic site, the directing influence of the hydroxyl group being much stronger than that of the methyl groups. This is well illustrated in the case of 2,6-dimethylphenol, where the two methyls are situated so as to increase the basicity of the C3 and C5 by ca. 10^6, no protonation in these positions could be detected.[66a,122,124]



(31)

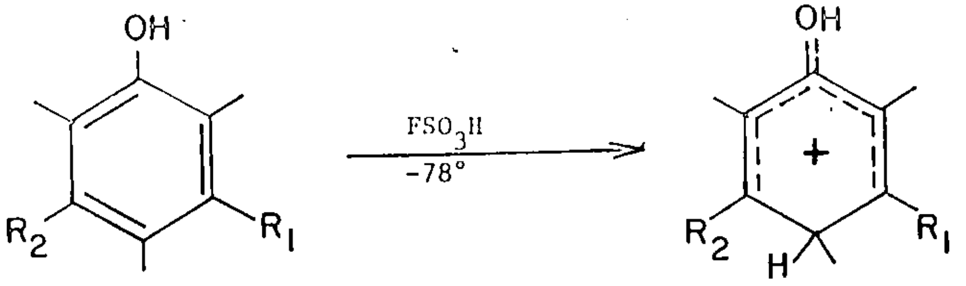
Olah,[119] Childs[124] and Wright[125] have independently shown that when the 4-position of a phenol bears a methyl substituent, proton addition at one of the two ortho positions or upon oxygen becomes possible, equation 32. This indicates that the effect of the methyl group is to reduce the basicity at C4. This effect has been attributed to the loss of hyperconjugative interaction energy between the methyl group and the ring in the cation.[125]



(32)

Protonation at C2 or C6 of these systems is only observed when at least one of these sites is unsubstituted. Thus <u>53</u>, <u>54</u> and <u>55</u>, which all have methyls on C2, C4 and C6, show no indication of being protonated on C2 or C6,[124] Scheme 8.

Scheme 8



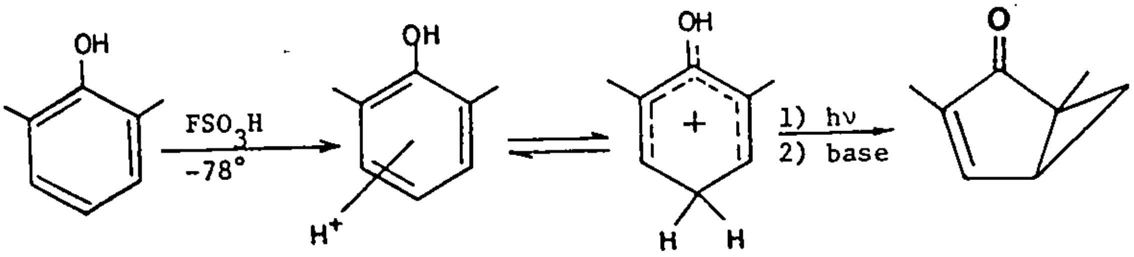
53, $R_1 = R_2 = H$
54, $R_1 = H$, $R_2 = Me$
55, $R_1 = R_2 = Me$

53H, $R_1 = R_2 = H$
54H, $R_1 = H$, $R_2 = Me$
55H, $R_1 = R_2 = Me$

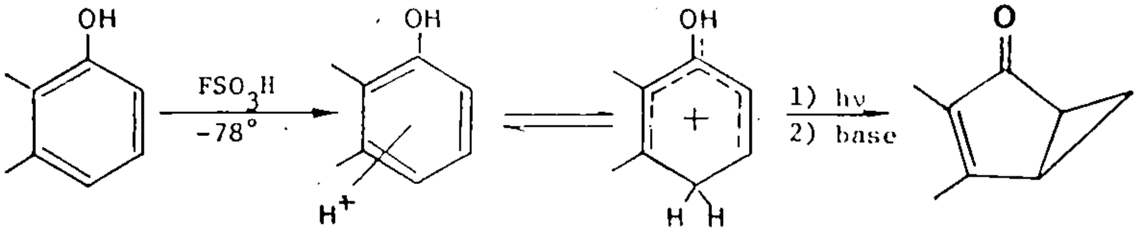
In FSO_3H-SbF_5, 2,4,6-trimethylphenol 53 was protonated only in the meta position. The electron donating properties of the hydroxy group must be modified by protonation or coordination with SbF_5 in this stronger acid.[124]

Photochemistry of Protonated Phenols

Examples of the photoisomerizations of C-protonated phenols date back to observations by Childs and Parrington some fifteen years ago.[113] It was reported then that C-protonated phenols undergo similar photorearrangements to those described for the protonated cyclohexadienones,[113,126,127] equations 33 and 34.



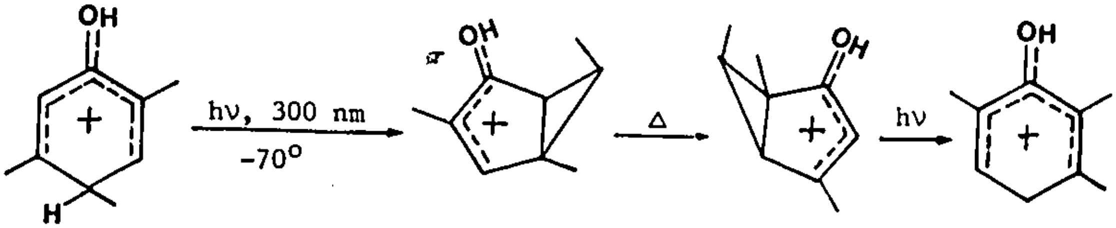
(33)



(34)

This facile photoisomerization of the C-protonated phenols stands in marked contrast to the general lack of photochemical reactivity of the parent phenols.[41c,128,129]

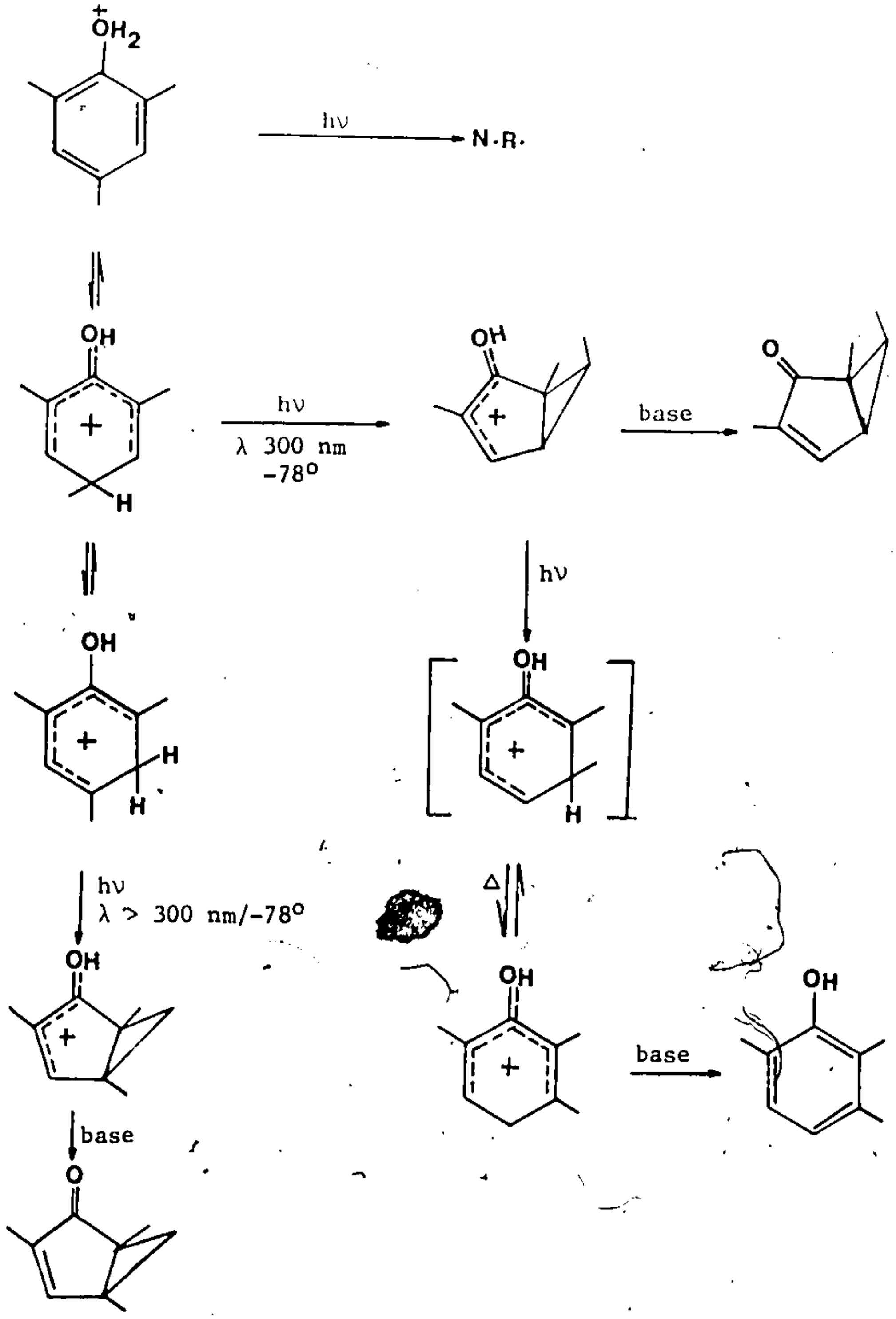
As in the photoisomerizations of protonated cyclohexadienones, protonated bicyclo[3.1.0]hexenones are also photochemically labile and can rearrange when irradiated (≥ 330 nm) to hydroxy benzenium ions,[113,126] equation 35.



(35)

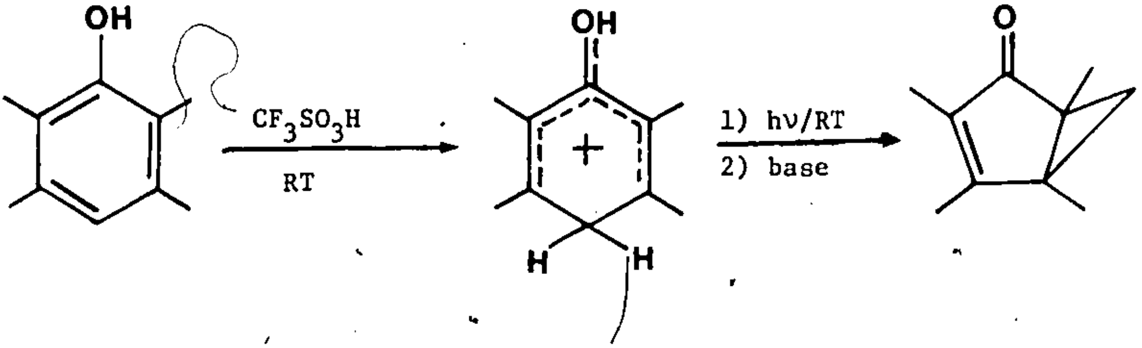
In a similar manner protonated 2,4,6-trimethylphenol is converted into protonated 2,3,6-trimethylphenol, Scheme 9. The meta-protonated form would also seem to be photochemically active, being converted to protonated 1,3,5-trimethylbicyclo[3.1.0]hexenone.

Scheme 9


$\overset{+}{O}H_2$
hν
N.R.
OH
H
hν
λ 300 nm
-78°
OH
base
O
OH
H
H
hν
λ > 300 nm/-78°
OH
base
O
hν
OH
H
Δ
OH
base
OH

The photoreactions of protonated phenols are attractive from a preparative point of view. However, their practical utility is diminished by two major drawbacks. First, the temperature of the acid solution has to be kept below -60°C during the irradiation in order to prevent fluorosulfonation of the phenol. Second, the maximum conversion of a protonated phenol to protonated bicyclohexenonone was less than 30%. These difficulties have recently been overcome by using trifluoromethanesulfonic (triflic) acid as solvent and modification of the wavelength of the light used.[126,127]

Triflic acid is a sufficiently strong acid to ring protonate most methyl substituted phenols giving solutions which are stable at room temperature, equation 36.[126] Photoisomerization of these solutions has been shown to occur on irradiation at room temperature.



(36)

Objectives of the Present Work

While the above review reveals the interest and the potential use of endothermic organic photoreactions for the utilization of solar energy, it is also evident that no organic photochemical latent heat storage system which makes efficient use of solar energy is yet known.

It appears from the work of Childs and co-workers that the acid catalysed photoreactions of polymethyl substituted benzenes hold some promise as candidates for photochemical latent heat solar energy storage.[61] The major problem associated with these benzenoid based systems lies in the low activation barrier for the thermal back reaction. Preliminary results show that a higher barrier can be obtained by introducing an hydroxy group on the benzene ring. The cheap and wide availability of methyl and chloro substituted phenols made it seem worthwhile to investigate the potential of these systems further.

The purpose of this present study was to examine in more detail the quantitative aspect of the photoisomerization of protonated phenols to protonated bicyclo[3.1.0]hexenones and the thermally induced reverse isomerizations.

In terms of the photoisomerizations of substituted phenols, it is necessary to identify the products formed upon irradiation, the nature of the excited states and to investigate the mechanistic pathways. In addition it is important to know the quantum efficiencies of these reactions and in particular to discover the effect substituents play in determining these efficiencies. A variety of methyl and chloro substituted phenols were examined.

Second major type of information needed to complete the evaluation of protonated phenols as potential candidates for energy storage purposes is a detailed knowledge of the thermal rearrangements of the protonated bicyclo[3.1.0]hexenones (i.e., the kinetic stability of these cations). In addition a systematic energetic studies of these cations are also required and is currently under investigation by other member of this group.

As shown earlier there is a dearth of information on the thermal chemistry of protonated bicyclo[3.1.0]hexenone cations. The ring opening seemed to depend on the substituents at C6. However, no systematic study of the effect of the substituents on the various pathways and on the activation energies of these isomerizations was so far attempted. In the present work a detailed study of these questions was undertaken by using a wide range of methyl substituted bicyclic ketones in triflic acid.

CHAPTER 2

RESULTS

PART I:

Protonation and Photoisomerization of Protonated Methyl Substituted Phenols

The only reported cases of photoisomerization of a protonated phenol in triflic acid is that of protonated 2,3,5,6-tetramethylphenol (durenol), reported recently by Childs[126] and Baeckström.[127] This work extend the above finding and shows that C4 protonated polymethyl substituted phenols are generally photoreactive at room temperature in CF_3SO_3H, undergoing similar isomerizations to those previously reported in FSO_3H at low temperature.[113]

In order to understand the photorearrangements of protonated phenols, it is important to know the structure of the cation formed by the protonation of these phenols in triflic acid.

Protonation

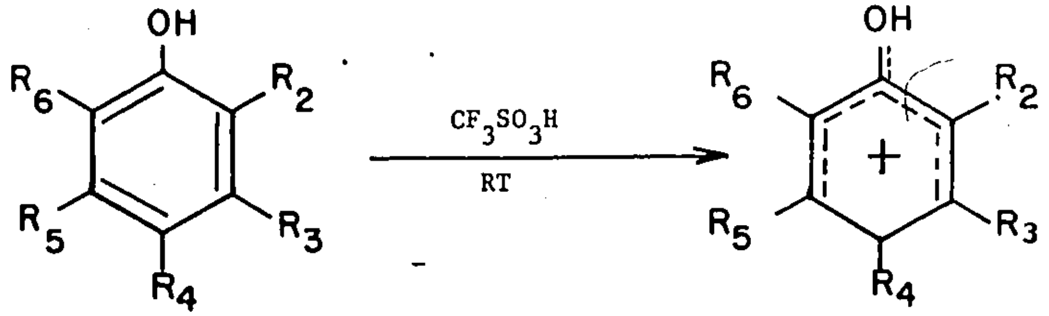
Triflic acid solutions of methyl substituted phenols were prepared by adding phenols to the acid at 0°C. The reaction mixtures were slowly brought to room temperature. The cations produced upon dissolving the phenols in CF_3SO_3H were identified by their room temperature Proton Nuclear Magnetic Resonance (^{1}H NMR) spectra, Table 2.1. In most of the cases protonation only occurred at one site of the phenol and the interpretation of the spectrum was relatively straightforward.

Phenols 56 to 58 and 60 to 65, shown in Scheme 10, were all protonated at the para ring carbon when dissolved in CF_3SO_3H. The ^{1}H NMR spectra of these cations were similar to those previously reported in FSO_3H at low temperature.[113,124,125] The marked similarity of the NMR spectra of these protonated phenols, to those of protonated 2,5-cyclohexadienones confirms the structural assignments.[99,100,130,131]

The chemical shifts given in Table 2.1 for the resonances of the hydrogens attached directly to the ring and the methyl hydrogens in the para protonated species fall into characteristic patterns. For example, protons at C_2 or C_6 give rise to signals in the δ 6.82 - 7.22 region where as those at C_3 or C_5 give signals at δ 8.0 - 8.23. Similarly, methyl substituents at C_2 or C_6 give signals in the δ 2.1 - 2.33 region while those at C_3 or C_5 appear at δ 2.39 - 2.51. Protons at C_4 show two ranges, δ 3.94 - 4.13 and δ 3.60 - 3.95 for C_4-hydrogen and C_4-methyl substituted phenols respectively.

The ^{1}H NMR spectra of cations 58H, 60H and 62H-64H, which are all unsubstituted at C_4, show no coupling between the protons on C_4 and protons on C_3 or C_5. Instead, a broad signal was observed for the C_4 protons at room temperature which became sharper at lower temperatures. This is illustrated in the case of protonated 2,6-dimethylphenol, 64H, (Figure 4). At 20°C a very broad signal at δ 4.1 is observed for the resonance of H_4 and a reasonable sharp singlet at δ 8.15 for the signals of H_3 and H_5. On cooling the solution to -20°C the resonance attributed to H_4 becomes a sharper singlet with no change in the multiplicity of the signal at δ 8.15 (Figures 5 and 6).

Scheme 10



	R$_2$	**R**$_3$	**R**$_4$	**R**$_5$	**R**$_6$	
<u>56</u>	Me	Me	Me	Me	Me	<u>56H</u>
<u>57</u>	Me	Me	Me	H	Me	<u>57H</u>
<u>58</u>	Me	Me	H	Me	Me	<u>58H</u>
<u>59</u>	Me	Me	Me	Me	H	<u>59H</u>
<u>60</u>	Me	Me	H	H	Me	<u>60H</u>
<u>61</u>	Me	Me	H	Me	H	<u>61H</u>
<u>62</u>	Me	H	H	Me	H	<u>62H</u>
<u>63</u>	Me	Me	H	H	H	<u>63H</u>
<u>64</u>	Me	H	H	H	Me	<u>64H</u>
<u>65</u>	H	Me	H	Me	H	<u>65H</u>

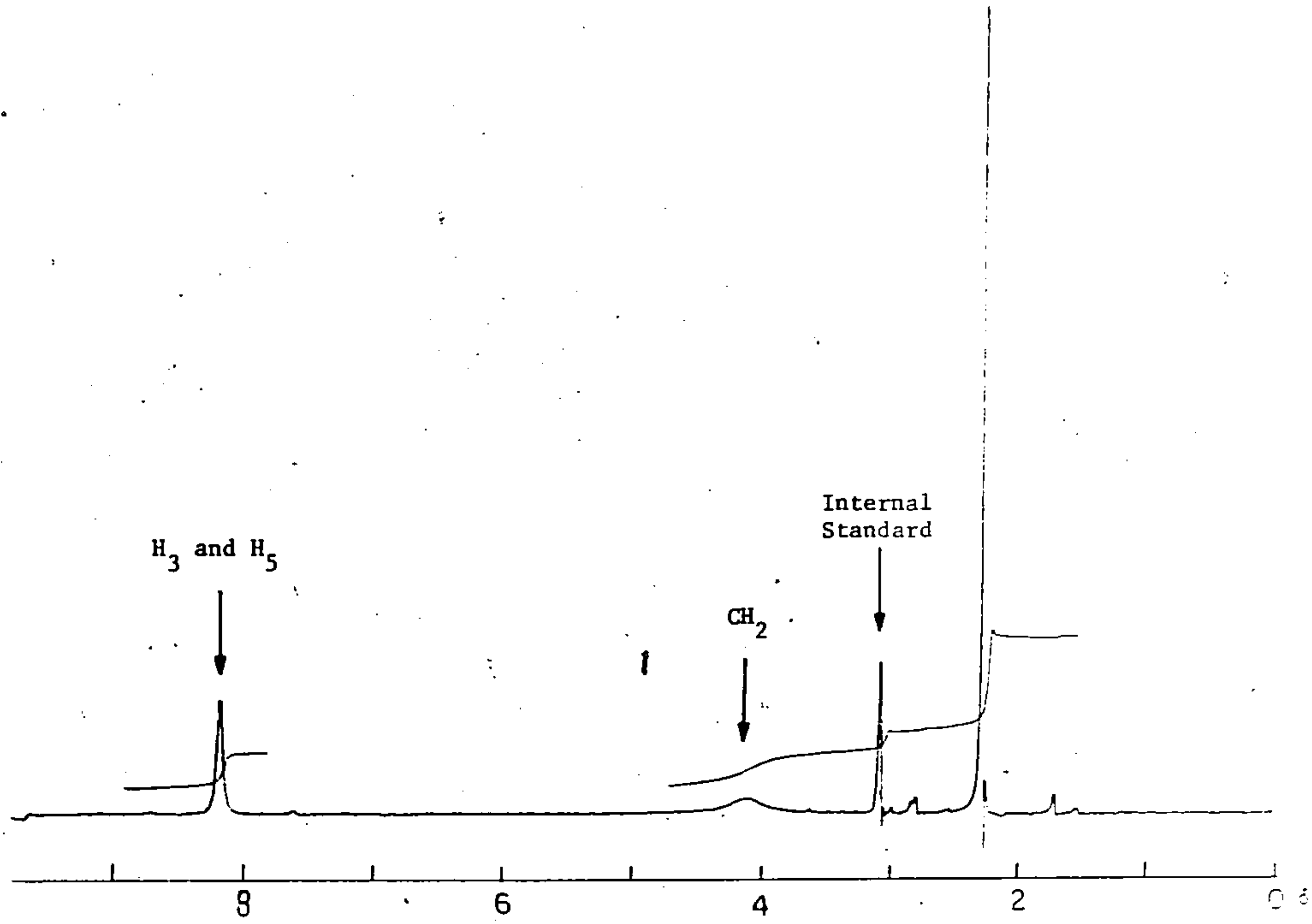


Figure 4. ^{1}H NMR spectrum of a solution of the phenol 64 in CF_3SO_3H at 20°C.

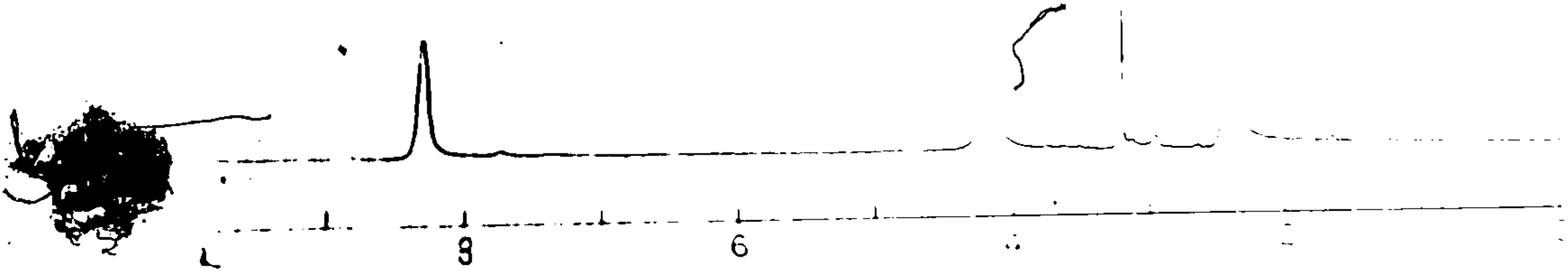


Figure 5. ^{1}**H NMR spectrum of a solution of the** phenol [illegible] in CF_3SO_3H at 0°C.

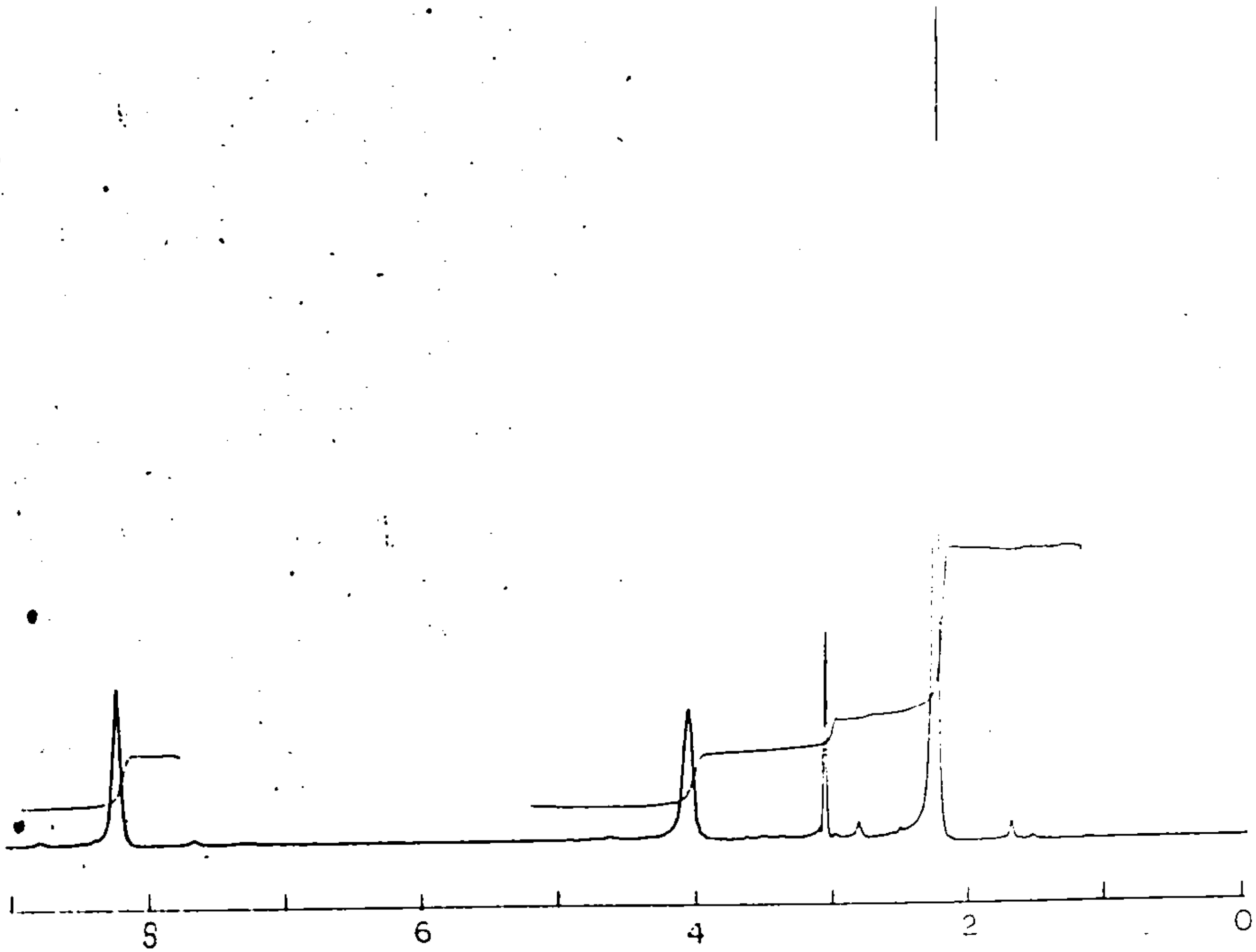


Figure 6. ^{1}H NMR spectrum of a solution of the phenol 64 in CF_3SO_3H at -20°C.

Table 2.1. ^1H NMR Chemical Shifts of Protonated Phenols in CF_3SO_3H[a]

Cation	Chemical Shift, ppm[b,c]						Coupling Constant Hz
	Positions 2 and 6		Positions 3 and 5		Position 4		
	Me	H	Me	H	Me	H	
56H	2.11		2.39		1.52d	3.6q	J_{Me-H} = 8.0
57H[e]	2.20,2.17		2.46	8.05	1.53d	3.73q	J_{Me-H} = 8.0
58H	2.08		2.42			4.03bs	
59H	2.10	6.82	2.40		1.52d	3.62q	J_{Me-H} = 8.0
60H	2.25,2.22		2.51	8.0bs		4.05bs	
61H	2.10	6.91	2.38			3.98	
62H	2.22	7.14	2.50	8.05bs		4.0bs	
63H	2.20	7.22bd	2.51	8.23bd		4.13bs	
64H	2.32			8.20		4.15	
64H[f]	2.32			8.20			
65H		6.93	2.42			3.94	

a) bd = broad doublet, bs = broad singlet, d = doublet, m = multiplet, q = quartet.

b) OH proton is not observable owing to rapid hydrogen exchange with the solvent.

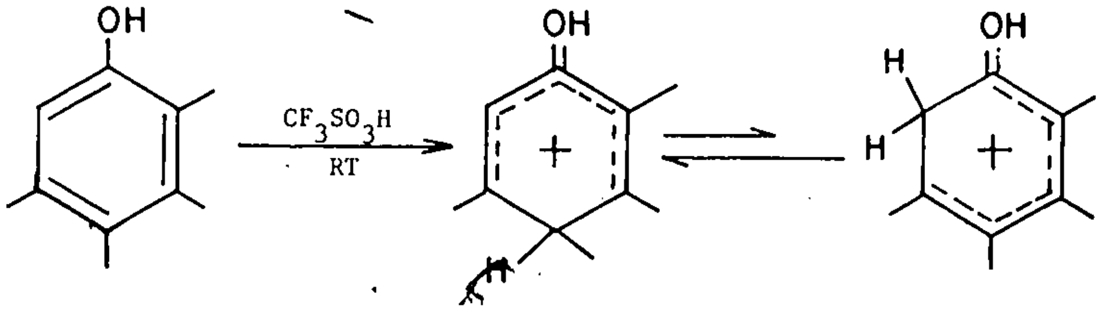
c) In ppm from $(CH_3)_4N^+BF_4^-$ (3.10 ppm) in CF_3SO_3H at room temperature.

e) In CF_3SO_3H at -20°.

f) In CF_3SO_3D at room temperature.

The room temperature (34oC) ^{1}H NMR spectrum of 57H (Figure 7) shows a very broad signal for the C_5 proton at δ 8.0, but no signal for H_4. On cooling the sample to 0oC (Figure 8), the resonances attributed to H_5 (δ 8.0) and H_4 (δ 3.73) appear as broad signals. In addition, the multiplicity of the C_4 methyl signal (δ 1.53) changes from a singlet to a doublet. Below 0oC (Figure 9) the two signals assigned to the resonances of H_5 and H_4 become a singlet and quartet respectively, while resonance of the C_4 methyl protons become a sharp doublet.

The protonation of 2,3,4,5-tetramethylphenol, 59, in CF_3SO_3H follows a different course, as the NMR spectrum of the products shows the presence of two cations in the ratio of 19:1. These were identified as 59H and 66. The identity of 59H, the cation resulting from para protonation, was evidenced by the presence of a high field doublet (δ 1.52, J = 8 Hz) and a quartet (δ 3.62) characteristic of 4-methyl and 4-methine protons, respectively. As is shown in Table 2.1, the other resonances of this para protonated cation are in accord with its assigned structure.[113]



59

95%
59H

5%
66

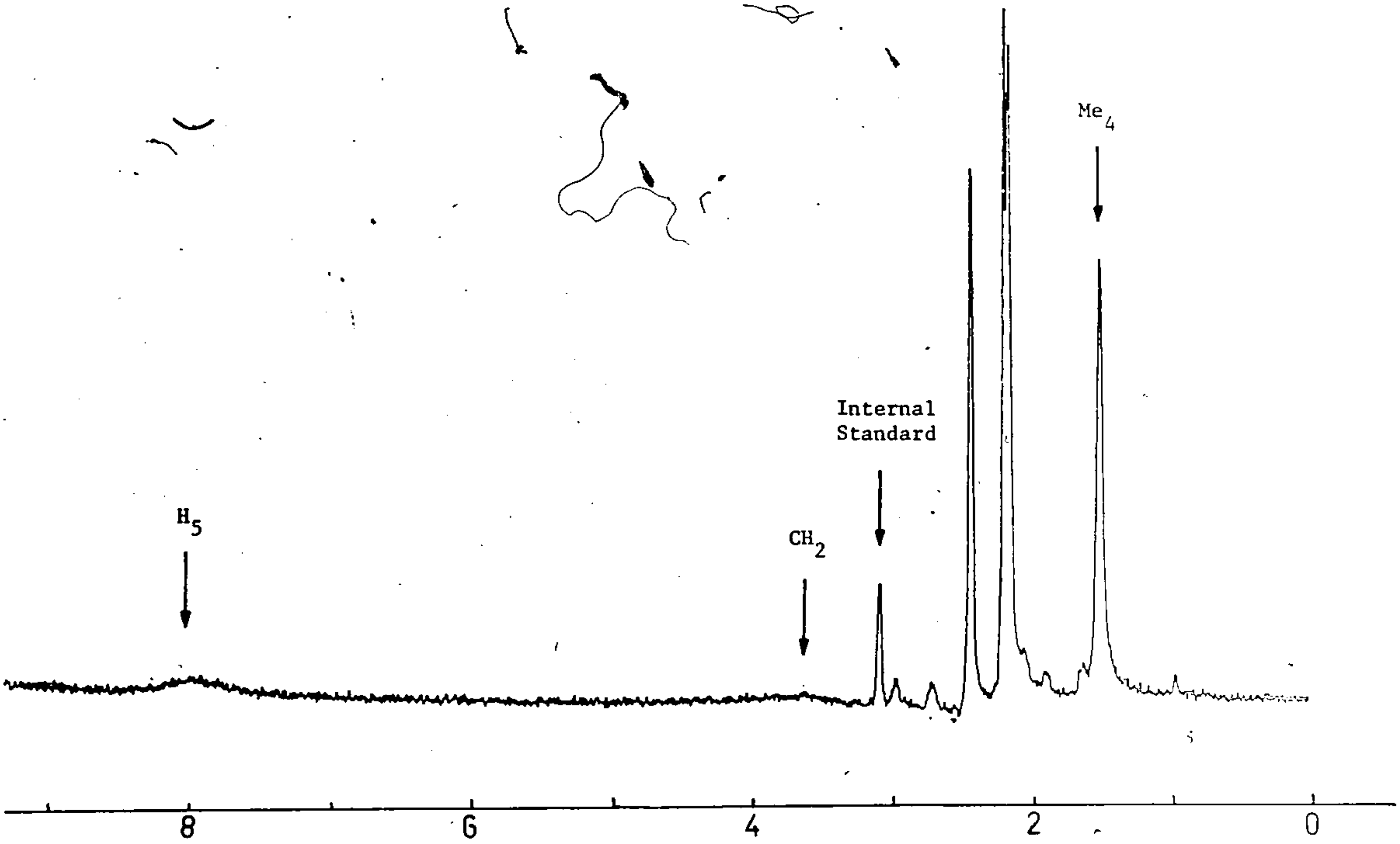


Figure 7. ^{1}H NMR spectrum of a solution of the phenol <u>57</u> in CF_3SO_3H at 34°C.

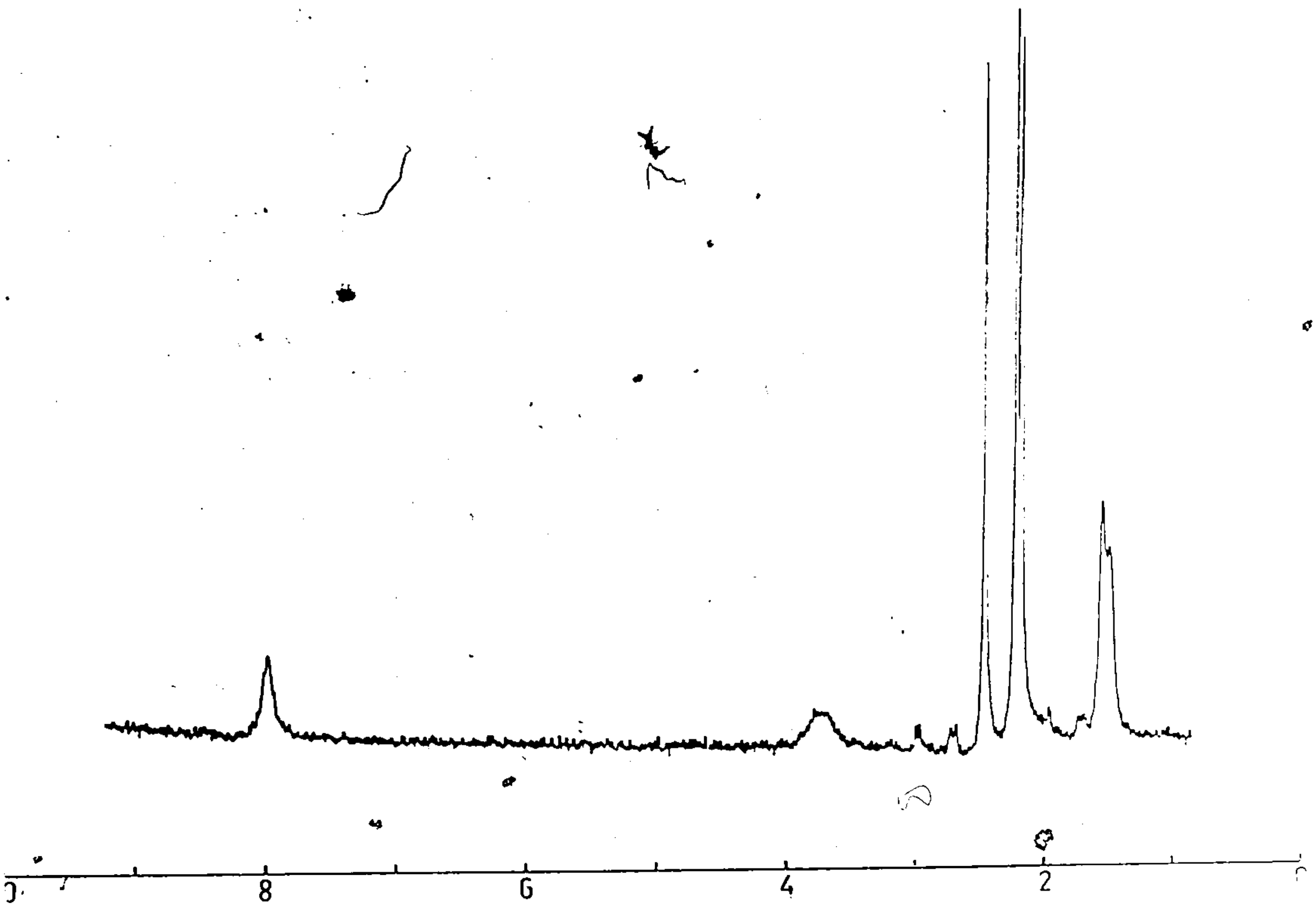


Figure 8. ^{1}H NMR spectrum of a solution of the phenol 57 in CF_3SO_3H at 0°C.

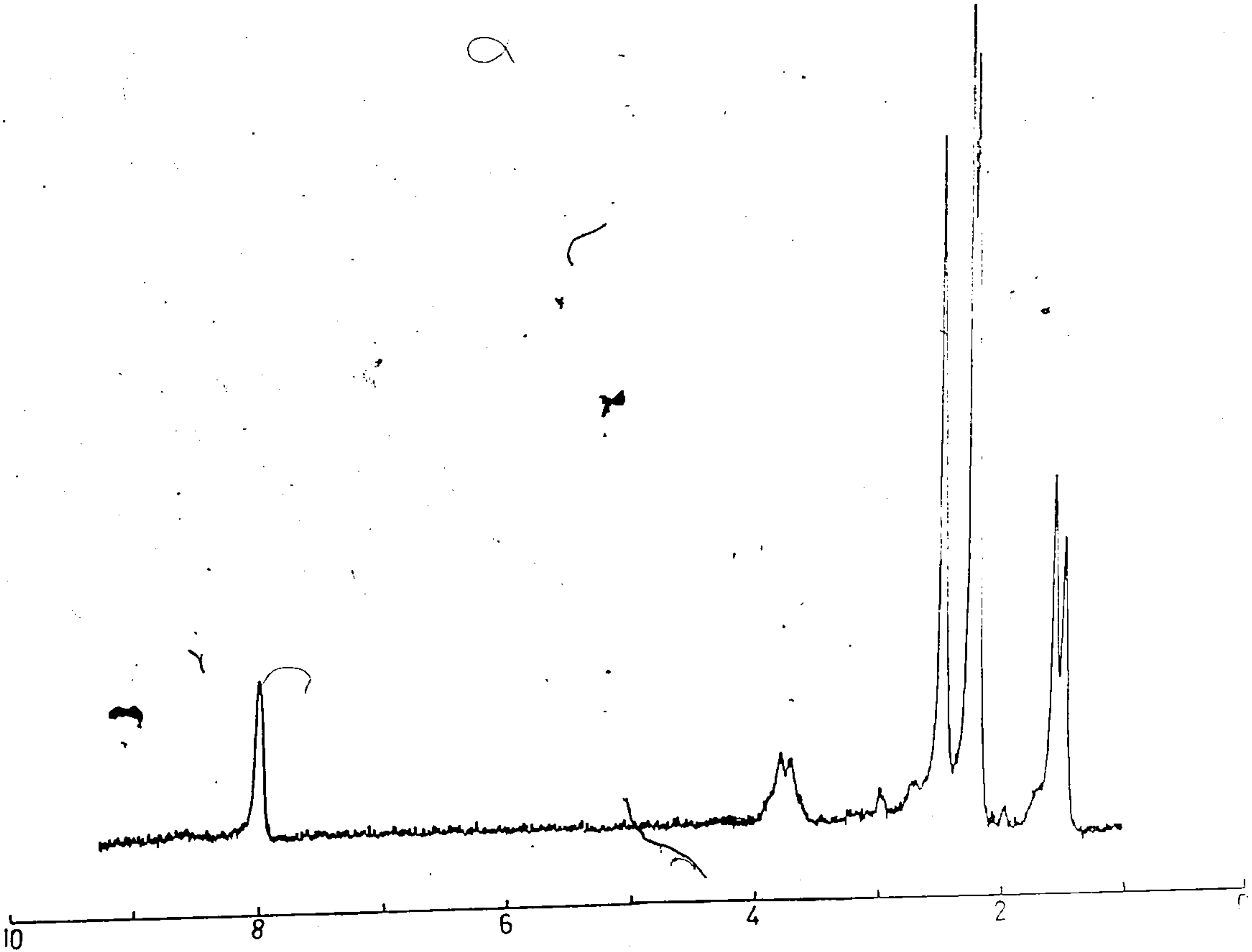


Figure 9. ^1H NMR spectrum of a solution of the phenol <u>57</u> in CF_3SO_3H at -20°C.

The minor isomer was identified as a cation formed by proton attachment at C_6, 66. It was characterized by a broad singlet attributed to the methylene protons at δ 4.0, and singlets at δ 2.6 and 2.25 for the signals of the protons at the two methyl groups at C_3 and C_4 respectively. Other resonances attributable to 66 were not detected, and are probably coincident with resonances of 59H. Similar observations have been reported by Wright et al.[125] for the protonation of 59 in FSO_3H at low temperature.

The UV absorption spectra of the protonated phenols 56H to 65H were measured at room temperature in triflic acid and the results are summarized in Table 2.2.

An attempt was made to measure the emission from cation 58H at room temperature in CF_3SO_3H. No fluorescence was observed.

Photoisomerization of the Protonated Phenols and Identification of Photoproducts

General

Direct irradiations of the protonated phenols were carried out using a Rayonet photoreactor and 300 nm lamps at room temperature, conditions which have been shown to generally maximize the formation of the bicyclic products. The photoisomerizations were followed by ^1H NMR spectroscopy at room temperature directly on the irradiated acid solutions. More detailed product analysis were carried out by GLC after neutralization of the irradiated acid solutions. Control experiments were carried out in each case to ensure that the observed products arose

Table 2.2: UV Spectra of Protonated Phenols in CF_3SO_3H at 25°C

Compound	λ_{max}(nm)	Log ϵ_{max}
<u>56H</u>	329	3.72
<u>57H</u>	324	3.79
<u>58H</u>	328	3.99
<u>59H</u>	385,310	2.63,4.06
<u>60H</u>	326	3.43
<u>61H</u>	328	3.61
<u>62H</u>	300	3.78
<u>63H</u>	305	3.75
<u>64H</u>	304	3.72
<u>65H</u>	306	3.87

photochemically and not thermally. The results are summarized in Table 2.3 and are outlined in succeeding sections.

Pentamethylphenol

A solution of protonated pentamethylphenol 56H in CF_3SO_3H was irradiated at room temperature. After 8 hours ~ 60% of 56H had reacted and from the ^1H NMR spectrum of the resultant acid solution it appeared that a single product had been formed. Neutralization of the irradiated acid solution and GLC analysis confirmed the presence of one photoproduct.

The photoproduct was shown to be the bicyclo[3.1.0]hexenone 67 from its spectroscopic properties. It displayed a strong carbonyl absorption at ca. 1695 cm^{-1}, typical of α,β-unsaturated ketones. Mass spectral analysis of 67 showed that it was isomeric with 56. The ^1H NMR spectrum of this compound (Table 2.3) exhibited five resonances at high field attributable to methyl protons. One of these was a doublet at δ 0.94 for the signal due to the C_6 methyl protons. A value of 6.4 Hz for this coupling constant was indicative for the presence of a proton on C_6,[104,113] consistent with that anticipated for 67. The assignments of the various resonances, shown in Table 2.4, were made by comparison of the chemical shifts to those found in the spectra of other ketones with different substitution patterns obtained in this work and those previously reported.[104,113,126,132]

The assignments of the Carbon^{13} Nuclear Magnetic Resonance (^{13}C) signals of the ring system, shown in Table 2.5, were made by considering the spectra of bicyclo[3.1.0]hexanone 82, 2-cyclopentenone 83, and bicyclo[3.1.0]hexenone 84, shown in the same table, together with the

Table 2.3: Summary of Photoisomerizations of Protonated Phenols

Protonated Phenol	Time of Irradiation hrs	Total Isomerization %	Products[a,b] (%)
<u>56H</u>[c]	8	66	<u>67</u>(100)
<u>57H</u>[c]	40	85	<u>70</u>(53),<u>71</u>(18),<u>72</u>(9),<u>58</u>(20)
<u>57H</u>[d]	32	85	<u>70</u>(28),<u>71</u>(29),<u>72</u>(19),<u>73</u>(7) <u>57</u> and <u>58</u>(19)
<u>58H</u>[c]	40	85	<u>70</u>(53),<u>71</u>(18),<u>72</u>(9),<u>57</u>(20)
<u>60H</u>[c]	40	60	<u>74</u>(82),<u>75</u>(16),others(2)
<u>60H</u>[d]	72	90	<u>74</u>(83),<u>76</u>(17)
<u>61H</u>[c]	253	< 20	unidentified products
<u>62H</u>[c]	216	60	<u>77</u>(35),others(65)
<u>63H</u>[d]	48	60	<u>78</u>(95),<u>79</u>(5)
<u>64H</u>[c]	48	70	<u>81</u>(100)
<u>65H</u>[c]	288	< 5	Unidentified products

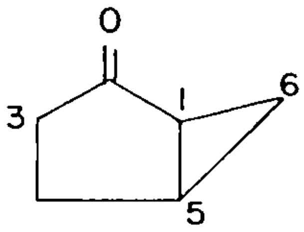
a) Express as a percentage of total products.

b) After neutralization of the irradiated solution with base.

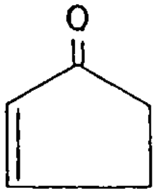
c) In CF_3SO_3H (room temperature).

d) In FSO_3H at -78°C.

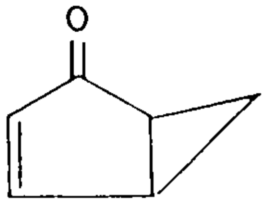
changes occurring in the spectra as the substitution pattern of the bicyclic ketones, is altered. The complexity of the spectra in the high field region (i.e., methyl carbon region) make precise analysis difficult and no assignments have been shown.



82

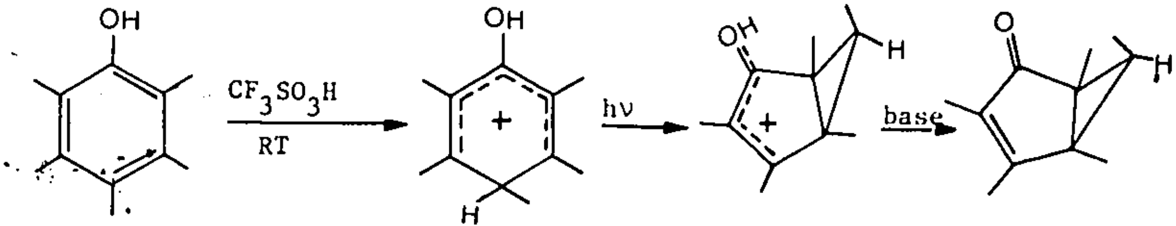


83



84

There are two possible stereoisomers of 67 with either an "endo" or an "exo" methyl group at C_6. The expected chemical shift range of exo- and endo methyl groups would be in the order of δ 1.1 - 1.2 and 0.9 - 1.0 respectively.[85-87,92,95,102,113] The position of the C_6 methyl signal (δ 0.94) in 67 indicates it is the endo isomer, (equation 37). Shielding of the endo methyl groups by the cyclopentenone ring in the bicyclo[3.1.0] ring systems have been adequately established.[93,102,135-141]



56 56H 67H 67

(37)

Table 2.4. ^{1}H NMR Chemical Shifts of Bicyclo[3.1.0]hexenones.[a]

Compound No.	H_1	H_3	H_4	H_5	H_6		Coupling Constants Hz
					endo	exo	
67	(1.34)	(1.63)	(1.92)	(1.25)	(0.94)d	1.41q	$J_{CH_3,H_6} = 6.4$
67H	(1.65)	(1.90)	(2.35)	(1.62)	(1.20)d	2.90q	$J_{CH_3,H_6} = 6.4$
70	(1.33)	(1.47)	(1.96)	(1.20)	0.83d	1.17d	$J_{CH_2} = 3.0$
70H	(1.65)	(1.80)	(2.40)	(1.60)	1.92d	2.85d	$J_{CH_2} = 3.2$
71	(1.35)	(1.63)	(1.98)	2.13d	(0.97)d	1.75m	$J_{5,6} = 7.3$; $J_{CH_3,H_6} = 6.2$
71H	(1.68)	(1.90)	(2.40)	3.50d	(1.25)d	3.35m	$J_{5,6} = 7.0$; $J_{CH_3,H_6} = 6.2$
72	(1.39)	(1.58)	(2.08)	1.64d	1.32m	(1.1)d	$J_{5,6} = 2.3$; $J_{CH_3,H_6} = 5.8$
72H	(1.68)	(1.81)	(2.43)	3.23d	2.83m	(1.35)d	$J_{5,6} = 2.5$; $J_{CH_3,H_6} = 6.0$
73	(1.35)	(1.65)d	6.9d	(1.20)	(0.97)d	1.43q	$J_{CH_3,H_6} = 6.4$; $J_{Me_3,H_4} = 1.4$
73H[e]	(1.70)	(2.03)	8.0	(1.65)	(1.36)d	2.20	$J_{CH_3,H_6} = 6.4$
74	(1.33)	(1.51)	(1.95)	1.88m	1.11m	1.20m	$J_{CH_2} = 3.20$, $J_{5,CH_2} = 3.1$ and 6.3
74H	(1.67)	(1.77)	(2.42)	3.35m	2.25m	2.75m	$J_{CH_2} = 3.0$, $J_{5,CH_2} = 3.0$ and 6.2

..... continued

Table 2.4. (continued)

Compound No.	H_1	H_3	H_4	H_5	H_6 endo	H_6 exo	Coupling Constants Hz
76	(1.35)	(1.56)d	6.95q	(1.24)	0.85d	1.31d	$J_{CH_3,H_4} = 1.3$; $J_{CH_2} = 3.0$
76H[e]	(1.71)	(1.81)d	8.23q	(1.67)	2.18d	3.26d	$J_{CH_3,H_4} = 1.4$; $J_{CH_2} = 3.5$
77	(1.40)	5.35bs	(2.13)	f	1.25m	1.34m	$J_{CH_2} = 3.2$; $J_{5,CH_2} = 3.3$ and 6.7
78	2.23m	(1.55)	(2.05)	2.11m	1.17m	1.43m	
78H	3.27m	(1.77)	(2.45)	3.55m	2.35m	2.60m	
79	(1.25)	5.38d	7.23d	(1.14)	0.75d	f	$J_{CH_2} = 3.1$, $J_{3,4} = 6.0$
81	(1.40)	(1.65)	7.26d	2.16m	1.22m	1.30m	$J_{CH_2} = 2.0$
81H	(1.70)	(1.85)	8.45d	3.55m	2.35m	2.95m	$J_{4,5} = 2.1$

a) Ketones in $CDCl_3$; protonated ketones in CF_3SO_3H; bs = broad singlet, d = doublet, q = quartet, m = multiplet.

b) Numbers in parentheses refer to chemical shifts of methyl resonances.

c) All the NMR spectra were recorded at room temperature unless otherwise specified.

e) At -10°C.

f) Position uncertain.

Table 2.5. ^{13}C NMR Data for Bicyclo[3.1.0]hexenones

Compound	Chemical Shift, ppm										
	C_1	C_2	C_3	C_4	C_5	C_6	Methyl Carbons				
67[a]	37.1	207.7	132.6	165.3	38.7	54.4	14.6	13.1	11.6	8.4	7.3
70[a]	32.5	208.0	128.4	169.4	33.6	46.8	13.5	11.5	10.3	7.66	
70H[b]	40.9	219.5	129.8	209.2	47.0	76.8	17.6	9.5	7.2	5.7	
71[c]	34.3	207.0	133.2	163.5	36.9	46.2	17.1	14.7	7.6	7.2	
72[c]	34.4	208.4	129.3	168.2	38.2	48.0	16.3	14.5	8.7	7.9	
74[d]	29.0	205.3	129.5	166.1	31.2	40.2	16.4	14.0	8.3		
74H[b]	37.4	219.6	131.1	209.6	41.9	70.8	19.4	10.4	6.6		
76[a]	31.9	208.6	134.7	159.2	33.6	48.8	13.3	10.5	10.0		
77[a]	28.3	e	123.8	168.8	33.8	41.7	19.2	13.8			
78[a]	24.4	206.6	129.5	168.2	30.8	34.0	16.3	7.6			
81[a]	29.4	208.0	135.8	155.7	27.3	42.8	13.1	10.0			
81H[b]	40.2	226.0	131.0	186.4	40.8	76.2	10.7	8.7			
82[f]		213.7									
83[g]		208.1	132.9	164.2							
84[h]	22.8	193.2	128.0	162.9	40.0	35.2					

a) In ppm from TMS in $CDCl_3$.

b) In ppm from TMS in CF_3SO_3H.

c) In ppm from TMS in CD_2Cl_2.

d) In ppm from TMS in CCl_4.

e) Position uncertain.

f) Data from reference 133a.

g) Data from reference 133b.

h) Data from reference 134.

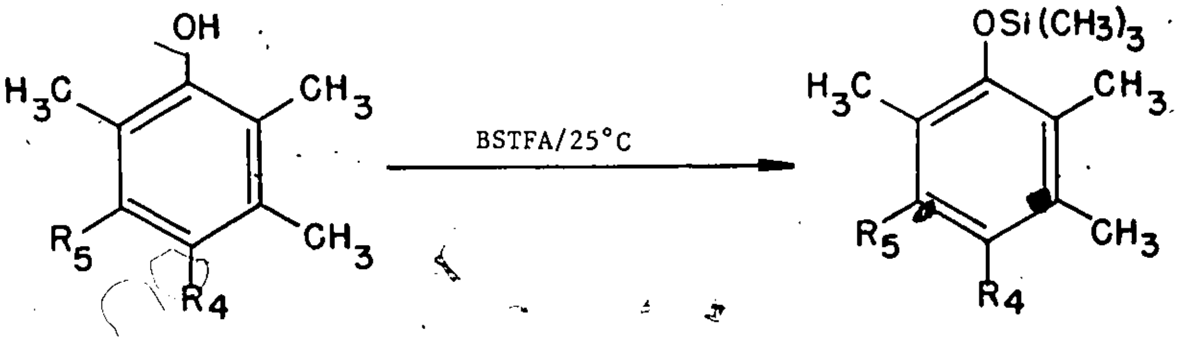
Dissolution of 67 in CF_3SO_3H gave 67H which has a ^1H NMR spectrum which was identical to that obtained from the irradiation of 56H. CF_3SO_3H solutions of 67H were thermally stable for prolonged periods of time.

Tetramethylphenols

Isodurenol in CF_3SO_3H

Irradiation of protonated 2,3,4,6-tetramethylphenol 57H, led to the formation of a mixture of cations. The irradiated acid solution was neutralized and analysed by GLC. The analysis showed four materials to be present in addition to the starting material 57. Three of these materials had very short retention times as compared to the starting material. The fourth material had a very similar retention time to that of 57 and was found to be 58.

A variety of GC conditions were tried in order to cleanly separate mixtures of the two phenols 57 and 58 but with little success. Treatment of a mixture of 57 and 58 with bis(trimethylsilyl)trifluoroacetamide[142] (BSTFA) gave the corresponding trimethylsilyl ethers which could readily be separated, equation 38.



(38)

57 R_4 = Me; R_5 = H

58 R_4 = H; R_5 = Me

68 R_4 = Me; R_5 = H

69 R_4 = H; R_5 = Me

The three short retention time photoproducts were separated by preparative GLC. The structural assignments of these products rests largely on their spectroscopic properties. Mass spectral examination showed that each of these products was an isomer of the starting material. The presence of an α,β-unsaturated carbonyl group in each of the products was clearly indicated by a strong absorption at ca. 1690-1705 cm^{-1} in the infrared spectrum characteristic of bicyclo[3.1.0]-hexenones.[136] The ^1H NMR spectra of each of these products was obtained and is summarized in Table 2.4.

The second component to be collected from the GLC column was shown to be 70 by comparing its spectral properties to those reported by Childs[126] and Baeckström.[127]

^1H NMR spectra of the other two products were very similar and the products were assigned to the structures shown as 71 and 72. No resonances were observed at low field in the ^1H NMR spectrum of either material which could be attributed to vinyl protons. Each spectrum exhibited three sharp singlets and a doublet, each of relative area three, which were attributed to methyl group protons. The presence of two doublets at δ 0.97 and δ 1.1 ($J \sim 6$ Hz) indicated the presence of a methyl group and a proton on C_6. The assignment of the methyl group to C_1 and not C_5 was made by comparison of the chemical shifts of the methyl resonances with other bicyclo[3.1.0]hexenones, Table 2.4, in which it was generally noted that proton resonances of a C_1 methyl substituent are deshielded (0.1 - 0.15 ppm) in comparison with the proton resonance of a methyl group on C_5. Similarly, the resonance of the C_1 hydrogens are also deshielded (0.1 - 0.13 ppm) in comparison with C_5 hydrogen resonances.[113] The latter appeared as doublets at δ 2.13 and 1.64 for 71 and 72 respectively.

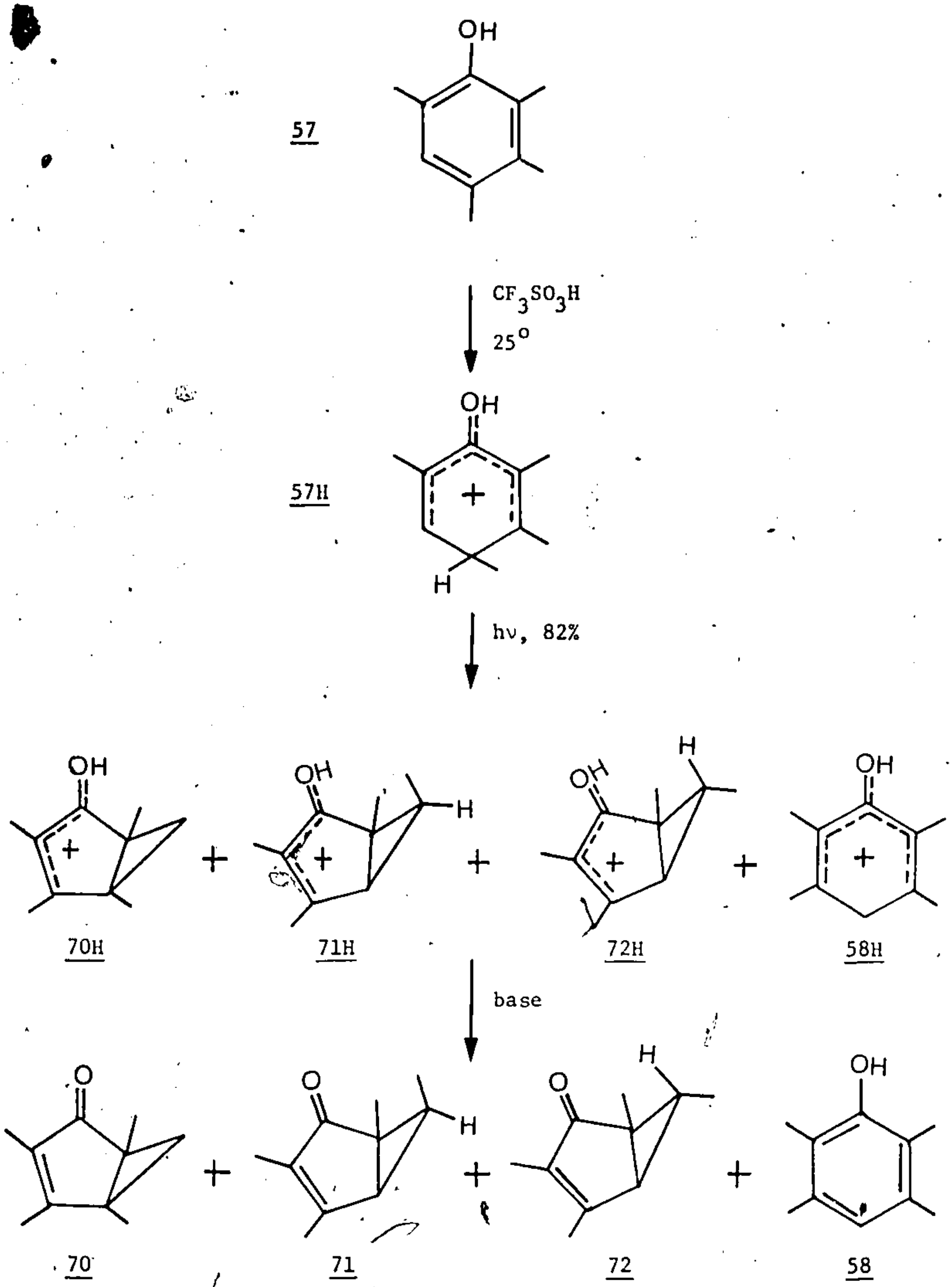
Assignment of the stereochemistry at C_6 was made by comparison of the chemical shifts of the C_6 methyl resonances of 71 and 72 with that of 67. This suggests that 71 is the endo- and 72 the exo-isomer. This assignment of the stereochemistry is confirmed by examination of the positions of the resonances of the C_5 proton. The C_5 proton is extensively deshielded (0.49 ppm) in 71 relative to 72. This is consistent with the above assignments since this proton is respectively anti and syn to the C6 methyl group in 71 and 72.

The ^{13}C NMR spectra, Table 2.5, of these ketones were consistent with the assigned structures. The structures of the products are summarized in Scheme 11.

Further confirmation of these structural assignments were made by dissolution of 70, 71 and 72 in CF_3SO_3H to form the corresponding hydroxy cations 70H, 71H and 72H. The ^1H NMR spectra, Table 2.4, of these cations and the ^{13}C NMR spectra, Table 2.5 of 70H were consistent with the assigned structures.

To establish a clear picture for the photoisomerization of 57H in CF_3SO_3H, it would be desirable to identify the products formed at different time intervals. Plots showing the disappearance of reactant 57H and the growth of photoproducts 70H, 71H, 72H and 58H measured as a function of time are shown in Figures 10 and 11. The latter Figure is simply an expansion of the initial portion of the curves in Figure 10.

In order to probe the mechanistic possibilities for the rearrangement process observed, an experiment in which protonated



Scheme 11

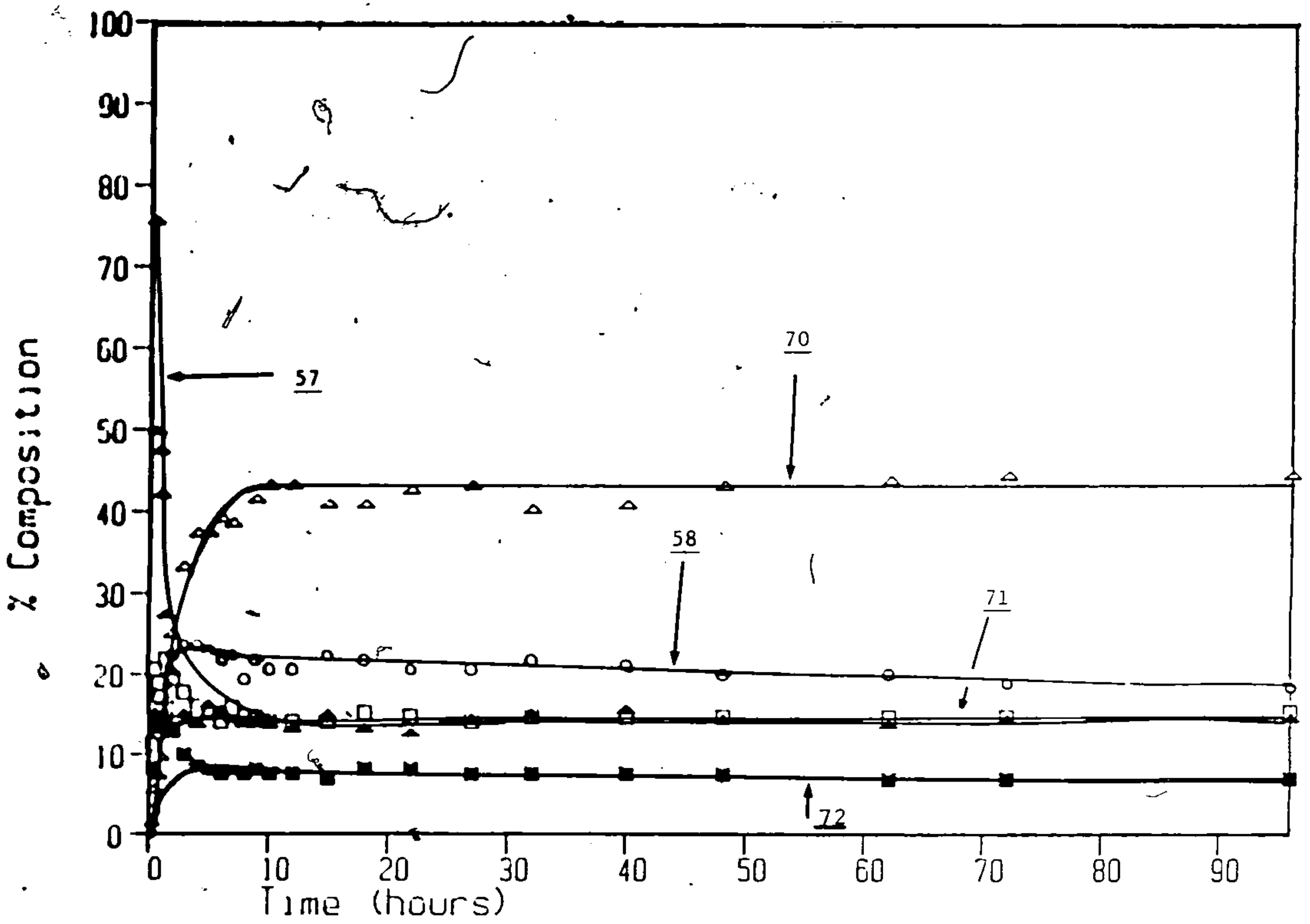


Figure 10. Photoisomerization of Protonated Isodurenol 57H

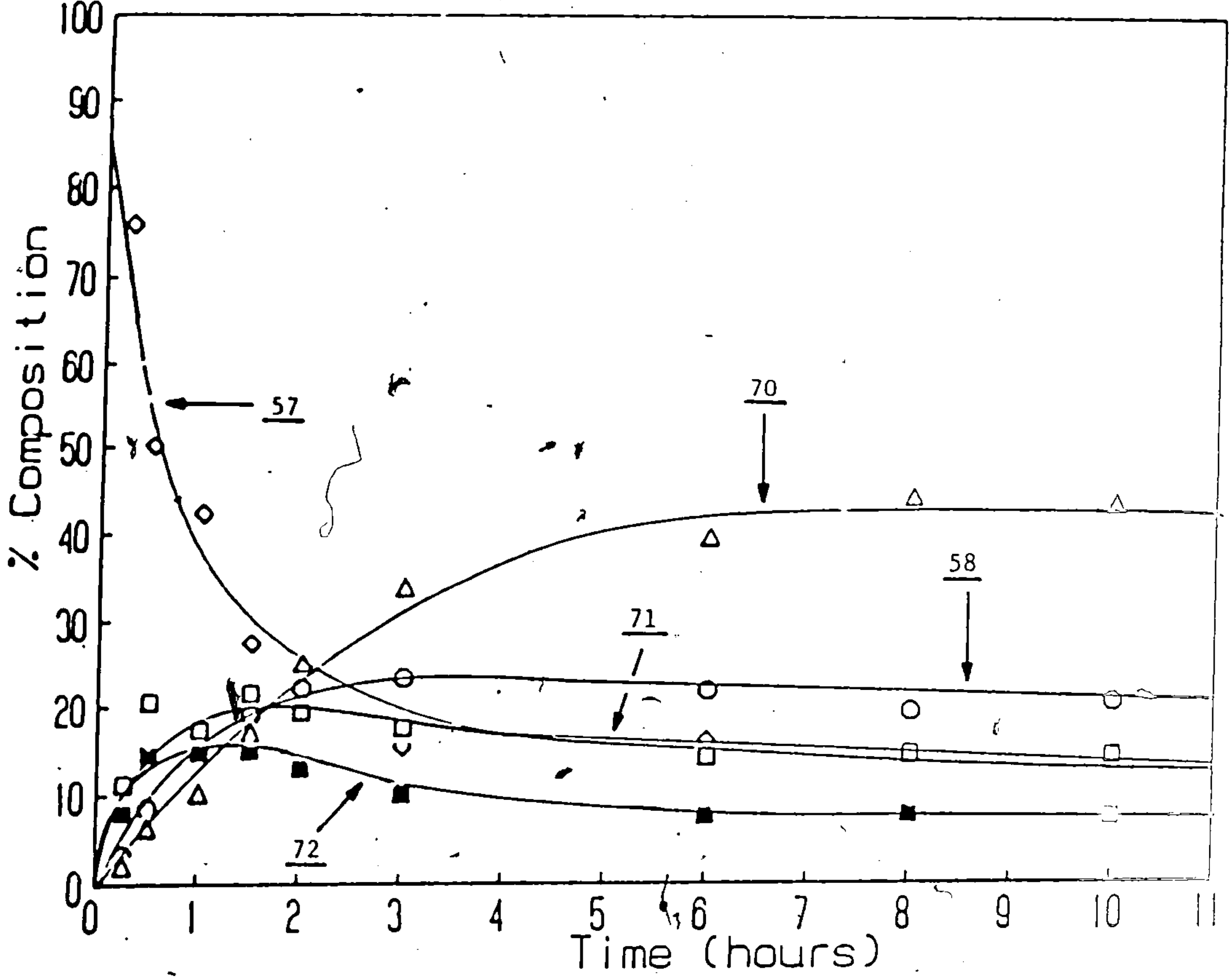


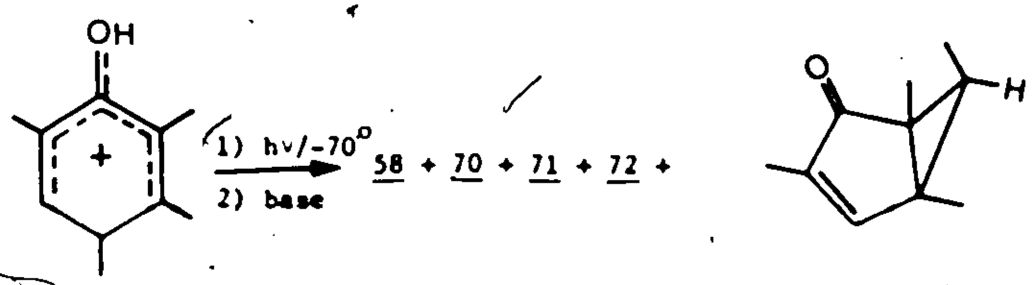
Figure 11. Photoisomerization of Protonated Isodurenol 57H

isodurenol was irradiated for a short time to allow low conversion was carried out at ambient temperatures using light of wavelength (365 nm). GLC analysis of the photolysate showed only the presence of <u>71</u> and <u>72</u> in a ratio of 2:1 with no detectable amount of <u>70</u>.

The photoisomerization of <u>57H</u> was investigated at low temperatures. Because of its relatively high freezing point, CF_3SO_3H is not suitable as a low temperature solvent and FSO_3H was used as the solvent. Irradiations were carried out at -70°C using the same light source as described above. The photoisomerization was followed by low temperature ^1H NMR directly on the irradiated acid solution.

Under these conditions a further minor photoproduct was isolated in addition to those formed at room temperature. Analysis of the ^1H NMR spectrum indicated that this product was <u>73</u>, Table 2.4.

The NMR spectrum of <u>73</u> in $CDCl_3$ exhibits three sharp singlets at δ 1.65, 1.35 and 1.20 corresponding to resonances of methyl protons at C_3, C_1 and C_5, respectively. Another singlet at δ 6.9 corresponding to a proton on C_4. The two remaining signals, δ 0.97 and 1.43, with an intensity ratio of 3:1 have coupling constants (J = 6.14 Hz) consistent with the presence of a methyl and a hydrogen at C_6. The similarity in the chemical shift of the C_6 methyl resonances of <u>67</u>, <u>71</u> and <u>73</u> indicates that this methyl is in the endo position at C_6, equation 39.



(39)

Protonation of 73 in CF_3SO_3H gave 73H. The ^1H NMR spectrum of 73H at -10°C was complelety consistent with the assigned structure. In particular a signal corresponding to the vinyl hydrogen was observed in a position which is characteristic of protonated cyclopentenones.[143,144] At room temperature, cation 73H was found to be thermally unstable and rearrange quantitatively to 57H (see thermal section).

Durenol

The irradiation of 58H was carried out at room temperture under the same conditions as were used for 57H. The reaction was followed by ^1H NMR spectroscopy and it was found that after 41 hours, most of the starting cation had reacted and a series of cations formed. The irradiated acid solution was neutralized to give a mixture which was shown by GLC to consist of four products whose retention times were the same as those obtained on irradiation of 57H. The products were shown to be 57, 70, 71 and 72 by comparing their spectroscopic properties with the corresponding materials isolated from the irradiation of 57H. The changes in the composition of the irradiates solution of 58H are shown in Figure 12.

A similar study on the photoisomerization of 58H in CF_3SO_3H was conducted recently by Baeckström et al.[127] Their results showed the formation of 57 (19%), 59 (7%) and 70 (31%) and three unidentified photoproducts (16%). In the present work, no resonances were observed at low field (δ 6.52) in the ^1H NMR spectra of either photoproducts of 57 or 58 which could be attributed to the aromatic proton of 59. The spectra of 57 and 58 exhibit sharp singlets at δ 6.82 and 6.61 respectively each

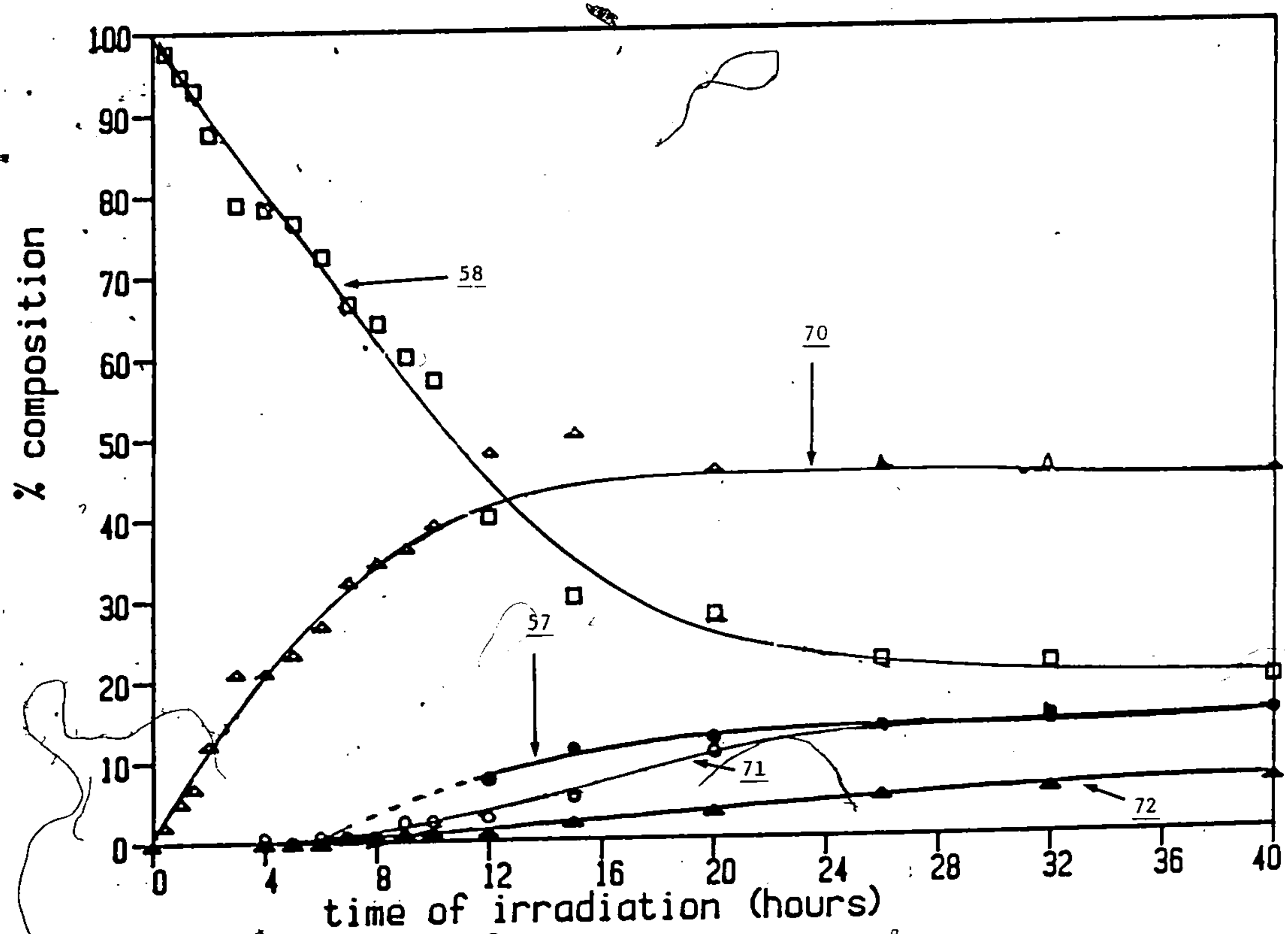


Figure 12. Photoisomerization of 58H

of relative area one and which were attributed to the aromatic protons. Furthermore, it is possible that two of the three unidentified products (m/e 150) observed by Baeckström and coworkers on the irradiation of 58 in CF_3SO_3H are 71 and 72.

Trimethylphenols

2,3,6-Trimethylphenol

Irradiation of protonated 2,3,6-trimethylphenol 60H in CF_3SO_3H at room temperature led to the formation of two products. The acid solution was neutralized and analysed by GLC. Two products in the ratio of 5:1 were shown to be present in addition to the starting material 60.

The major product had a molecular weight of 136 and a strong absorption in the IR at 1694 cm^{-1}, indicating an α,β-unsaturated ketone that is isomeric with the starting material. Analysis of the ^1H NMR indicated that this product was 74, Table 2.4. The ^1H NMR spectrum in $CDCl_3$ shows two sharp singlets at δ 1.95 and 1.51 for the signals corresponding to the C_4 and C_3 methyl groups respectively. Confirmation that these methyl substituents were on the vinylic carbons comes from the absence of any resonance which could be attributed to a vinyl proton. Signals were observed as a singlet at δ 1.33 for the resonance of methyl protons at C_1, a one proton multiplet at δ 1.88 for the signal of H_5, and two multiplets each of relative area one are at δ 1.20 and 1.11 corresponding to the resonance for the methylene protons at C_6. The positions of the ^1H and ^{13}C NMR resonances observed for 74 are very similar to those of other bicyclo- [3.1.0]hexenones. Dissolution of 74 in CF_3SO_3H gave 74H. The ^1H and ^{13}C NMR spectra of 74H was again consistent with the assigned structure.

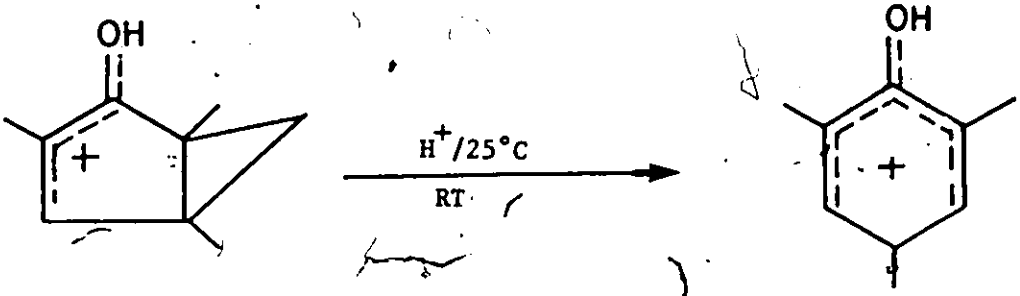
The minor product was shown to be 2,4,6-trimethylphenol, 75, by comparing its ^1H NMR spectrum and GC retention time to those of an authentic sample.

The photoisomerization of 60H at room temperature is summarized in Scheme 12.

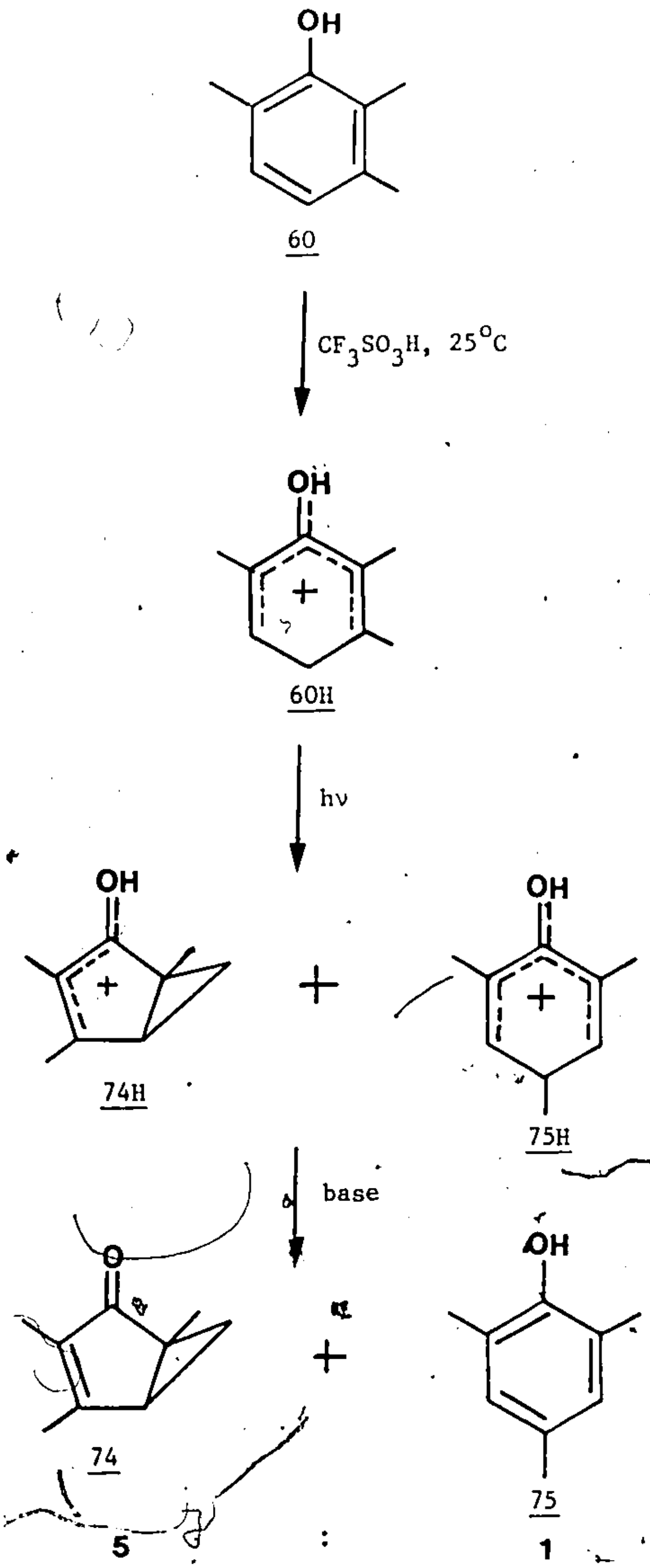
A solution of 60H was irradiated at low temperatures (-70°C) in FSO_3H. The low temperature ^1H NMR spectrum of the resultant acid solution suggested a mixture of products was present. Recovery of the neutral photoproducts by quenching the acid solution gave a mixture which was shown by GLC to consist of two products in the ratio of ~ 5:1. These two products were collected by preparative GLC.

The major product was shown to be 74 by comparing its ^1H NMR spectrum and GLC retention time with an authentic sample.

The ^1H NMR spectrum of the minor product suggested this product was 76. Comparison of this spectrum with that previously reported by Childs et al.[113] confirmed the assignment. Dissolution of 76 in CF_3SO_3H gave 76H. The ^1H NMR spectrum of 76H at -10°C was completely consistent with the assigned structure, Table 2.4. Cation 76H was found to be thermally unstable and rearranged quantitatively to 75H at room temperature, equation 40.



76H 75H (40)



Scheme 12

2,3,5-Trimethylphenol

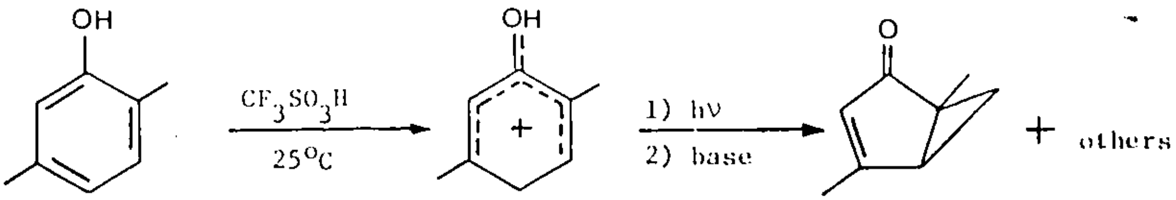
Prolonged irradiation of protonated 2,3,5-trimethylphenol, <u>61H</u>, at room temperature in CF_3SO_3H led to the formation of several new cations. The irradiated acid solution was neutralized to give a mixture which was shown by GLC to consist of at least five materials (total yields < 10%) in addition to the starting material. Their short retention times, suggested that these materials were isomeric bicyclo-[3.1.0]hexenones. However, they were not isolated and characterized because of the small amounts present and the difficulty of their separation. No further attempt was made to investigate this reaction.

Dimethylphenols

2,5-Dimethylphenol

Protonated 2,5-dimethylphenol <u>62H</u> gave a series of cations on irradiation. Recovery of the neutral photoproducts by quenching the acid solution gave a mixture which was shown by GLC to consist of one major and several minor products. The major product was collected by preparative GLC. However, the additional minor photoproducts which had short retention times characteristic of bicyclic ketones, were not isolated and characterized because of the small amounts present.

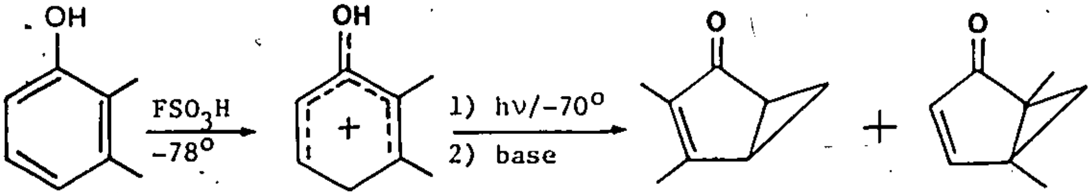
The infrared spectrum of the major photoproduct revealed the presence of an α,β-unsaturated carbonyl group (1701 cm^{-1}). Determination of the molecular weight of the product by mass spectrometry indicated that this photoproduct was isomeric with the starting material. The ^1H NMR spectrum of the material was consistent with <u>77</u>. The spectrum exhibits a singlet at low field (δ 5.35) assigned to the resonance of H_3, another singlet at δ 2.13 due to the methyl resonance at C_4, a further singlet at δ 1.4 for the resonance of the methyl protons at C_1, and a pair of multiplets at δ 1.34 and 1.25 corresponding to the resonances for the methylene protons. The resonances of the vinyl proton on C_3 and the vinyl methyl group on C_4 occur in the region expected on the basis of the spectra of the previous ketones, e.g., 73 and 76, Table 2.4, equation 41.



(41)

2,3-Dimethylphenol

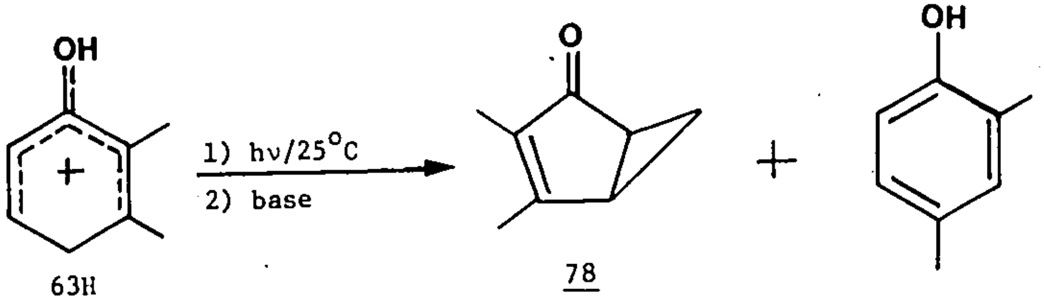
It has been previously reported that the irradiation of protonated 2,3-dimethylphenol 63H in FSO_3H at low temperature (-70°) gave 78 after quenching the acid solution.[113] In this study a further minor photoproduct (~ 5%) was observed on irradiation in FSO_3H in addition to 78 in the GC analysis of the quenched reaction mixture. A sufficient amount of the minor component was obtained for ^1H NMR examination, and it appeared to be 79, equation 42.



(42)

The ^1H NMR spectrum of 79 exhibits two doublets (J = 6 Hz) at δ 5.38 and 7.23 attributed to the signals of the two vinyl hydrogens at C_3 and C_4 respectively. A pair of sharp singlets at δ 1.25 and 1.14 correspond to the resonances for the methyl protons at C_1 and C_5 respectively. The remainder of the spectrum consists of a doublet (J = 4 Hz) at δ 0.74 for the signal of H_6, while the other H_6 signal overlaps the C_5 methyl signal at δ 1.14.

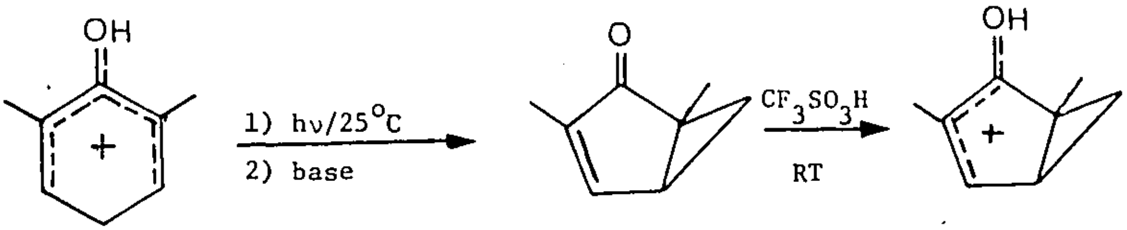
Irradiation of 63H at room temperature in CF_3SO_3H gave, after neutralization of the acid solution, 78 and a further compound identified as phenol 80, equation 43. Compound 80 was identified by comparing its GLC retention time to that of authentic material.



(43)

2,6-Dimethylphenol

Irradiation of 64H in CF_3SO_3H was carried out under the conditions described earlier to give a solution whose ^1H NMR spectrum was simple enough to suggest the formation of only one product. The neutralized solution contained a single photoproduct, as shown by GLC. This product was obtained in pure form by preparative GLC and assigned the structure 81. The identity of 81 was based on the comparison of its ^1H NMR spectrum with that previously reported by Childs et al.[113] In addition protonation of 81 in CF_3SO_3H resulted in the formation of 81H whose ^1H NMR spectrum, Table 2.4, was very similar to that previously reported in FSO_3H,[113] equation 44.



64H 81 81H

(44)

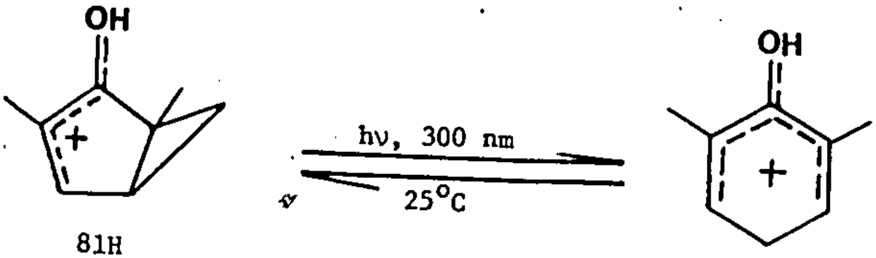
3,5-Dimethylphenol

In contrast to the ease of photoisomerization of the above dimethylphenols, no photorearrangement could be detected by ^1H NMR spectroscopy after irradiation of a solution of protonated 3,5-dimethylphenol 65H for 12 days. Neutralization of the acid solution gave a mixture which was shown by GLC to consist primarily of 65 (96%) and a complex mixture (~ 4%) of photoproducts. No attempt was made to separate these small amounts.

Photoisomerization of Protonated Bicyclo[3.1.0]hexenone

The UV absorption spectra of a number of protonated bicyclic ketones were measured at room temperature, Table 2.6. As in the case of other previously reported examples of protonated bicyclic ketones,[113] all the protonated bicyclic ketones exhibit absorption maxima at ca. 330 nm.

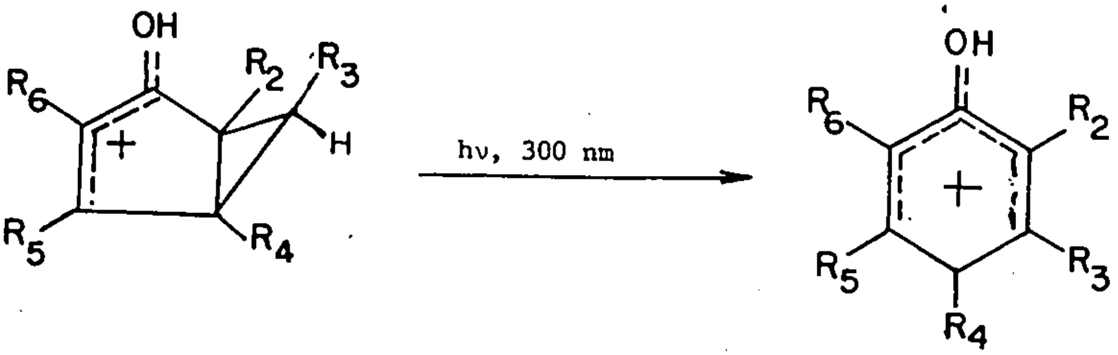
Ketone 81 dissolved in triflic acid, was irradiated at room temperature with 300 nm light. This led to the formation of <u>64H</u> as shown by ^{1}H NMR. A photostationary mixture consisting of <u>81H</u> (70%) and <u>64H</u> (30%) was rapidly formed. Irradiation of <u>64H</u> under similar conditions gave a reaction mixture of the same composition as when starting with protonated ketone <u>81H</u>, equation 45.



<u>81H</u> <u>64H</u> (45)

Similar photoinduced isomerizations of protonated bicyclic ketones have been examined and the results are summarized in Scheme 13.

<u>Scheme 13</u>



<u>67H</u> $R_2 = R_3 = R_4 = R_5 = R_6 = $ Me

<u>70H</u> $R_2 = R_4 = R_5 = R_6 = $ Me; $R_3 = $ H

<u>74H</u> $R_2 = R_5 = R_6 = $ Me; $R_3 = R_4 = $ H

<u>78H</u> $R_5 = R_6 = $ Me; $R_2 = R_3 = R_4 = $ H

<u>56H</u> $R_2 = R_3 = R_4 = R_5 = R_6 = $ Me

<u>58H</u> $R_2 = R_3 = R_5 = R_6 = $ Me; $R_4 = $ H

<u>60H</u> $R_2 = R_3 = R_6 = $ Me; $R_4 = R_5 = $ H

<u>63H</u> $R_5 = R_6 = $ Me; $R_2 = R_3 = R_4 = $ H

Table 2.6. UV Spectra of Bicyclo[3.1.0]hexenones[a,b,c]

Compound No.	λ_{max}, nm	log ε
67H[a]	332	3.65
71H[a]	336	3.50
72H[a]	332	3.40
78H[b]	330	3.50
74[c]	266	3.42
78[c]	262	3.67
81[c]	260	3.43

a) In H_2SO_4 at room temperature.

b) In CF_3SO_3H at room temperature.

c) In absolute ethanol.

Quantitative Measurements

The quantum efficiencies for the photoisomerization of a number of protonated methyl substituted phenols in CF_3SO_3H were measured at 25° relative to the photodecomposition of potassium ferrioxalate.[145] An optical bench set up was employed with a high pressure mercury lamp as the light source. A monochromator was used to select the irradiation wavelength of 313 nm with a 24 nm band width. After irradiation the neutral photoproducts were recovered by quenching the acid solution with base. The photolytic conversion of the starting material to products was assayed by quantitative analytical GLC. In all cases the reactions were carried out to less than 10% conversion. The results of this study are summarized in Table 2.7.

The effect of dissolved oxygen on the quantum yields was determined by degassing with dry argon bubbled throught the samples prior to irradiation. Data are included in Table 2.7.

Since the sample concentrations were relatively high, it seemed possible that a layering effect might occur. The results, Table 2.7, showed no detectable change in the measured quantum efficiencies when the solution was stirred by an argon stream during the irradiation.

All the quantum yields given in Table 2.7 are for the forward reactions and are not corrected for any back photoreaction. The quantum efficiencies of a number of reverse (protonated bicyclo[3.1.0]hexenones → protonated phenols) reactions, Scheme 13, were also measured at 313 nm, using an analogous procedure to that described above, Table 2.8.

Table 2.7. Quantum Yields for Formation of Bicyclo[3.1.0]hexenones

Reaction	Quantum Yield[a]	
	Aerated[b]	Degassed & Stirred[c]
56H → 67H	0.20 ± 0.03	0.19 ± 0.02
57H → $\frac{\text{71H}}{2} \overset{+}{:} \frac{\text{72H}}{1}$	0.49 ± 0.01	
58H → 70H	0.24 ± 0.01	0.24 ± 0.01
60H → 74H	0.50 ± 0.01	
63H → 78H	0.38 ± 0.02	0.38 ± 0.03
64H → 81H	0.65 ± 0.02	
65H → Product	0.018 ± 0.001	

a) Measured relative to the photodecomposition of potassium ferrioxalate[145] at 313 nm.

b) Errors are standard deviation of at least three runs.

c) Errors are the deviation from the mean.

Table 2.8. Quantum Yields of Isomerization for Bicyclo[3.1.0]hexenone Cations

Reaction	Quantum Yields[a,b]
<u>67H</u> → <u>56H</u>	0.21 ± 0.02[c]
<u>70H</u> → <u>57H</u>	0.19 ± 0.02[c]
<u>74H</u> → <u>60H</u>	0.24 ± 0.02
<u>78H</u> → <u>63H</u>	0.16 ± 0.01

a) Measured relative to the photodecomposition of potassium ferrioxalate[145] at 313 nm.

b) Errors are the deviation from the mean.

c) Same value for aerated or argon degassed solution.

Part II:

Protonation and Photoisomerization of Protonated Chlorophenols

This section extends the previous studies on polymethyl substituted phenols to include excited state reactions of protonated chloro substituted phenols.

Protonation of Chloro Substituted Phenols

The chlorophenols studied were 2-chloro-, 3-chloro, 3,5-dichloro-, and 2-chloro-5-methylphenols, 85, 86, 87 and 88 respectively. There are previous reports on the protonation of 85 and 86 in a variety of superacid media.[119] The protonation of 87 and 88 have not been reported.

The protonation of phenols 85 and 86 were reexamined in super-acid media not used by Olah and Mo.[119] Two acids were used for the protonation, FSO_3H at low temperture (acid I), and a mixture of CF_3SO_3H-SbF_5 (3:1) at room temperature (acid II). The results are summarized in Table 2.9.

Protonation of 2-Chlorophenol

Protonation of 85 in FSO_3H (acid I) at -78° gave two isomeric ions, these were identified from their ^1H NMR spectra, Table 2.10, as the C-protonated species 85H (30%), and the O-protonated species 89 (70%), equation 46. The chemical shifts of the proton resonances of the two cations are very similar to that which has been reported by Olah and Mo.[119]

Table 2.9. Site of Protonation of Chlorosubstituted Phenols

Compound No.	Acid[a,b]	Ion Formed (%)	
		C_4	oxygen
<u>85</u>	I	<u>85H</u> (30)	89(70)
<u>86</u>	I	<u>86H</u> (100)	0
<u>86</u>	II	<u>86H</u> (100)	0
<u>87</u>	I	<u>87H</u> (60)	90(40)
<u>87</u>	II	<u>87H</u> (100)	
<u>88</u>	I	<u>88H</u> (100)	
<u>88</u>	II	<u>88H</u> (100)	

a) Acid I is FSO_3H at -60°.

b) Acid II is a mixture of $CF_3SO_3H-SbF_5$ (3:1) at room temperature.

Table 2.10. ^{1}H NMR Chemical Shifts of Protonated Chlorophenols

Compound No.	H_2	H_3	H_4	H_5	H_6	Coupling Constant Hz
85^c	–	8.97	4.83	9.11	7.90^e	
86^c	7.70	–	4.67d	8.73(d,t)	7.54d	$J_{5,6} = 9.0$; $J_{5,CH_2} = 2.0$
87^{c,f}	7.34	–	4.55	–	7.34	
88^{c,f}	–	8.32t	4.37d	2.63 (Me)	7.25	$J_{3,CH_3} = 4.5^g$
90^c	7.40	–	7.56	–	7.40	

a) d = doublet, m = multiplet, t = triplet.

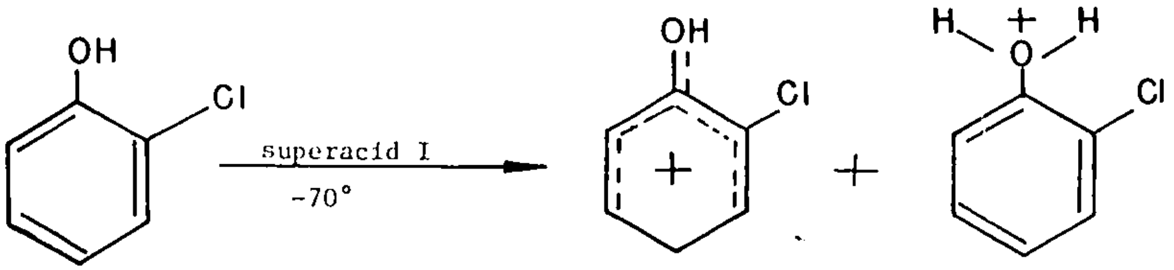
b) OH proton is not observable owing to rapid hydrogen exchange with the solvent.

c) In ppm from $(CH_3)_3N^+BF_4^-$ (3.10 ppm) in FSO_3H at -60°.

e) Hidden under aromatic protons of III 89.

f) In ppm from $(CH_3)_4N^+BF_4^-$ (3.10 ppm) in CF_3SO_3H-SbF_5 at room temperature.

g) Multiplicity was only observed with method f.

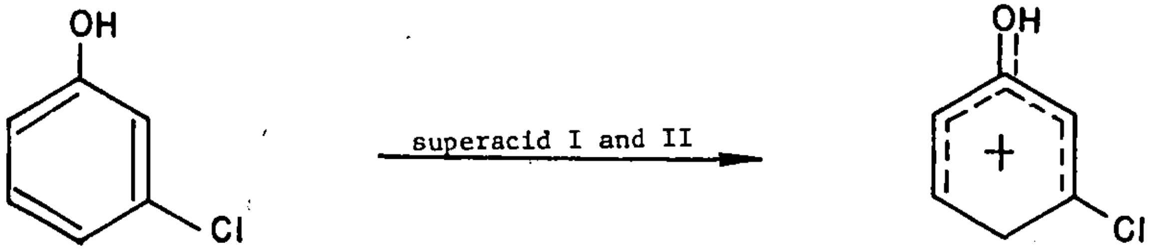


85 85H 89

(46)

Protonation of 3-Chlorophenol

The cation 86H, was prepared by dissolving 86 in superacids I or II, equation 47. The ^1H NMR spectrum of this cation, Table 2.10, corresponds to that previously reported for 86H in different acid media.[119]

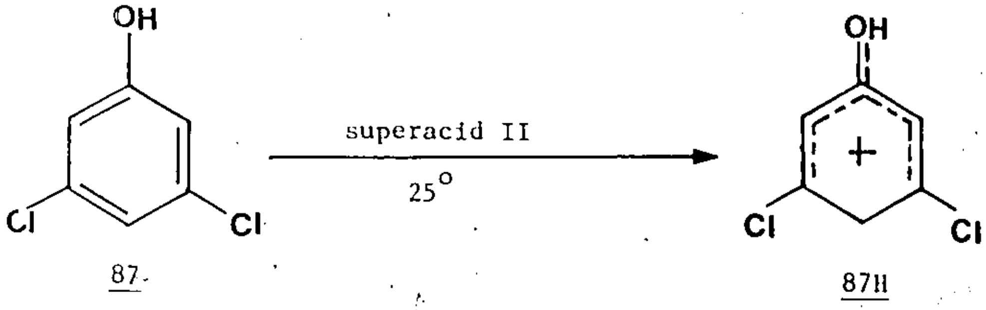


86 86H

(47)

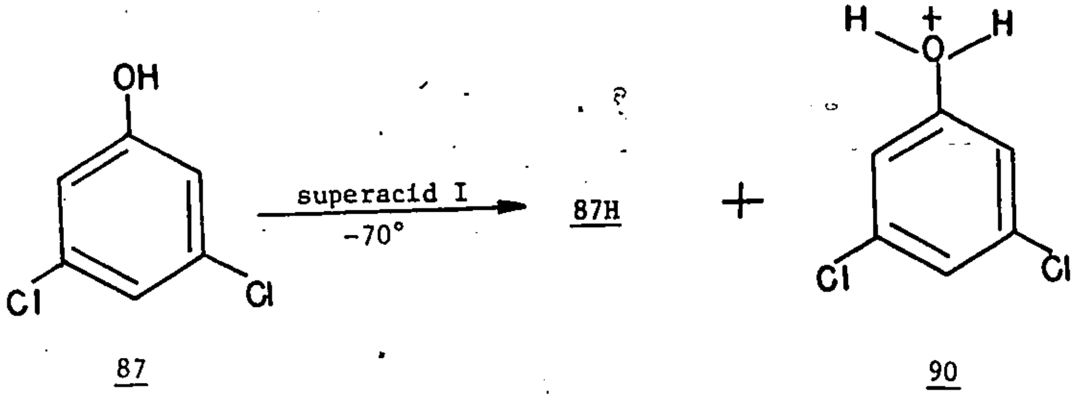
Protonation of 3,5-Dichlorophenol

Dissolution of 87 in superacid II gave the corresponding C_4-protonated benzenium ion 87H. Evidence for the formation of this benzenium ion came from the ^1H NMR spectrum which shows two sharp singlets (δ 4.55 and 7.34), each of relative area two. These were assigned to the methylene and the two equivalent hydrogens at C_2 and C_6, respectively.



(48)

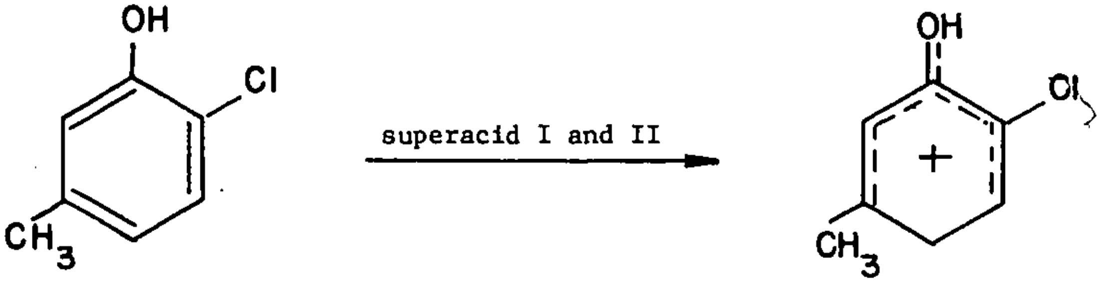
When 87 was protonated in superacid I, the ^{1}H NMR spectrum of the solution exhibited, two additional sharp singlets at δ 7.40 and 7.56 with a relative area of 2:1, respectively. The positions of these two signals, along with their relative ratio, suggest the presence of the oxonium ion 90, equation 49. The ratio of ions 87H:90, was determined by integration of the NMR spectrum.



(49)

Protonation of 2-Chloro-5-Methylphenol

The phenol, 88, readily dissolved in superacid I and II to give one product whose ^1H NMR spectrum was consistent with the C_4 protonated species 88H, equation 50. The low field region of the ^1H NMR spectrum, Table 2.10, consisted of a triplet (δ 8.32; J = 4.5 Hz) and a sharp singlet (δ 7.25) each of relative area one attributed to H_3 and H_6 respectively. The high field region of this spectrum exhibited one sharp singlet at δ 2.63 and a doublet δ 4.37 (J = 4.5 Hz) of relative area three and two respectively. These were assigned to the methyl and methylene protons, respectively.



88 88H (50)

The absorption spectra of FSO_3H solutions of phenols 85 to 88 were obtained, Table 2.11. These protonated phenols exhibit absorption maxima in the same range of those of C-protonated methyl substituted phenols, Table 2.2, and protonated 2,5-cyclohexadienones (i.e., 300 - 330 nm).[99,100,130,131] It can also be seen that both 85 and 87 have strong absorption maxima at wavelengths below 300 nm. Similar UV spectra have been reported for O-protonated phenols.[146]

Table 2.11. UV Spectra of Protonated Chlorophenols*

Compound	λ_{max}(nm)	Log ϵ_{max}
<u>85</u>	262,306	3.87,3.78
<u>86</u>	304	3.28
<u>87</u>	259,332	4.19,3.10
<u>88</u>	313	3.18

* In FSO_3H at -70°C.

Photochemistry of Protonated Chlorophenols

Direct irradiation of solutions of the protonated chlorophenols 85 - 88 in superacid I and II were carried out. Use of acid II was not promising because of decomposition, therefore only reactions in acid I were studied in detail. The reactions were followed by low temperature ^1H NMR spectroscopy directly on the irradiated acid solutions.

2-Chlorophenol

Low temperature (-70°) irradiation of protonated 2-chlorophenol, 85H, in FSO_3H at 300 nm led, as indicated by ^1H NMR, to the formation of a new product. The irradiated acid solution was neutralized to give a solid which, after sublimation, gave colorless crystals.

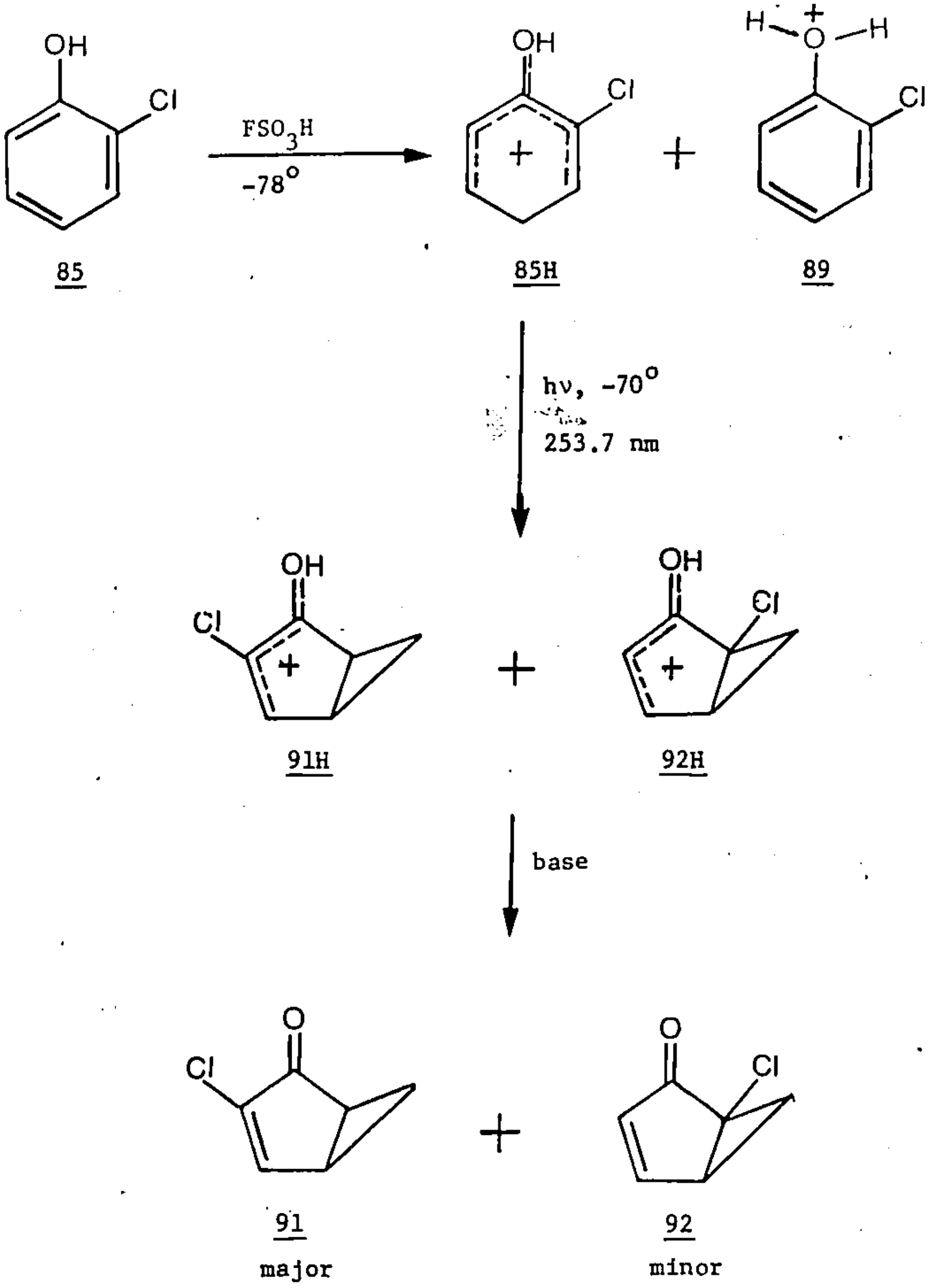
Mass spectral analysis of the solid revealed a molecular weight of 210 corresponding to the presence of fluorosulfonated product. Evidence to support this comes from the strong absorptions in the IR spectrum at 1410 and 1210 cm^{-1} attributed to the antisymmetric and symmetric stretch of the $-SO_2F$ group respectively.[147] The low field resonances of the ^1H NMR spectrum suggest the presence of more than one product. These results seem to indicate the formation of a mixture of fluorosulfonated isomers of the corresponding starting material. No attempts were made to separate or identify these isomers.

In contrast, irradiation of 85H in FSO_3H at 253.7 nm using quartz apparatus led to the formation of different products to those obtained above. Neutralization of the irradiated solution gave a mixture which was shown by GLC to consist of two products in a 6:1 ratio. The two photoproducts were separated by preparative GLC.

The structural assignments of the products rests largely on their spectroscopic properties. Mass spectral examination showed that each of the two products were isomers of the starting material. The presence of an α,β-unsaturated carbonyl group in each of the products, was clearly indicated by a strong absorption at 1703 and 1720 cm^{-1} in the infrared spectra, an absorption typical of bicyclo[3.1.0]hexenones.[136] The ^1H NMR spectra of each these products was obtained and is summarized in Table 2.12.

^1H NMR spectra of the major product in $CDCl_3$ exhibited a doublet (J = 2.7 Hz) of relative area one at δ 7.55 for the signal corresponding to H_4, and a pair of multiplets of relative area one at δ 2.27 and 2.54 corersponding to the resonances for H_1 and H_5 respectively. The remainder of the spectrum consisted of two multiplets at δ 1.43 and 1.51 which were assigned to the cyclopropyl methylene proton resonances. These results are consistent with the structure indicated by <u>91</u>, Scheme 14.

The ^1H NMR analysis of the minor product indicated that this product was <u>92</u>, Table 2.12. The NMR spectrum in $CDCl_3$ showed a doublet of relative area one at δ 5.73 (J = 6 Hz) for the signal of H_3, and a doublet of doublets of relative area one at δ 7.55 (J = 6 and 2.7 Hz) for the signal corresponding to H_4, a multiplet of relative area one at δ 2.76 for the resonance of H_5. The presence of two multiplets each of relative area one at δ 1.81 - 1.90 is due to the resonances of the methylene protons at C_6.


OH
Cl
FSO3H
-78°
85
OH
Cl
+
85H
+
H
O
H
Cl
89
hν, -70°
253.7 nm
OH
Cl
+
91H
+
OH
Cl
+
92H
base
O
Cl
91
major
+
O
Cl
92
minor

Scheme 14

Table 2.12. ^1H Chemical Shifts of Chlorobicyclo[3.1.0]hexenones[a]

Compound No.	Chemical Shift, ppm H_1	H_3	H_4	H_5	H_6		Coupling Constant Hz
91	2.27	-	7.55d	2.54m	1.51m[b]	1.43m[b]	$J_{4,5} = 2.7$, $J_{1,5} = 4.5$, $J_{CH_2} = 3.2$ $J_{5,CH_2} = 7$ and 5.3
92	-	5.73d	7.55d,d	2.76m	1.81 -	1.90m	$J_{3,4} = 6$, $J_{4,5} = 2.7$, $J_{CH_2} = 3.1$ $J_{5,CH_2} = 7.4$ and 1.0
93	2.32m	5.62	-	2.62m	1.55 -	1.61m	$J_{1,5} = 4.4$, $J_{5,CH_2} = 7$ and 5.8 $J_{CH_2} = 3.1$
94	2.47m	5.65d,d	7.54d	-	1.90 -	1.96m	$J_{3,4} = 5.8$, $J_{3,1} = 1.5$ $J_{1,CH_2} = 7.1$ and 1.1, $J_{CH_2} = 3.3$

a) Ketones in $CDCl_3$, d=doublet, d,d = doublet of doublet, m = multiplet.

b) Assignments may be reversed.

3-Chlorophenol

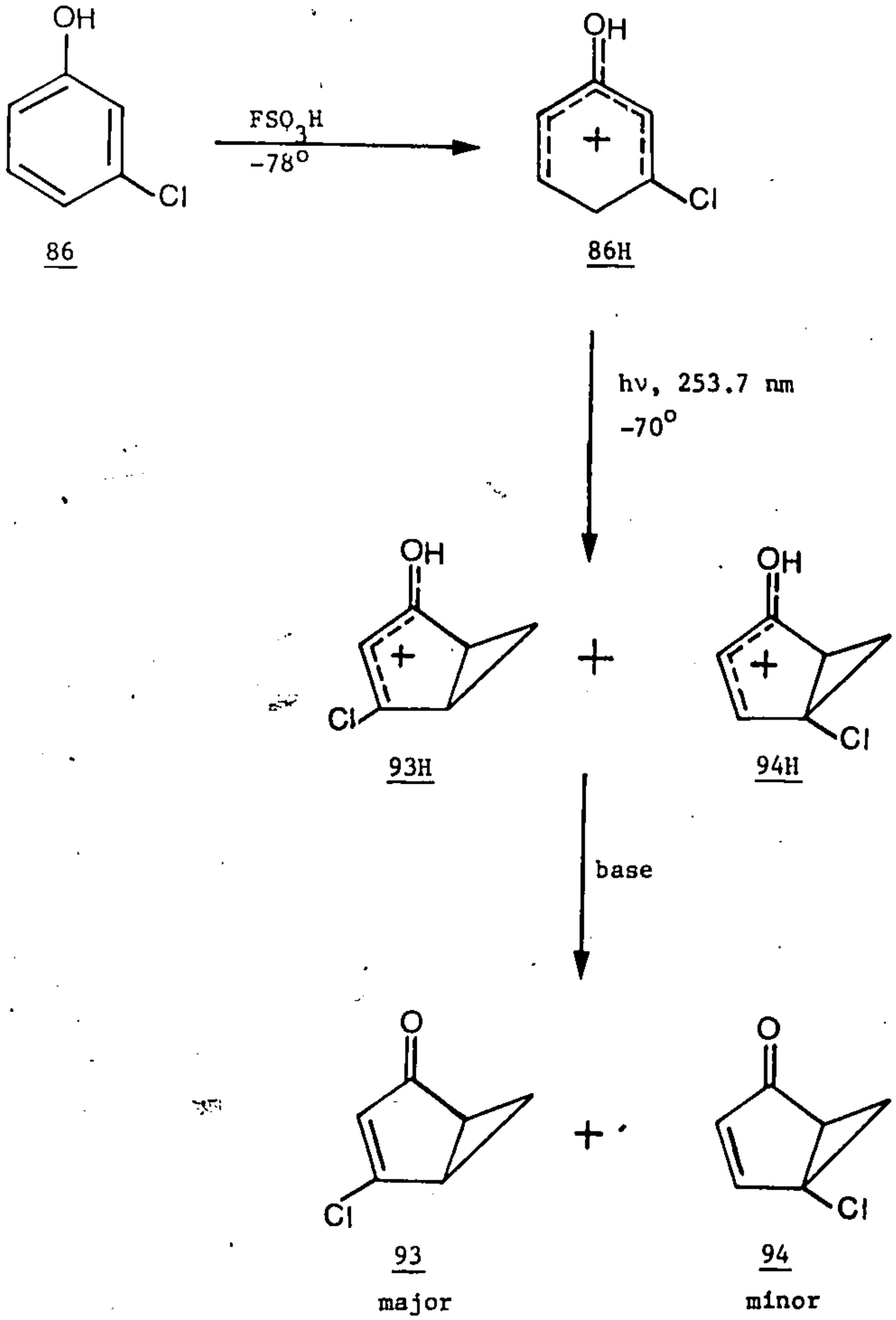
As in the previous case, irradiation of 86 in FSO_3H at 300 nm gave a solid product after neutralization of the acid solution.

The spectroscopic properties of this solid (IR, MS and NMR) again indicated the presence of a mixture of fluorosulfonated isomers derived from the corresponding starting material.

When the above experiment was repeated using 253.7 nm lamps, the photoisomerization took a different course. Neutralization of the acid solution followed by separation using preparative GLC gave two products in a ratio of 9:1.

The major photoproduct was shown by mass and IR spectroscopy to be an α,β-unsaturated ketone that was isomeric with 86. The ^1H NMR spectrum, Table 2.12, showed a pair of multiplets each of relative area one at δ 2.32 and 2.62 for the signals corresponding to the protons at C_1 and C_5 respectively, and a singlet of relative area one at δ 5.62 for the resonance of H_3. The presence of a multiplet of relative area two at δ 1.61 - 1.55 is indicative of the presence of methylene protons at C_6. These data are similar to those obtained for the ketone 91, except for the C_3 and C_4 hydrogens in the NMR spectrum, and suggest that this compound has structure 93.

The minor component was shown to be 94. This ketone had IR and mass spectra which were similar to those of ketones 91 - 93. The ^1H NMR spectrum of this ketone showed a doublet at δ 7.54 (J = 5.8 Hz) for the signal of H_4, a doublet of doublets at δ 5.65 (J = 5.8 and 1.5 Hz) for the signal corresponding to H_3, a multiplet at δ 2.47 for the resonance


OH
Cl
86
FSO$_3$H
-78°
86H
hν, 253.7 nm
-70°
93H
94H
base
O
93
major
94
minor

Scheme 15

of H_1, and a two proton multiplet at δ 1.90 – 1.96 corresponding to resonances for the methylene protons at C_6, Scheme 15.

Disubstituted Chlorophenols

In contrast to the photoisomerizations seen with <u>85H</u> and <u>86H</u>, no isomerization could be detected on irradiation of protonated <u>87H</u> and <u>88H</u> with light of wavelengths 253.7 at 300 nm in either super acids I or II, Table 2.13.

PART III:

Thermal Isomerization of Protonated Bicyclo[3.1.0]hexenones

All the protonated methyl substituted bicyclo[3.1.0]hexenones were found to isomerize cleanly to protonated phenols when heated in triflic acid. No products other than protonated phenols could be detected by ^{1}H NMR at any time during these isomerizations or by GLC after quenching the reaction mixture.

The rate constants for these isomerizations were determined by heating an acid solution of the appropriate cation in a constant temperature both for known lengths of time and quenching the reaction by rapidly cooling the sample to room temperature. The composition of the solution was determined using ^{1}H NMR spectroscopy. At least two independent runs were made for each reaction.

In each case good first-order kinetics were observed, e.g. Figures 13 and 14. The results of this study are summarized in Table 2.14.

Table 2.13. Summary of the Photoisomerization of Protonated Chlorophenols

Protonated Phenol	Wavelength (nm)	Time of Irradiation (hrs.)	Total Isomerization (%)	Products[c,d] %
85H[a]	300	60	-	fluorosulfonated
85H[a]	253.7	20	10	91(84), 92(16)
85H[a]	-	60	0	-
86H[a]	300	60	-	fluorosulfonated
86H[a]	253.7	20	40	93(90), 94(10)
86H[a]	-	60	0	-
87H[a]	300	16	0	-
87H[a]	253.7	48	0	-
87H[b]	253.7	10	0	-
88H[a]	300	20	0	-
88H[a]	253.7	28	0	-
88H[b]	253.7	12	0	-

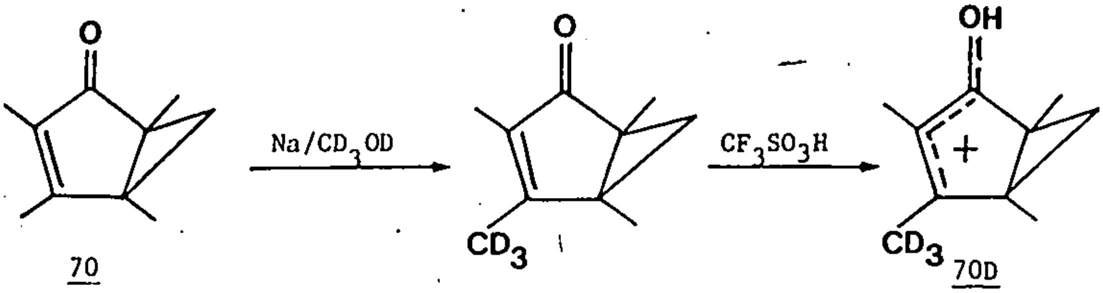
a) In FSO_3H at -70°C.

b) In $CF_3SO_3H-SbF_5$ (3:1) at room temperature.

c) After neutralization of the irradiated acid solution with base.

d) Expressed as a percentage of total products.

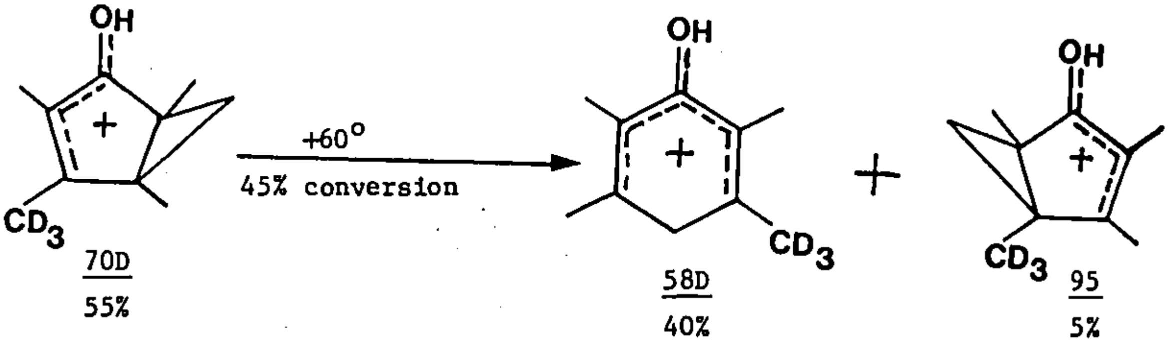
In order to gain further insights into the nature of the rearrangement processes involved, the isomerization of cation 70D was examined.



(51)

A circumambulatory rearrangement of 70D would result in equilibration of the CD$_3$ label, initially at C$_4$, with the methyl upon C$_5$. If this process occurred it could be followed experimentally by observing the increase in the intensity of the signal for the C$_4$ methyl protons and decrease in the intensity of the signal for C$_5$ methyl protons, in the ^{1}H NMR spectrum of 70D. The deuteration of 70 was carried out using CD$_3$ONa/CD$_3$OD.[111] The degree of D incorporation was 98%. Protonation gave 70D in which the ^{1}H NMR was identical with that of unlabelled 70D except that the peak at δ 2.40 was absent.

On warming 70D in CF$_3$SO$_3$H to +40°, the ratio of the integrals for the methyl groups of C$_4$ and C$_5$ signal in the ^{1}H NMR spectrum did not change. At +60°, 70D rearranged to give (after 45% conversion) two new cations. Based on their ^{1}H NMR spectra the structures 58D (40%) and 95 (5%) were assigned to these cations, equation 52.



(52)

Table 2.14. Isomerizaton rate constants for the bicyclo[3.1.0]hexenones in CF_3SO_3H

Reaction	rate constant[a], sec^{-1}			$\Delta G^{\ddagger}$[b] kcal/mole
	60 ± 0.5°C	100 ± 0.5°C	Other (Temp.)	
7H → 56H	$7.3 \pm 0.3 \times 10^{-5}$	$5.30 \pm 0.50 \times 10^{-3}$		25.8 ± 0.8
70H → 58H	$6.2 \pm 0.40 \times 10^{-5}$	$2.90 \pm 0.2 \times 10^{-3}$		26.2 ± 0.8
71H → 58H	$1.70 \pm 0.10 \times 10^{-5}$	1.50×10^{-3}[c]		26.8 ± 0.8
72H → 57H	$3.1 \pm 0.2 \times 10^{-4}$	2.40×10^{-2}[c]		24.9 ± 0.7
73H → 57H			$5.3 \pm 0.30 \times 10^{-4}$ (20°)	21.5 ± 0.5
74H → 60H	$3.30 \pm 0.40 \times 10^{-6}$	$2.80 \pm 0.2 \times 10^{-4}$		27.9 ± 0.9
76H ± 75H			$5.20 \pm 0.60 \times 10^{-4}$ (30°)	22.4 ± 0.6
78H → 63H	4.80×10^{-8}[d]	$8.70 \pm 1.5 \times 10^{-6}$		30.7 ± 1.0
81H → 64H	$9.30 \pm 0.5 \times 10^{-6}$	$5.40 \pm 0.40 \times 10^{-4}$		27.2 ± 0.8
70D → 95	$7.7 \pm 0.8 \times 10^{-6}$			27.3 ± 0.8

a) errors quoted are standard deviations.

b) errors quoted are based upon a temperature error of ±0.5°.

c) extrapolated from data at 60°.

d) extrapolated from data at 100°.

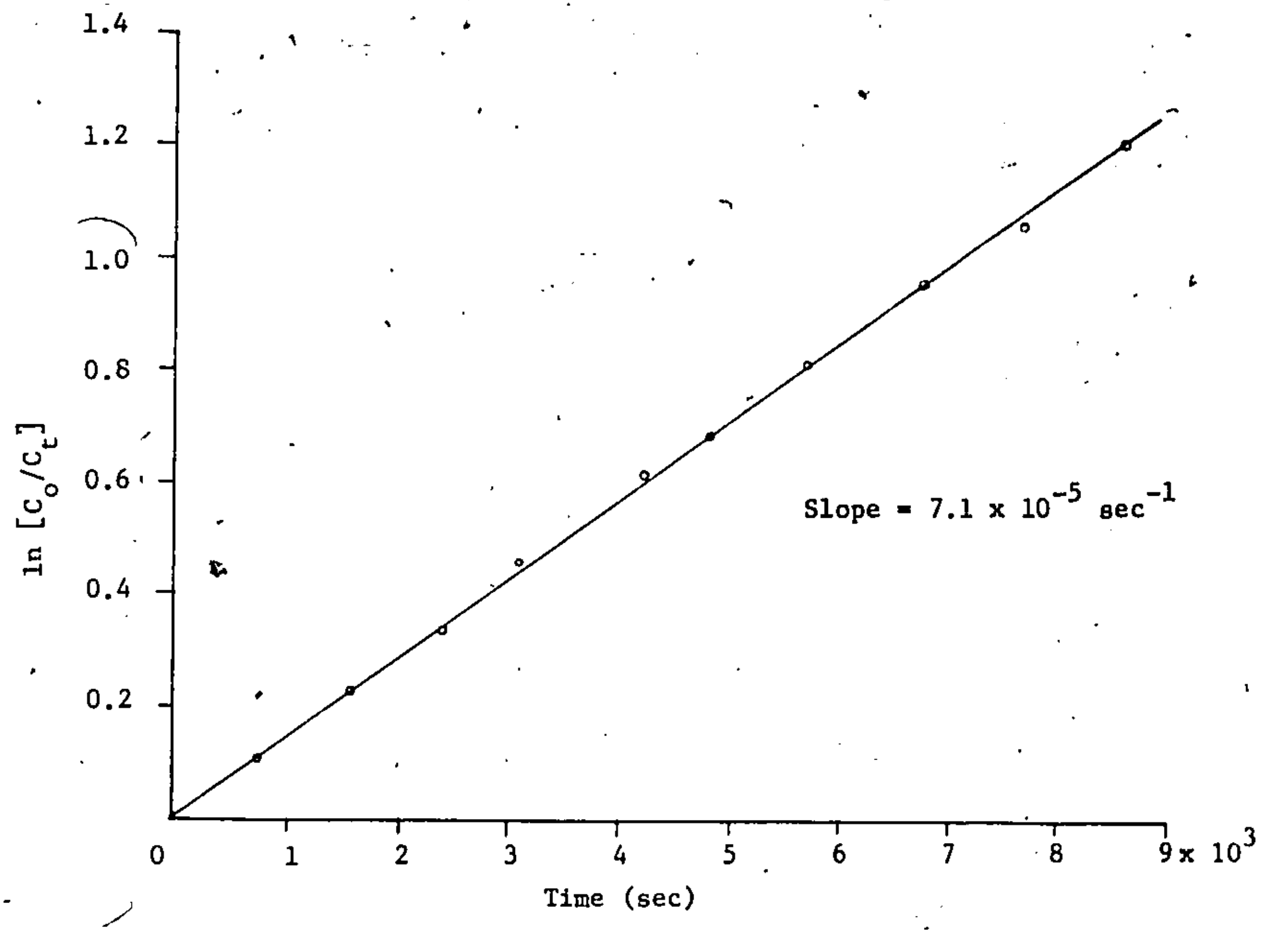


Figure 13. Thermal isomerization of 67H at 60°C.

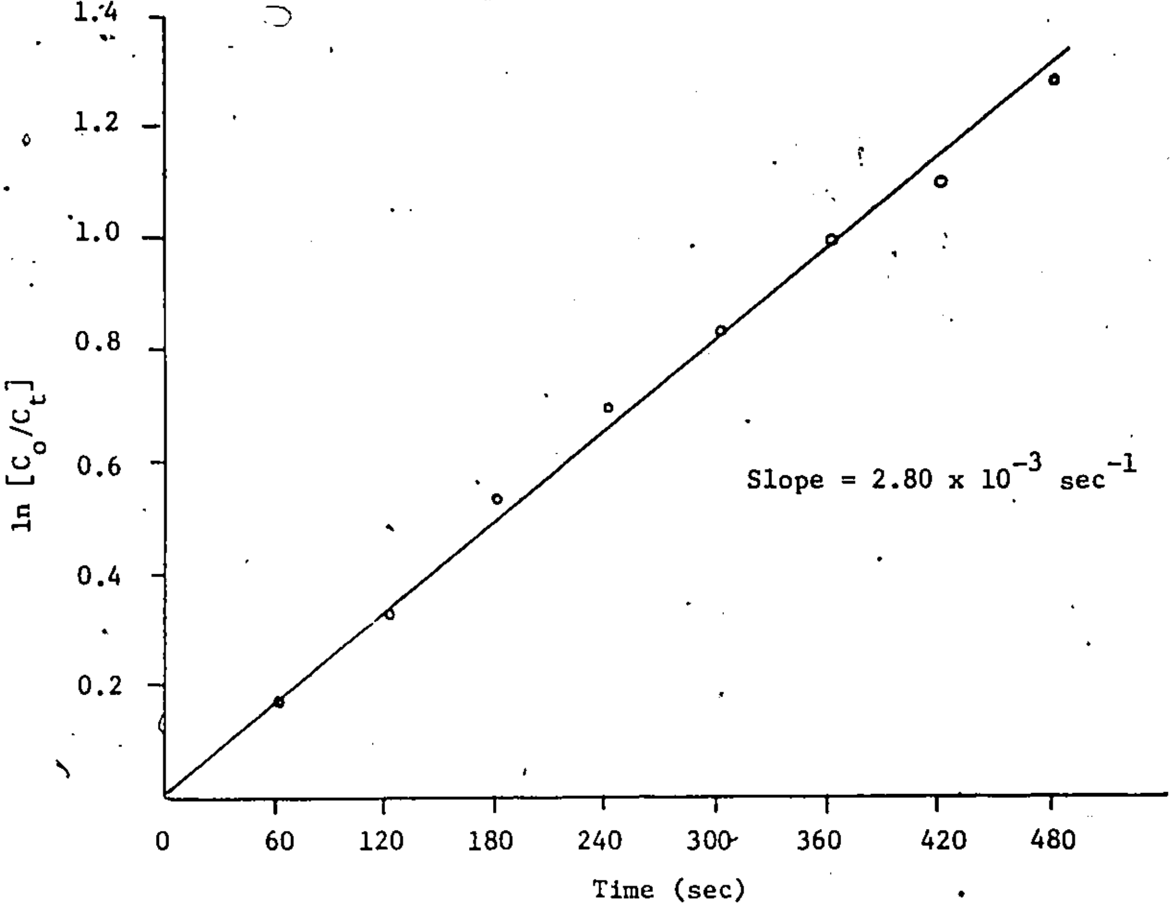


Figure 14. Thermal isomerization of <u>70H</u> at 100°C.

CHAPTER 3

DISCUSSION

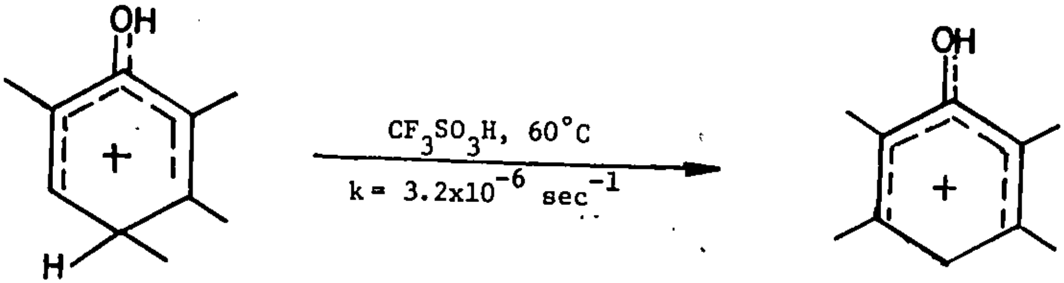
PART I:

Protonation of Phenols

The disolution of phenols in FSO_3H at low temperatures and the resulting formation of protonated phenols has been previously investigated by several workers.[113,124,125] The major conclusions reached have been previously summarized in the Introduction to this thesis.

CF_3SO_3H is reported to be a weaker acid than FSO_3H with an H_o of 14.1[148-150] as compared to 15.1[151] for FSO_3H. From the results presented in the previous chapter this reduction in acidity does not seem to alter to any significant extent the site of proton attachment to a phenol. Further, the ^1H NMR spectral changes associated with the protonation of methyl substituted phenol, 56-65 in CF_3SO_3H at room tempertaure are very similar to those reported in FSO_3H at low temperatures. The maximum difference in chemical shift of any proton in the two acids is 0.12 ppm. By comparing the results obtained in this work with those previously reported the cations resulting from protonation of 56-65 in CF_3SO_3H were assigned the structures 56H-65H.

CF_3SO_3H solutions of the cations 56H-65H were stable at ambient temperatures and no thermal isomerizations such as the migration of a methyl group around the ring could be detected by ^{1}H NMR. Even heating samples of 56H, 58H-65H at 60°C for several hours produced no change in their NMR spectra. In contrast, heating a solution of 57H at 60°C resulted in the formation of new cation. The rate constant for this process was $(3.2 \pm 0.36)\times10^{-6}$ sec^{-1} ($\Delta G^{\neq}$ = 27.9 kcal/mole), equation 53.



57H

58H

(53)

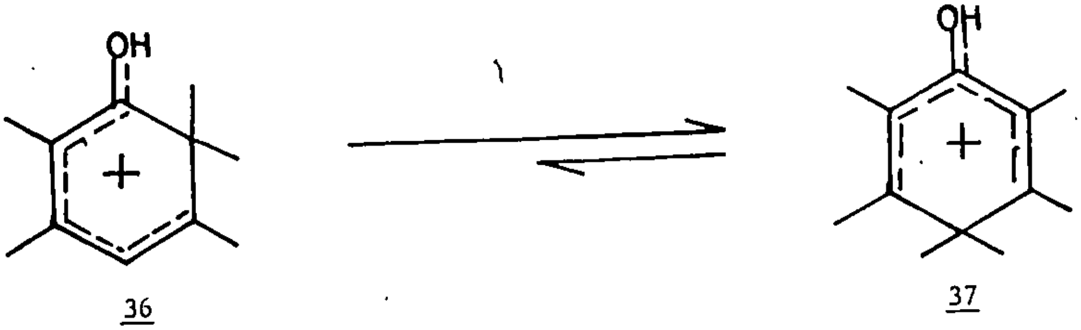
Similar isomerization has been previously observed with other C_4 protonated methyl substituted phenols in different acid media.[152,153]

Dissolution of 57, 60, 63 and chlorophenols 85-88 in FSO_3H at -78° and observation of the resulting cations at -60° by ^{1}H NMR showed the formation of the C_4-protonated cations 57, 60H, 63H and 85H-88H. In the case of 85 and 87 some O-protonation was also detected yielding 89, 70% and 90, 40%. As mentioned earlier, the chemical shifts of the proton resonances of the resulting cations from 85 and 86 are very similar to those which have been reported by Olah and Mo.[119] The above cations were stable up to -30°. Above this temperature fluorosulfonation and decomposition of these cations was observed as indicated by the formation of new signals in the ^1H NMR spectra of these solutions. Neutralization of the acid solution of these cations at room temperature resulted in the formation of colorless solids which were found to be fluorosulfonated products of the starting phenols.

Further support for the structure of the cations resulted from protonation of methyl- and chlorosubstituted phenols comes from the UV spectra of these cations, Tables 2.2 and 2.11. The phenols protonated at the para position exhibited strong absorption bands in the 300 - 330 nm region with the position of the maximum depending on the ring substituents. Absorptions in this range are consistent with the formation of para protonated cations. For example, protonated cyclohexa-2,5-dienones exhibit very similar UV spectra.[99,100,131]

It is well established that when the 4-position of a phenol bears a methyl substituent, proton attachment to an unsubstituted ortho position or the oxygen atom becomes possible.[113,124] Thus 2,3,4,5-tetramethylphenol, 59, which has no methyl on C_6, is protonated at C_4, 59H (95%) and C_6, 66 (5%), equation 35. The UV spectrum of 59 in CF_3SO_3H exhibits bands at 310 (log ϵ = 4.06) and 385 nm (log ϵ = 2.63). The low intensity longer wavelength maximum is consistent with the formation of the C_6 protonated species 66. Protonated cyclohexa-2,4-dienones exhibit maxima in this region.[99,100,102,131]

Overall it is clear that there is a preference for para over ortho protonation of phenols. This is consistent with the known equilibrium position between 36 and 27 which lies in favor of 37,[101,132,135] equation 54.

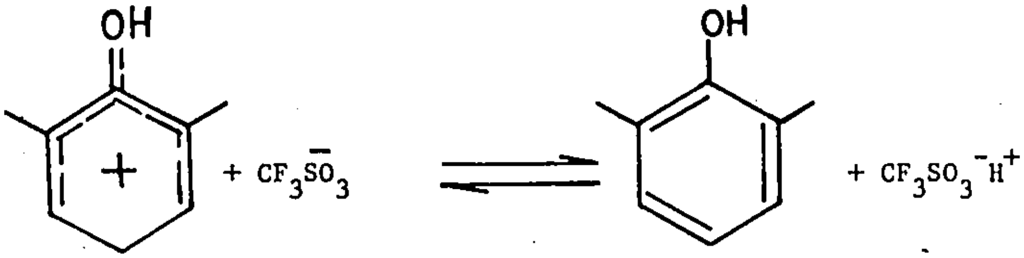

36

37

(54)

A more detailed examination of the ^{1}H NMR spectra of 57H and 64H in CF_3SO_3H revealed an interesting temperature dependence of the resonances of the aromatic protons of these cations. Thus at -20°C the spectrum of 64H in CF_3SO_3H was consistent with the formation of this cation with resonably sharp resonances being exhibited (Figure 6). At 0° (Figure 5) the signal due to the CH_2 protons was broadened. At still higher temperatures, 20°C the CH_2 signal was further broadened (Figure 4). On cooling the samples, the original low temperature spectrum was regenerated. There was no detectable change in the signal attributable to the protons at C_3 and C_5 over the temperature range studied.

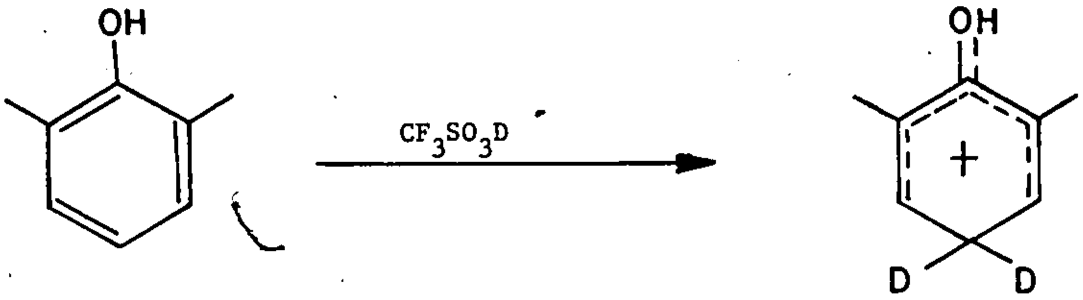
The broadening of the CH_2 signal of 64H clearly indicates a reversible intermolecular proton transfer with acid, equation 55. At temperatures higher than 0°, the para ring protons undergo a relatively rapid exchange with the solvent which results in the observation of a broad signal for the resonance of the protons at C_4. The narrowing of the absorption for the CH_2 signal at low temperature (-20°) indicates a slowing of the rate of exchange at lower temperatures. The lack of observable coupling between C_3 and C_5 with C_4 protons indicate that even at -20° a slow exchange with solvent is taking place. Kinetic measurements for these exchange reactions were not carried out.



64H 64

(55)

Direct evidence for this exchange process comes from the results of the protonation of 64 with CF_3SO_3D, in which complete exchange of the C_4 proton with deuterium occured prior to observation by ^1H NMR spectra, equation 56.

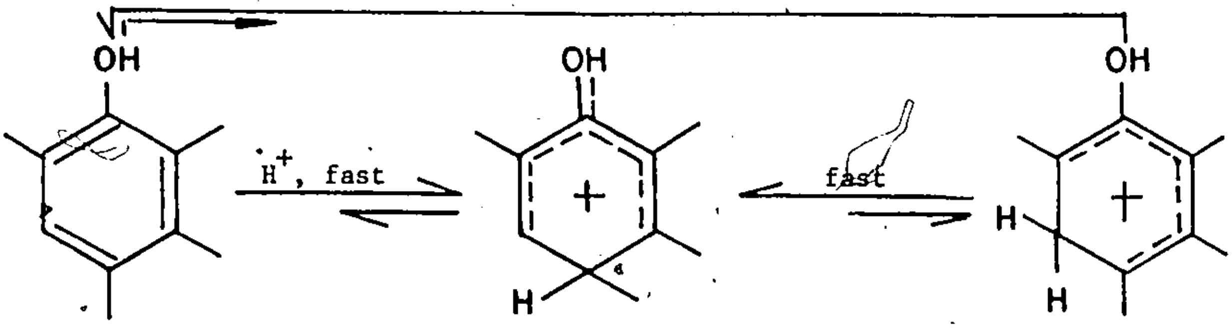


64 64D

(56)

A temperature dependent ^1H NMR spectrum was also observed for 57H in CF_2SO_3H. The changes observed are consistent with the exchange of both ring protons (i.e. protons at C_4 and C_5) with the solvent (Figures 7-9). As the temperature is raised, the ring proton absorptions broaden indicating a rapid exchange. It can be seen from Figures 7-9 that the line broadening for H_4 occurs at a lower temperature than H_5.

These findings can be understood in terms of intermolecular exchange of H_4 with the solvent, as was shown above for 64H, coupled with an intramolecular exchange of H_5 with H_4. The exchange of H_5 with H_4 could take place by a 1,2-hydride shift to give the C_5 (meta) protonated species 96. Similar shifts are known to occur very rapidly at room temperature in related cations.[154,155] Cation 96 could then revert to 57H leading to an exchange of H_4 and H_5. Proton loss from 96 to give 57 is another possible exchange route. Comparable exchange reactions are well known to occur with methylated benzenes in CF_3SO_3H.[66b,150]

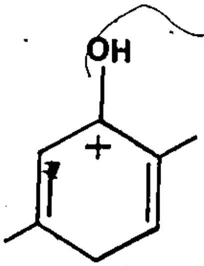


57 57H 96

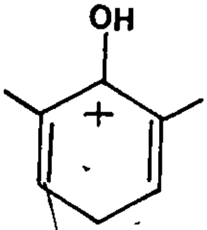
The results presented above leave one question to be answered, namely why protonated isodurenol shows exchange of both C_4 and C_5 protons but 2,6-dimethylphenol 64H shows exchange of the C_4 protons only.

A detailed examination of the room temperature ^1H NMR spectra of CF_3SO_3H solutions of 2,5- and 3,5-dimethylphenols, 62 and 65, respectively shows that the rate of exchange for the C_4 and C_6 protons is dependent on the positioning of the methyl groups.

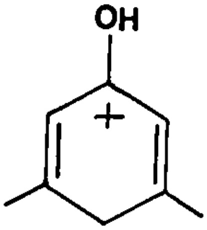
Thus the ^1H NMR spectrum of 65H at 34°C shows the resonances of the C_4 proton to be very sharp, Figure 15, suggesting that exchange of these protons with solvent is slow in the NMR time scale. In the case of 62H, the C_4 proton resonance is somewhat broadened (Figure 16) while in 64H no resonance for these protons can be detected in CF_3SO_3H at room temperature. These results can be understood in terms of the relative stability of the cations 65H, 62H and 64H resulting from the effect of C_3 and C_5 methyl groups in stabilizing the positive charge.



62H



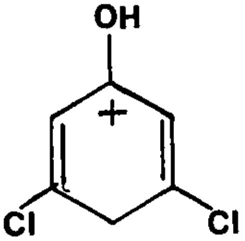
64H



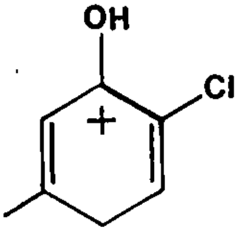
65H

The absence of signals attributable to the C_3, C_4 and C_5 protons in the ^1H NMR spectrum of a CF_3SO_3H solution of 2,4,6-trimethylphenol at room temperature again indicates that a fast exchange of these protons with solvent is occurring.

The preference for protonation at the different sites of 3,5-dichloro and 2-chloro-5-methylphenols, 87 and 88 respectively, can be understood in a similar manner to that outlined above for the methyl substituted phenols. Protonation of 88 results in the formation of only the para protonated species, i.e. 88H. Protonation of 86 led to the formation of C_4 (86H, 60%) and O- (90 , 40%) protonated species. These observations can again be understood in terms of the greater effect of the methyl group at C_5 in stabilizing the positive charge in 88H compared to two chlorine atoms in the case of 87H.



87H



88H

It is instructive to compare the ^1H NMR spectral data for the C_4-methylsubstituted cations 56H, 57H and 59H with those cations lacking a methyl substituent at C_4, i.e. 58H, 60H and 61H, Table 2.2. It can be seen that the signals for the tertiary hydrogen of 56H, 57H and 59H appear at remarkably high field positions, 3.60, 3.73 and 3.62 ppm respectively. The signal of a methinic proton is normally found at a lower field than that of a methylene proton in the corresponding position.[156] The reverse is the case with these protonated phenols, Scheme 17.

It has been suggested by E.L. Mackor and coworkers[73,157,158] and H.M. McConnell[159] that protonated hexamethylbenzene is non planar with

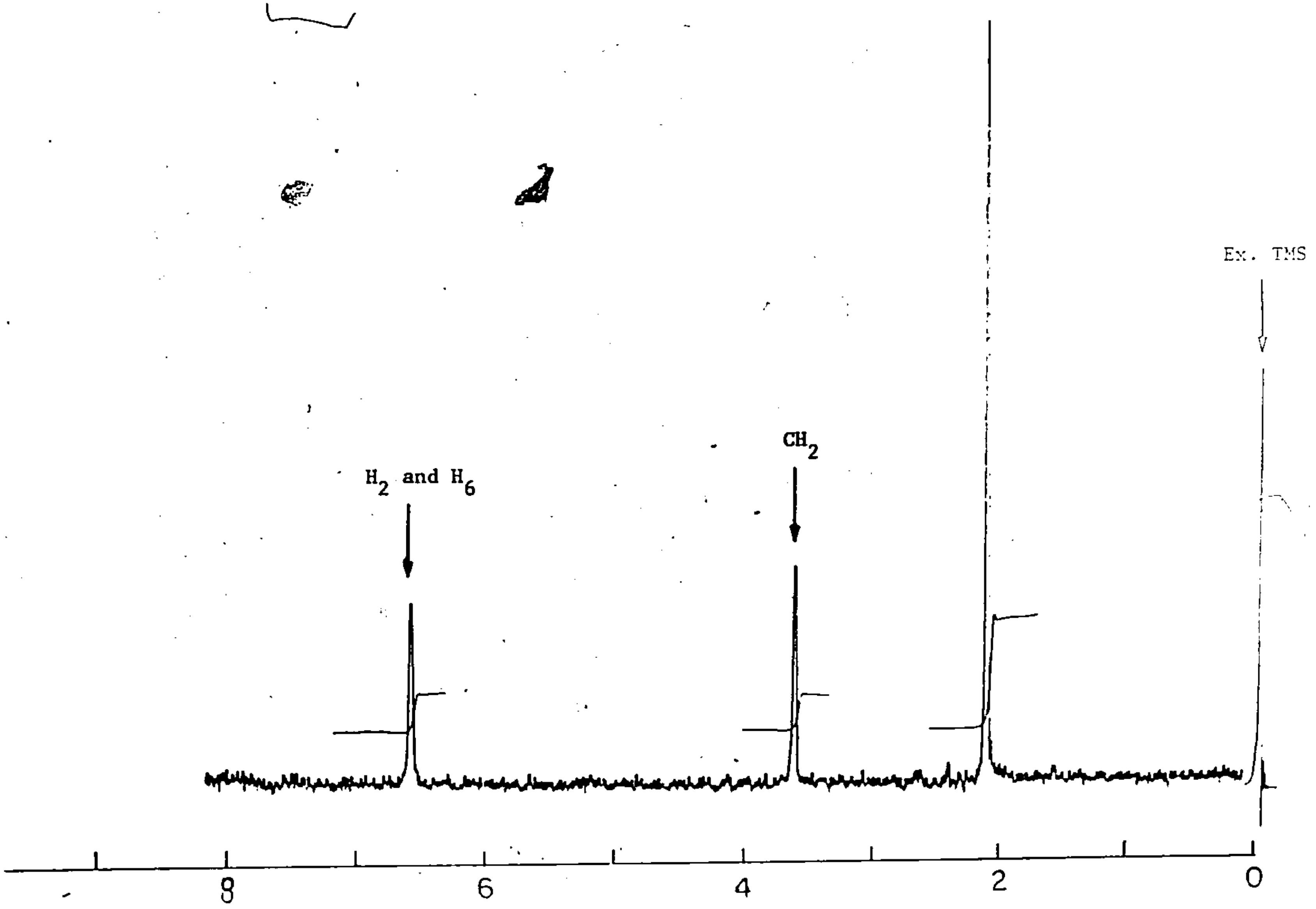


Figure 15. ^1H NMR spectrum of a solution of the phenol <u>65</u> in CF_3SO_3H at 34°C.

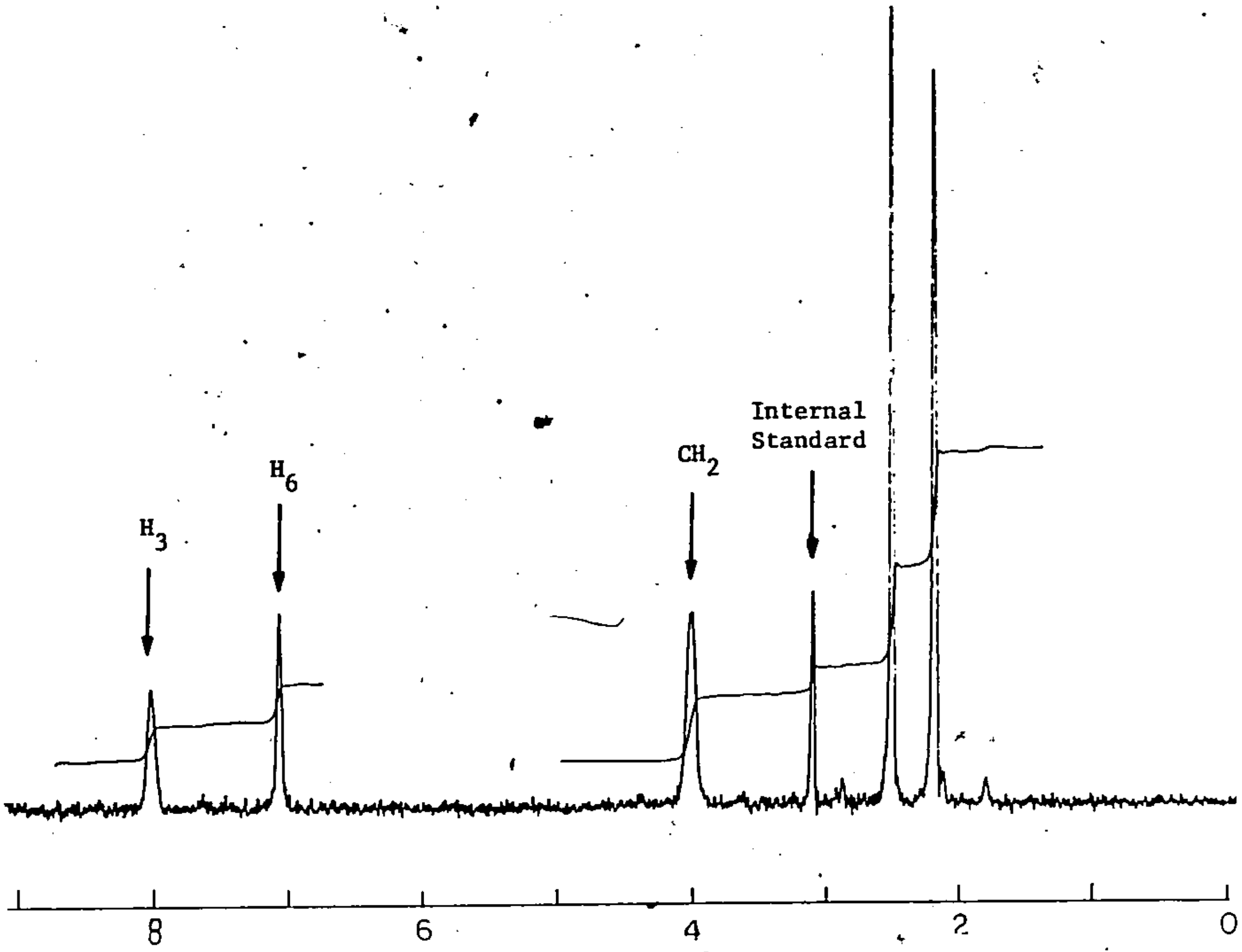
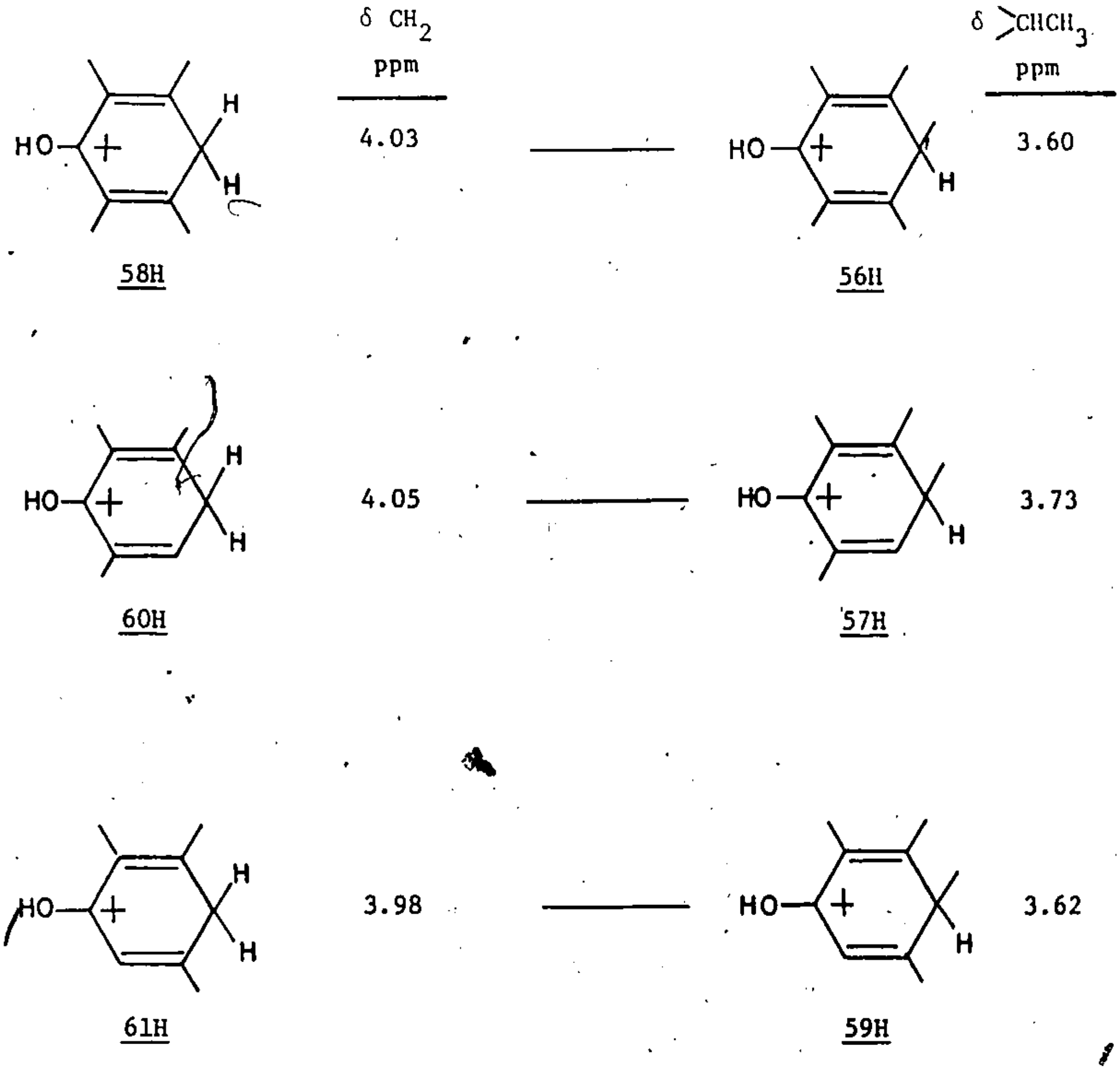
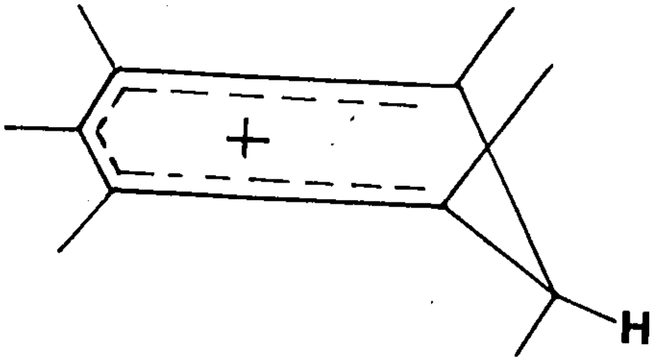


Figure 16. ^1H NMR spectrum of a solution of the phenol 62 in CF_3SO_3H at 34°C.

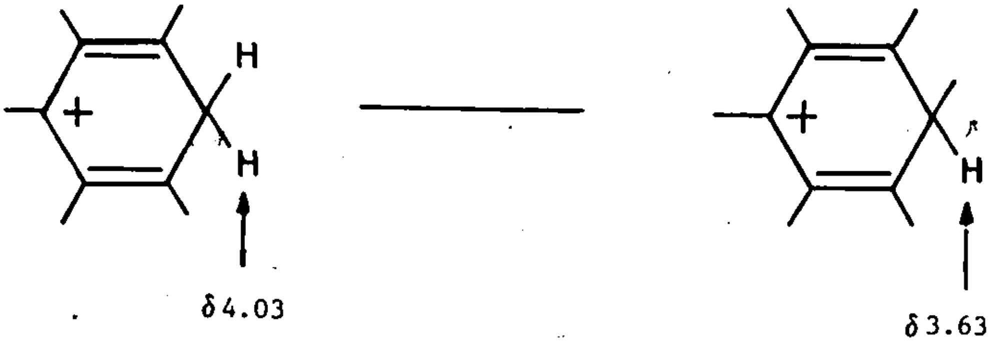

δ CH$_2$
ppm
δ >CHCH$_3$
ppm
HO
H
H
4.03
HO
H
3.60
58H
56H
HO
H
H
4.05
HO
H
3.73
60H
57H
HO
H
H
3.98
HO
H
3.62
61H
59H

Scheme 17

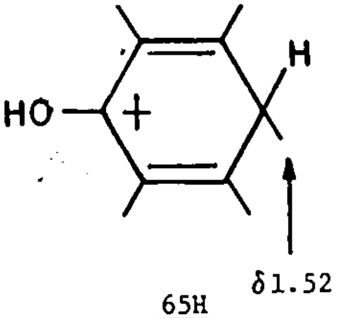
the sp^2 carbon being tilted out of the plane of the other ring carbons so as to relieve the steric repulsion between the bulky methyl groups. Evidence to support this suggestion comes from the coupling constant (J = 2 Hz) between the proton on C$_4$ and the protons of the C$_4$ methyl group in the hexamethylbenzenium ion. This is smaller than that for the CH$_2$ protons of pentamethylbenzenium ion (J = 3.5 Hz). A similar non planar configuration of the para protonated phenols 56H, 57H and 59H would seem to be likely.



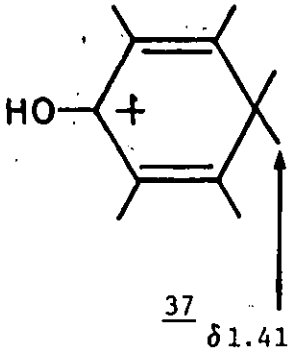
A similar effect to that outlined above for the methyl substituted phenols is observed in benzenium ions as is shown below.[73,82,154]



The positions of the C_4 methyl resonances in cations 56H, 57H and 59H is also consistent with a non planar system. The signal of a C_4 methyl resonances of these cations is considerably further downfield (1.52 - 1.53 ppm) compared to the case of cation 37 (1.41 ppm).[124]



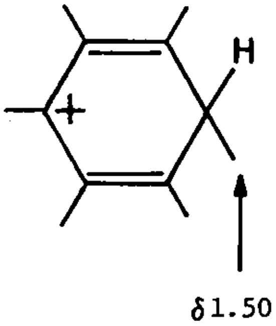
65H

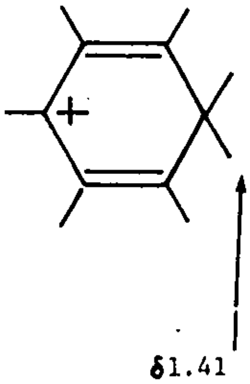


37

One effect of such a distortion is that the methine hydrogen will lie much closer to the plane of the remaining five carbons of the protonated phenols or benzenium ion. As such the magnetic environment of this hydrogen is different from that of hydrogens in planar systems such as 58H, 60H and 61H. This will result in a different magnetic environment of the tertiary hydrogen.

A similar observation to the above C_4 methyl substituted phenols is obtained in benzenium ions as shown below.[85]





PART II:

The Structure of Protonated Bicyclo[3.1.0]hexenones

There are a substantial number of reports in which the structure of bicyclo[3.1.0]hexenyl cations has been discussed.[93,98,141,160-164] It is generally agreed that they are non aromatic cations with the external rather than the internal cyclopropane bonds being involved in electron delocalization.[93,98,163,164]

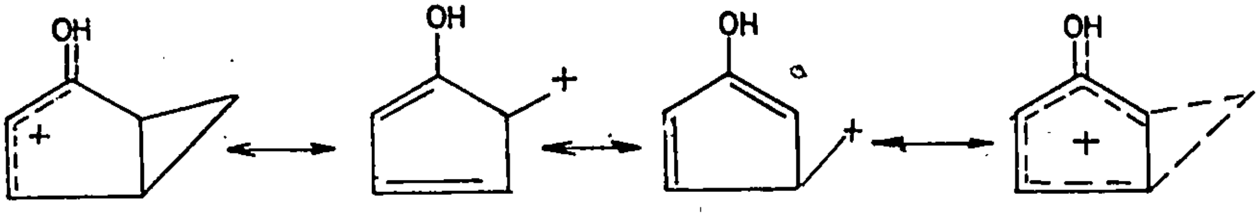
In the current study, a wide range of methyl substituted bicyclo[3.1.0]hexenones were protonated in CF_3SO_3H at room temperature and their spectra recorded. ^1H NMR spectral data of these cations (Table 2.4) show a very similar pattern of chemical shifts to these observed previously and are completely consistent with the above conclusion. No ^{13}C NMR spectral data has been previously reported for these hydroxy substituted bicyclo[3.1.0]hexenes.

In this work the ^{13}C NMR spectra of solutions of a number of a neutral and protonated bicyclo[3.1.0]hexenones were obtained (Table 2.5).

In terms of probing the changes in charge distribution occurring in these systems on protonation of the oxygen atom it is useful to examine the changes in chemical shift ($\Delta\delta$) of the various resonances. These are summarized for the various ring carbon atoms in Table 3.1. Also given are some corresponding values obtained on protonation of cyclopentenone and some cyclohexenones.

Overall, it is generally accepted that the presence of a full positive charge on a carbon atom will result in a deshielding of its ^{13}C resonance by ca. 160 ppm.[165] The present ions are delocalized systems with positive charge being distributed over several atoms. Examination of the data in Table 3.1 shows that the largest downfield shifts and presumably positive charge are found for C_4 and C_6 with C_2 in 81H also showing a large shift. The very large downfield shifts found for the resonances of C_6 on protonation of ketones 70, 74 and 81 clearly substantiate involvement of the external cyclopropane bonds in charge delocalization, Scheme 18.

Scheme 18



A more detailed examination of the changes in chemical shift induced on protonation 70, 74 and 81 reveals some interesting further observations. First, the $\Delta\delta$ value for C_4 in 81H is 9.1 and 12.8 ppm smaller than those of cations 70H and 74H, respectively. This large difference of the carbon shifts resulting from protonation is likely due to changes in charge distribution. This is in good agreement with the previous observations made upon protonation of aromatic and olefinic compounds.[143,166] For example, a deshielding of ca. 16.0 ppm at the carbon upon replacement of hydrogen by methyl has been demonstrated in cyclohexenone and 3,5-dimethylcyclo- hexenone cations,[143] Table 3.1.

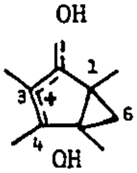
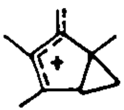
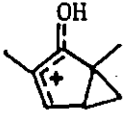
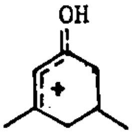
Coupled with the reduced $\Delta\delta$ value of C_4 in 81H is an increased downfield shift of C_2, C_6 in this ion as compared to 70H and 74H. This would indicate that there is more positive charge at these carbons in 81H than in 70H and 74H.

Overall the results in Table 3.1 shows that the sum of the chemical shift difference ($\Sigma\Delta\delta$) value of the ring carbons in 70H, 74H and 81H are very similar, 104.5, 105.1 and 102.7 ppm, respectively. This would indicate that while the total fraction of positive charge on the cation is very similar, the charge distribution depends on the position of the methyl groups.

The changes in chemical shift observed for the cyclopropyl carbons (C_1 and C_5) on protonation of these ketones are consistent with the resonance structures 97 and 98, Scheme 18. Typically, a positively charged carbon will cause an inductive deshielding of between 5 to 26 ppm at neighboring carbon atom.[167,168]

From the results presented above, it is quite clear that the formulation of the structure of a protonated bicyclo[3,1,0]hexenone[169] as shown in Scheme 18 agrees with the result of a recent structure determination of the tetramethyl substituted cation 70H as its $SbCl_6^-$ salt.[163,164] An important feature of this structure is the bond distances found in the cyclopropyl ring of 70H. It is interesting that there were substantial change in the C_1,C_6 bond distance of 1.547 Å from the normal value expected for a cyclopropane in a bicyclo[3.1.0]hexenone of 1.510 Å.[170] It is not clear at this stage whether the bond lengths of the cyclopropane would change with the position of the methyl substituents in these hydroxybicyclic cations. Clearly one needs to examine the crystal structure of a wider range of these cations to establish this point.

Table 3.1. Chemical shift differences ($\Delta\delta$)[a,b] for ring carbons observed upon protonation of bicyclo[3.1.0]hexenones,[c] cyclopentenone[d,e] and cyclohexenones.[d,e]

Cation	$\Delta\delta$ ^{13}C Values observed (ppm)						
	C_1	C_2	C_3	C_4	C_5	C_6	$\Sigma\Delta\delta$
70H 	8.4	11.5	1.4	39.8	13.4	30.0	104.5
74H 	8.4	14.3	1.6	43.5	10.7	30.6	105.1
81H 	11.8	18.0	4.8	30.7	13.5	33.4	102.7
82H 		23.0		38.9			
		23.0		41.8			
		14.7		57.7			

a) $\Delta\delta = \delta_{cation} - \delta_{neutral}$.

b) Positive sign indicates downfield shift for the carbon in question.

c) This work

d) Results are taken from reference 143.

e) To aid comparison the three monocyclic cations have been numbered using the bicyclic cations numbering scheme, i.e. the carbonyl carbon is C_2.

In conclusion it is evident that the ^{13}C NMR results described above furnish strong evidence for the involvement of the external cyclopropane bonds of these bicyclic cations in charge delocalization. It would also appear that the pattern of methyl substituents on those cations has an important effect on the total charge distribution and it would be interesting to examine the crystal structures of some further cations of this type which differ in substitution pattern of methyl groups.

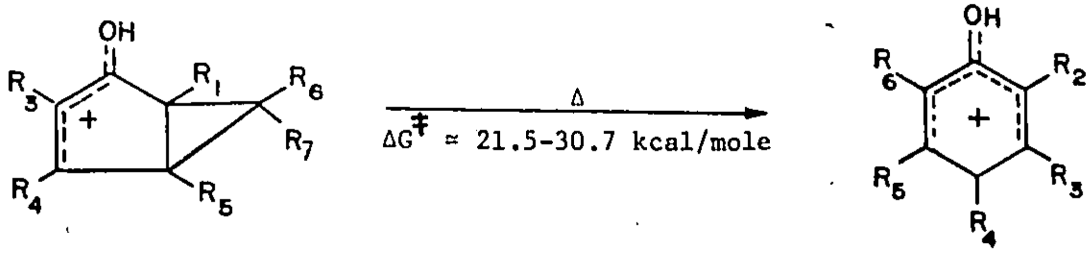
PART III:

Thermal Chemistry of Protonated Bicyclo[3.1.0]hexenones

Both Hart[97,112] and Childs[113] have reported the occurance of a degenerate rearrangement of protonated bicyclo[3.1.0]hexenones in which the cyclopropyl group migrates around the five membered ring, equations 26 and 28 respectively.

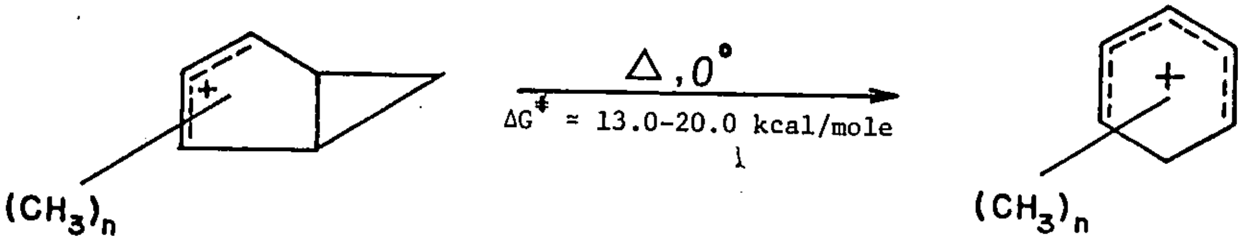
The use of CF_3SO_3H as an acid medium permits the extension of this earlier work to cover a much wider range of systems in which the rearrangement processes have higher activation energies. In this present study a quantitative investigation of the thermal isomerization of the protonated bicyclo[3.1.0]hexenones (76H, 70H-74H, 76H, 78H and 81H) to protonated phenols (Scheme 19) has been examined. The thermal conversions were found to be very clean in CF_3SO_3H with good first-order kinetics being observed. No side products or decomposition products were detected in these reactions. The products, identified as outlined in the results section, are summarized in Table 2.14.

Scheme 19



<u>67H</u>	$R_1=R_3=R_4=R_5=R_6=Me$; $R_7=H$	<u>56H</u>	$R_2=R_3=R_4=R_5=R_6=Me$
<u>70H</u>	$R_1=R_3=R_4=R_5=Me$; $R_6=R_7=H$	<u>58H</u>	$R_2=R_3=R_5=R_6=Me$; $R_4=H$
<u>71H</u>	$R_1=R_3=R_4=R_6=Me$; $R_5=R_7=H$	<u>58H</u>	$R_2=R_3=R_5=R_6=Me$; $R_4=H$
<u>72H</u>	$R_1=R_3=R_4=R_7=Me$; $R_5=R_6=H$	<u>57H</u>	$R_2=R_3=R_4=R_6=Me$; $R_5=H$
<u>73H</u>	$R_1=R_3=R_5=R_6=Me$; $R_4=R_7=H$	<u>57H</u>	$R_2=R_3=R_4=R_6=Me$; $R_5=H$
<u>74H</u>	$R_1=R_3=R_4=Me$; $R_5=R_6=R_7=H$	<u>60H</u>	$R_2=R_3=R_6=Me$; $R_4=R_5=H$
<u>76H</u>	$R_1=R_3=R_5=Me$; $R_4=R_6=R_7=H$	<u>75H</u>	$R_2=R_4=R_6=Me$; $R_3=R_5=H$
<u>78H</u>	$R_3=R_4=Me$; $R_1=R_5=R_6=R_7=H$	<u>63H</u>	$R_2=R_3=Me$; $R_4=R_5=R_6=H$
<u>81H</u>	$R_1=R_3=Me$; $R_4=R_5=R_6=R_7=H$	<u>62H</u>	$R_2=R_5=Me$; $R_3=R_4=R_6=H$

A much higher activation barrier ($\Delta G^{\ddagger}$) to isomerization of the above hydroxy bicyclohexenyl cations ($\Delta G^{\ddagger} \simeq 21.5$-$30.5$ kcal/mole) was noted as compared to that of the bicyclohexenyl cations lacking a hydroxy group[94] ($\Delta G^{\ddagger} \simeq 13.0$-$20.0$ kcal/mole), equation 57 . This difference can be attributed to the greater stabilization of the positive charge in the hydroxy bicyclic cations by the hydroxyl group. Similar differences have been noted earlier in the case of protonated hexamethyl (<u>38</u>, Scheme 6)[97,112] and 3,5,6-endo trimethyl bicyclo[3.1.0]hexenones (<u>54</u>, equation 28).[113]



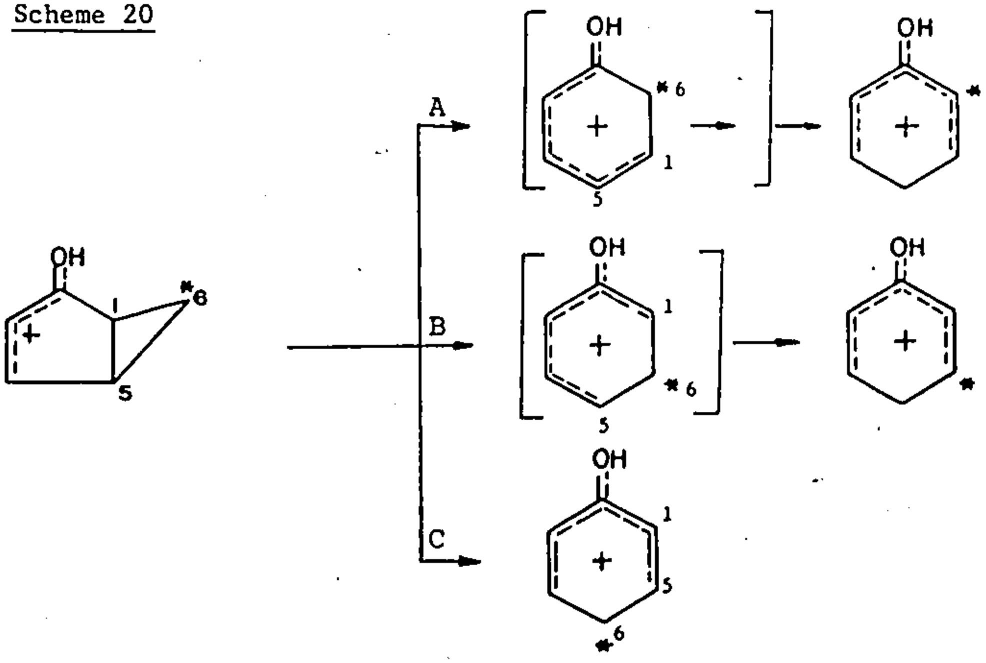
(57)

The interconversion of a bicyclo[3.1.0]hexenyl cation with the corresponding benzenium ion can be considered to proceed by a disrotatory electrocyclic reaction. As has been discussed previously, such a $4e^-$ electrocyclic reaction is formally forbidden in the ground state and allowed in the first excited state.[54,55,91] In order for orbital symmetry to be conserved in the thermally induced conversion of a bicyclo[3.1.0]hexenyl cation to a benzenium ion would have to proceed in a conrotatory mode leading to a trans double bond in the product. Such a process would be energetically unfavourable and as a result the thermal isomerizations involve substantial activation barriers.

The control experiments conducted on the protonated phenols showed that they are stable under the conditions used for thermal conversion of the protonated bicyclic cations. This means that while there can be proton reorganization on the phenolic rings, the positions of the methyl groups remain unchanged once the ring opening of the bicyclic ketones has occurred. Thus the position of the methyl groups in the products as compared to the starting bicyclic ketones indicate the location of C_6, the cyclopropane carbon.

An analysis of the products of the thermal isomerizations summarized in Scheme 20 reveals that at least three different types of processes are occurring, only one of which corresponds to the direct ring opening (Path B), Scheme 20. In the other two cases the cyclopropyl carbon C_6(*) is no longer bonded to C_1 and C_5 but a more deep skeletal rearrangement has occurred.

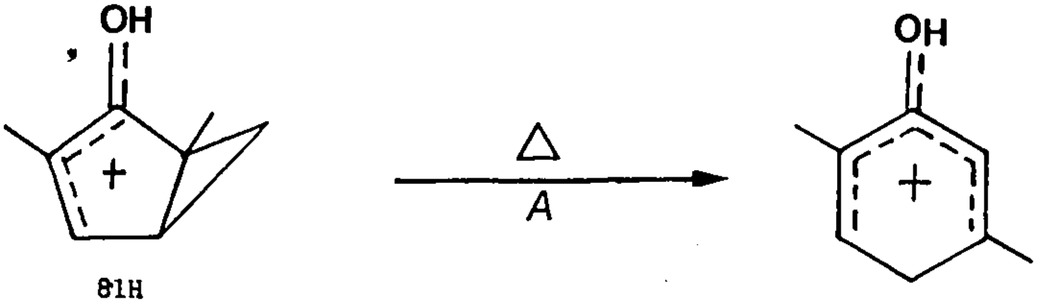
Scheme 20



The transfer of C_6 to the ortho position, Path A in Scheme 20, corresponds directly to the reaction observed by Hart and co-workers on the isomerization of hexamethylbicyclo[3.1.0]hexenyl cation 38, Scheme 6.[97,112] Path C is clearly analogous to this reaction.

The ring opening reactions in Pathways A and B would initially give ortho or meta protonated phenols respectively. Subsequent hydride shifts occur to give the more stable para protonated forms. Hydride shifts are well known to occur more rapidly than methyl shifts in cations of this type.[66,154]

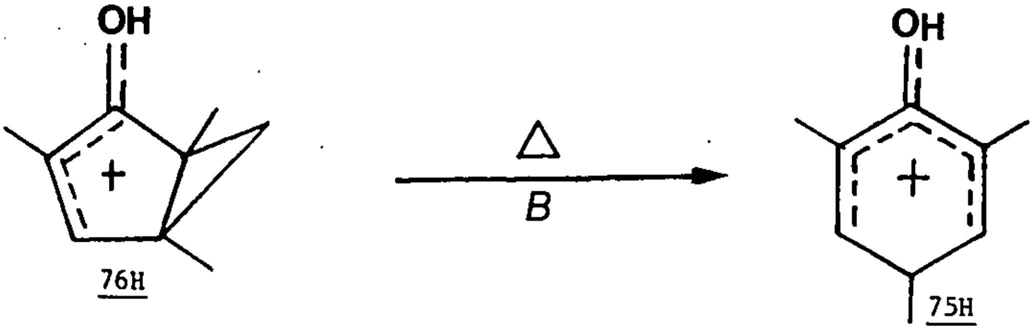
Not all the examples of the isomerization provide unambiguous evidence for the operation of a single isomerization pathways. However, there are four cases where it is possible to distinguish between the above pathways. These are shown below, equations 58-61.



81H

62H

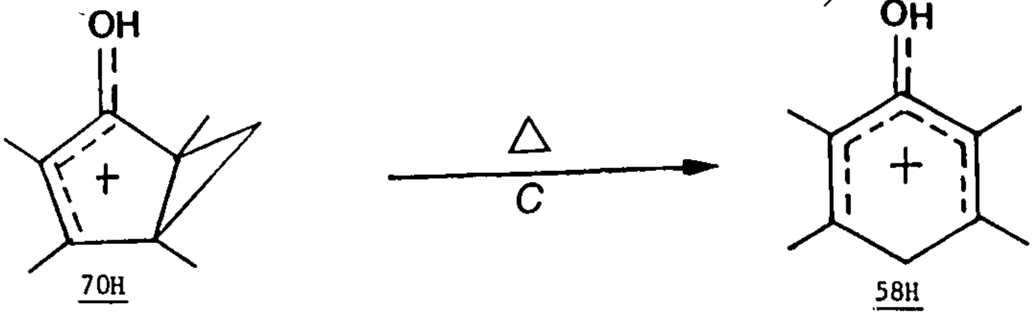
(58)



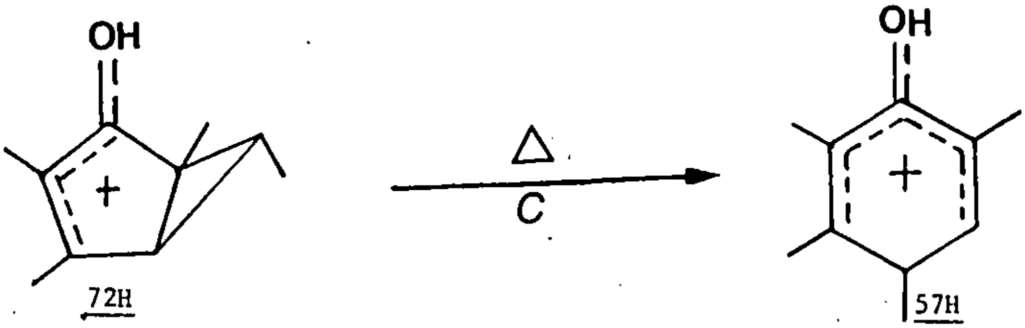
76H

75H

(59)



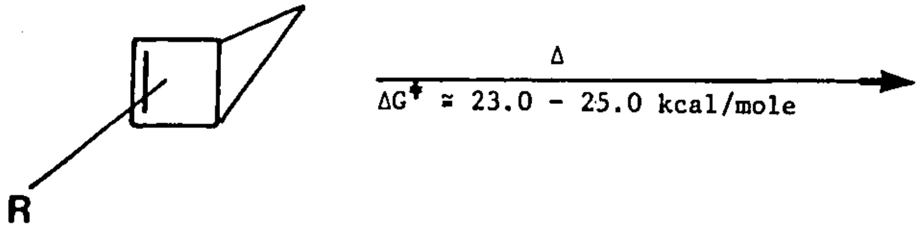
(60)



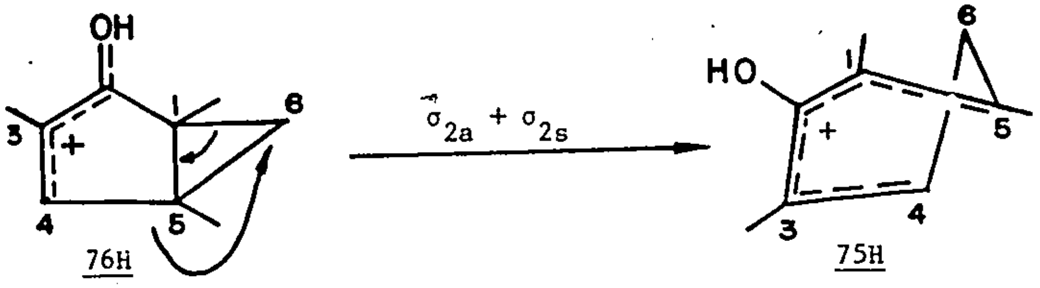
(61)

The isomerization of 76H to 75H provides a clear cut example of the intervention of a direct ring opening process, Path B. As has already been pointed out, such a ring opening is symmetry forbidden in the ground state and would thus be expected to involve a relatively high activation energy. As in the related isomerization of bicyclo[2.1.0]-pentenes,[171,172] equation 62, it is attractive to consider alternative more complex reactions which are symmetry allowed. The retention of the methyl substitution pattern during the rearrangement of 76H, equation 63, requires that the C_1-C_5 bond of this cation be broken. Thus, while a

$[\sigma_{2a} + \sigma_{2s}]$ route is a formally symmetry allowed isomerization pathway in that it circumvents the forbidden electrocyclic process, such a pathway can be rejected from consideration in the case of the conversion of 76H to 75H as it would leave the C_1–C_5 bond intact,[170] equation 63.

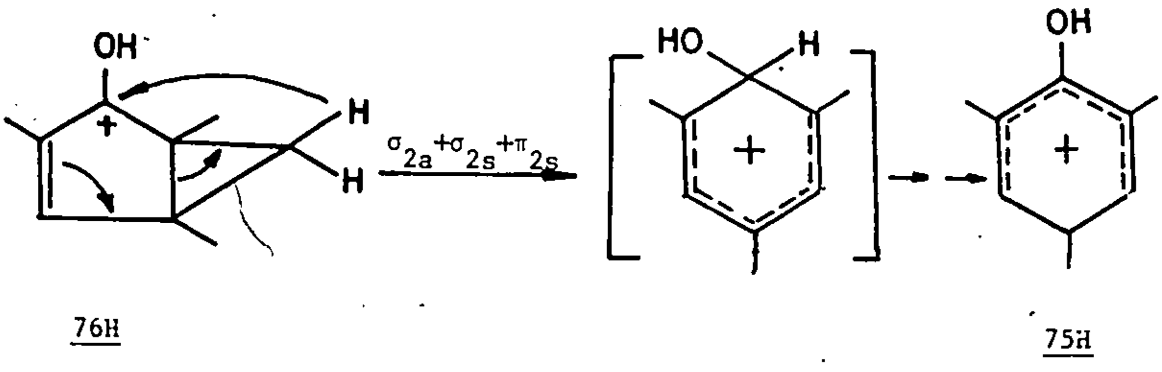


(62)



(63)

A retroene $(\sigma_{2s} + \sigma_{2s} + \pi_{2s})$ satisfies both the need to conserve orbital symmetry while the C_1–C_5 bond is broken.[172]

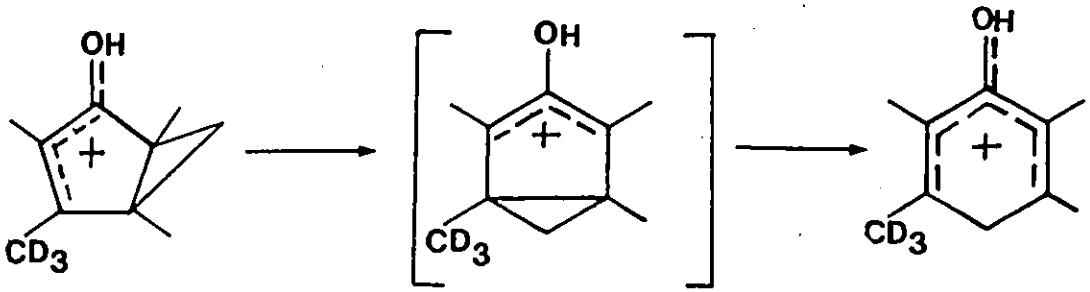


(64)

While it is not possible to rule out this mechanism on the basis of the observed reaction and no C_6 deuterated samples were examined in order to see if there is kinetic deuterium isotope effect present, this process is considered to be very unlikely. First, in the thermal rearrangement of bicyclo[3.1.0]hexenyl cations, this mechanism was specifically tested for and found not to occur.[93-95] Furthermore, none of the evidence requires or supports such a comparable process in the thermal isomerization of the isoelectronic bicyclo[2.1.0]pentenes to cyclopentadienes.[173,174] .In this case Baldwin[173] and Farneth[174] have shown that the major course of the reaction involves cleavage of the central bond by a formally symmetry forbidden electrocyclic process to give cyclopentadiene.

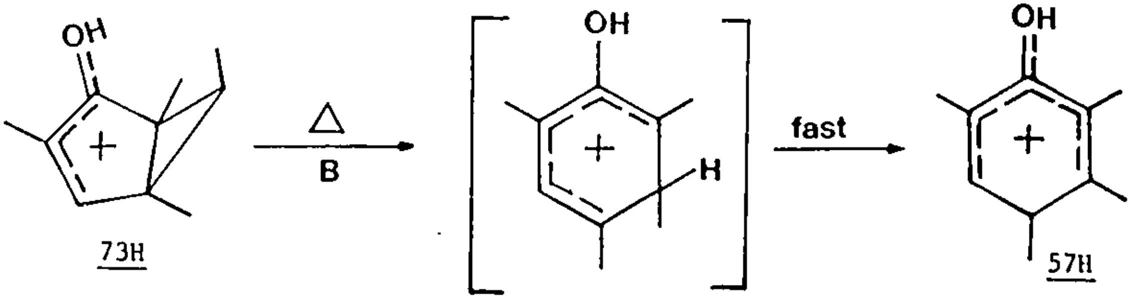
Thus it would seem likely that the ring openings of the hydroxy bicyclic cations presented in Scheme 19 proceed by symmetry forbidden electrocyclic rearrangements.

While the "simple" ring opening process is the lowest energy pathway for ring opening of <u>76H</u>, it is quite clear that the ions <u>70H</u>, <u>72H</u> and <u>81H</u> isomerize by different pathways. As mentioned earlier, many investigators have previously reported the occurrance of cyclopropyl migrations in bicyclo[3.1.0]hexenyl cations[86,87,94,95] and protonated bicyclo[3.1.0]hexenones.[95,97,112] Similarly, in this work the formation of <u>95</u> in the isomerization of <u>70D</u>, equation 68, again would indicate the occurrence of a circumambulatory rearrangement in this system. This strongly suggests that the intermediate <u>101</u> is involved in the ring opening process. It would seem most likely that isomerizations of <u>70H</u>, 72H and 81H which proceed by Paths A and C shown in Scheme 20 do so by an initial circumambulatory step followed by an electrocyclic ring opening. This is illustrated for the isomerization of 70D, equation 65.



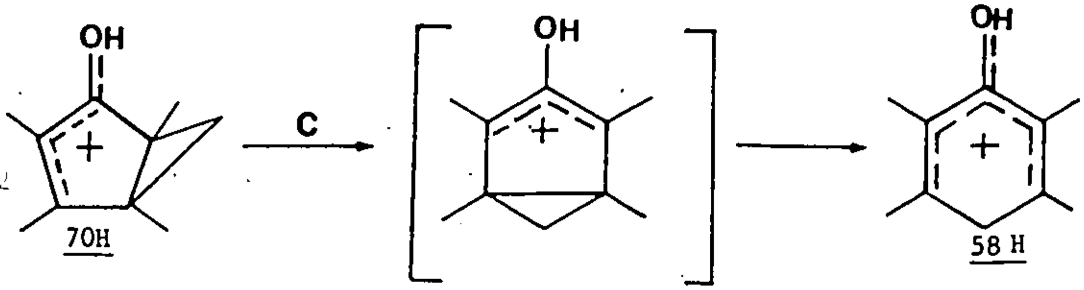
70D 101 95 (65)

To gain an understanding of the factors which determine the preferred pathway for isomerization, it is useful to consider first the direct ring opening for the conversion of 76H to 75H (equation 62). Examination of the data in Scheme 6 and Table 2.14 shows that apart from 38 and 73H, that 76H isomerizes much more rapidly than the rest of the systems studied. The methyl substitution pattern in 73H does not allow a clear definition of the isomerization pathway to be made. However, related studies on the ring openings of bicyclo[3.1.0]hexenyl cations has shown that addition of an endo methyl substituent at C_6 of a bicyclohexenyl cation lowers the barrier to the ring opening reaction by a small amount, Table 1.3.[95] In this present case, the barrier to the conversion of 73H to 57H is 0.9 kcal/mole lower than that of 76H. This would strongly suggest that 73H also isomerizes by Path B, equation 66.

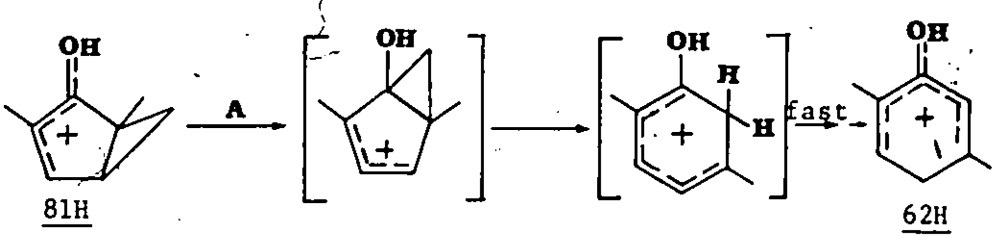


(66)

In contrast to the direct ring opening mechanism for the isomerization of 76H neither 70H or 81H isomerize by direct ring opening, but by an initial circumambulation, equation 67 and 68, respectively. Protonated ketones 70H and 81H are related to 76H by the presence of a methyl group at C_4, 70H, and the absence of C_5 methyl group, 81H. This change in the substitution pattern must clearly lead to an increase in the activation barrier of the direct ring opening reaction by at least 3.8 or 4.8 kcal/mole, respectively. These are large effects for the introduction or removal of a methyl group on the barrier of an electrocyclic reaction.[175-178]

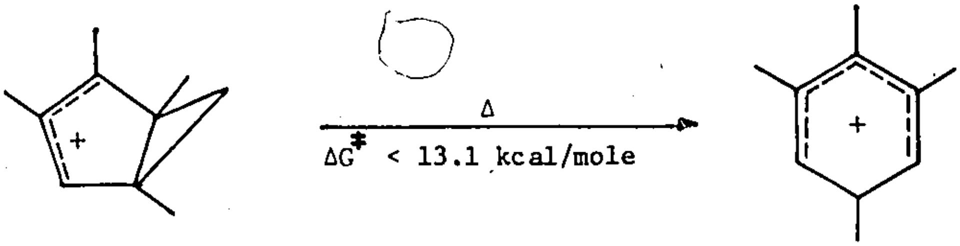


(67)

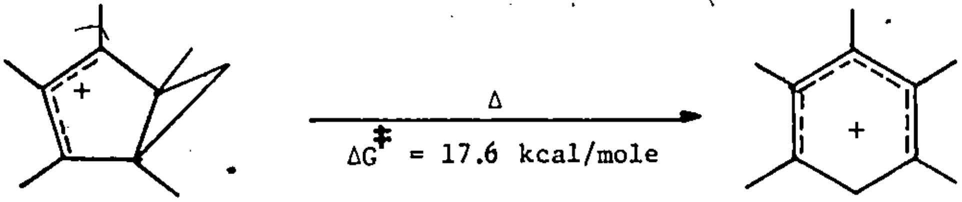


(68)

The common feature of both 73H and 76H which sets them apart from all of the other protonated bicyclic ketones is that in addition to the lack of methyl substituent at C_4 these cations are substituted at C_1 and C_5. A methyl group at C_4 would affect the activation barrier for ring opening by changing the relative stabilities of the starting cations. A C_4 methyl group in 70H would stabilize this cation as compared to 76H and presumably raise the barrier to isomerization with respect to 76H. A comparable effect of a methyl group on the barriers to the electrocyclic ring opening with the methyl substituted bicyclo[3.1.0]hexenyl cations has been reported,[94,95] equations 69 and 70.



(69).

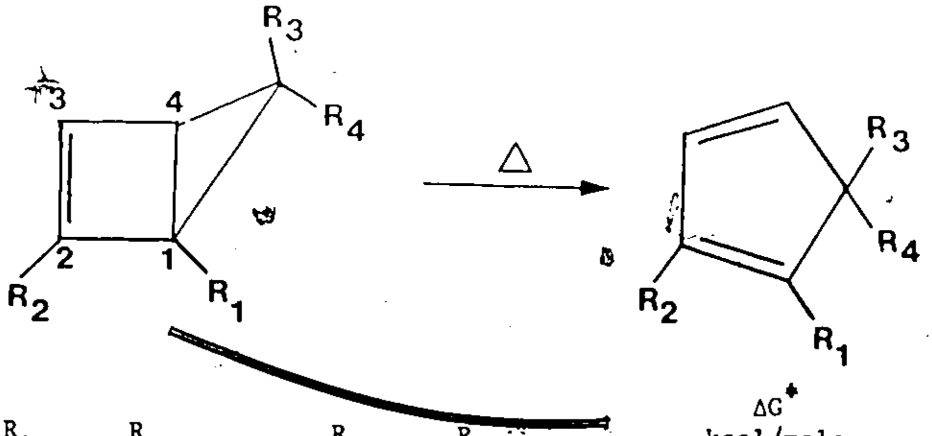


(70)

Results obtained on the isomerizations of bicyclo[2.1.0]pentenes and cyclobutenes have shown that methyl substituents at the bridgehead positions lower the barrier to the ring opening reactions.[175-178]

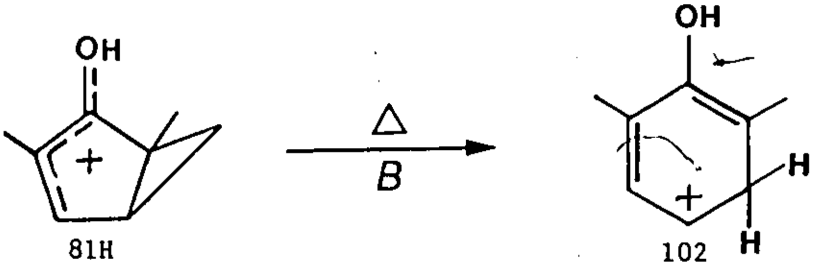
It is instructive to note that similar but smaller effects were observed by Klärner in the thermal isomerization of substituted bicyclo-[2.1.0]pentenes.[179,180]

Scheme 21

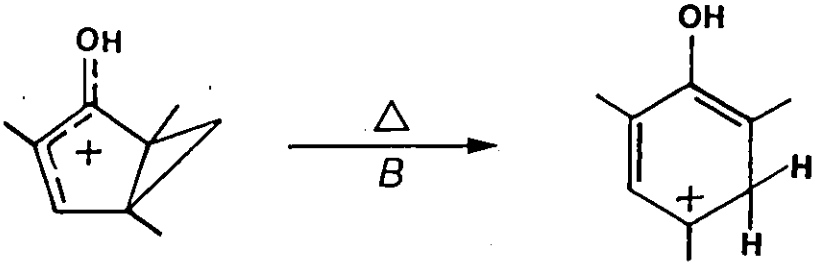


$\underline{R}_1$	$\underline{R}_2$	$\underline{R}_3$	$\underline{R}_4$	$\Delta G^{\neq}$ kcal/mole
H	H	H	H	24.9
H	H	CH_3	CO_2CH_3	24.5
CH_3	H	CH_3	CO_2CH_3	23.1
H	CH_3	CH_3	CO_2CH_3	25.2

In the present case, the effect of methyl substituents at the bridgehead positions (C_1 and C_5) can be seen clearly in the isomerizations given in Table 2.14. The presence of methyl groups at C_1 and C_5 of the bicyclic cations will have relatively little effect on the stability of the starting cation, however, they are ideally placed to stabilize the initially formed intermediate in the direct ring opening reaction (i.e. Path B). In the case of 81H, the absence of a C_5 methyl group causes the energy barrier for the direct ring opening to be greater than 27.2 kcal/mole as compared to 22.4 kacl/mole for 76H. The direct ring opening reaction of 81H would give rise to intermediate 102 which is less stable than 103 which is obtained from 76H by an analogous process, equations 71 and 72, respectively.

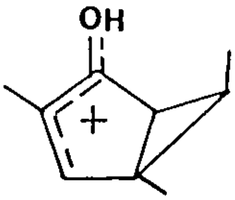


81H 102 (71)

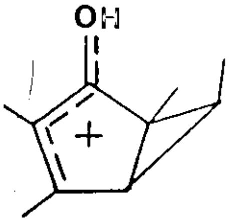


76H 103 more stable (72)

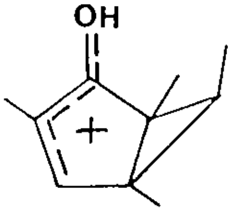
The importance of the two methyl groups on C_1 and C_5 for the direct ring opening reaction can also be seen when comparing the thermal isomerization of 54, 73H and 76H. As mentioned earlier, Childs and co-workers observed a circumambulatory migration in the rearrangement of 54, equation 28.[113] In this case, circumambulation must be a lower energy process than any of the ring opening pathways. Such a circumambulatory rearrangement might have been expected to occur in cations such as 73H and 76H producing the more stable bicyclic cations 71H and 74H, respectively.



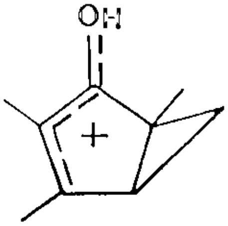
54H



71H



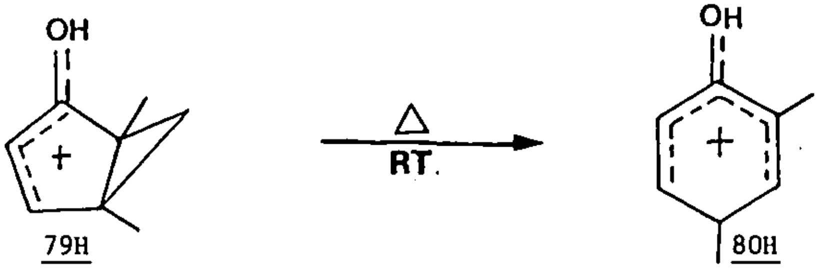
73H



74H

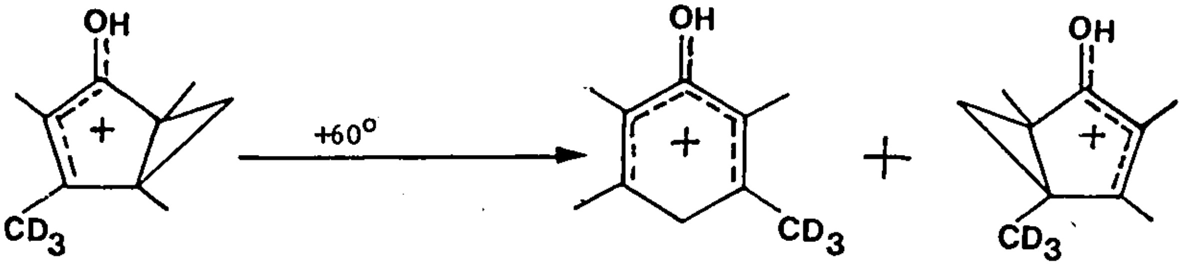
However, in the current study, neither 73H or 76H undergo circumambulatory rearrangements in preference to direct ring opening. This result can be understood in terms of the difference in the methyl substitution pattern at the bridgehead positions (i.e. C_1 and C_5) of 54, 73H and 76H. Cation 54 lacks the two methyl substituents at C_1 and C_5 which would seem to be a requirement for the direct ring opening, i.e. Path B.

It is interesting to note that the effect of methyl substitution at C_1 and C_5 is consistent with the results obtained from the irradiation of 63H at different temperatures. While, at -70°C a mixture of 78H (95%) and 79H (5%) are formed on irradiation of 63H (equation 42), when this same photoisomerization is carried out at room temperature 78H and protonated 2,4-dimethylphenol 80H are formed in the same ratio (equation 43). This result can be understood in terms of the thermal conversion of 79H at room temperature to 80H via Path B, equation 73.



(73)

In examining the effect of substituents on the barriers to isomerziation by Paths A and C, it is necessary to know what is the rate determining step in the two reactions. According to Hart[97,112] and Childs,[95] the circumambulatory migration process in protonated hexamethylbicyclo[3.1.0]hexenone 38 (equation 26) is faster than the ring opening, Scheme 6. In the present study, the identity of the slow step in the isomerization of 70H was established by examining the rearrangement of the deuterated bicyclic cation 70D, equation 52. On heating the CF_3SO_3H solution of 70D to +60° the concentration of the deuterated cation decreased in favour of the other two cations 58D (40%) and 95 (5%). This result indicates that the barriers for circumambulation ($\Delta G^{\ddagger}$ = 27.3 kcal/mole) and ring opening ($\Delta G^{\ddagger}$ = 26.20 kcal/mole) via Path C are now comparable.



(52)

70D
55%

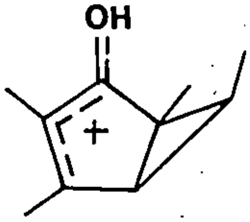
58D
40%

95
5%

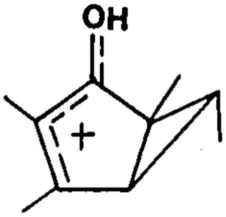
Previous work on the thermal isomerization of bicyclo[3.1.0]-hexenyl cations has shown that an exo methyl substituent at C_6 greatly enhances the circumambulation process in these cations while an endo methyl group as mentioned earlier has much less effect, Table 1.3.[95]

This important difference has been discussed in terms of the steric requirements for the reactions.[95]

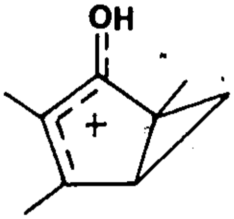
The effect of a methyl substituents at C_6 in the ions studied here can be seen clearly in the various isomerizations given in Table 2.14. While the methyl substitution pattern present in 71H and 74H does not enable a clear differentiation between the three isomerization pathways to be made. However, comparison of the effect of the C_6 substituents on the rate of isomerization of these ions as compared to 72H support the suggestion that they isomerize by a two step process in which the barrier to cyclopropyl migration is higher and it determines the overall rate of the reaction. In particular, it is important to note that 72H, which isomerizes by path C has the lowest activation barrier. This is consistent with the presence of an exo C_6 methyl group in this ion.



71H



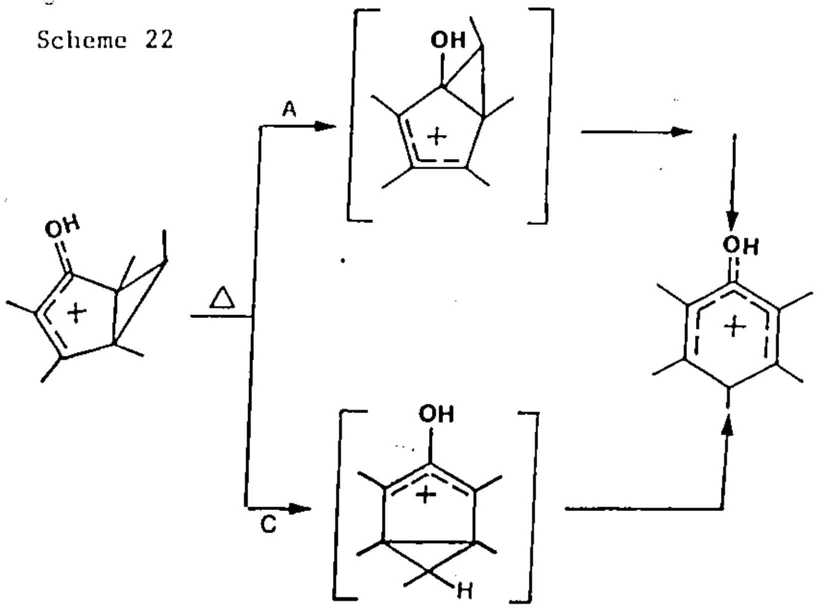
72H



74H

The barrier to isomerization of 67H is similar to that of 70H. In the former cation, there is more than one possible pathway by which 67H can be converted to 56H, however, in view of the behaviour of both 38 and 70H it would seem likely that 67H also isomerizes by either Path A or C, Scheme 22. Indeed it is likely that the endo C_6 methyl substituent on 67H is not altering the barrier to circumambulation by very much, as would be expected from the previous results summarized in Table 1.3.

Scheme 22



At this point it is still not clear as to what determines the choice of ring opening between Paths A and C. The above results have shown that, in general, such a choice between either pathway becomes applicable only when the energy barriers for the direct ring opening, Path B, is higher than for the circumambulatory routes, i.e. Paths A and C. One thing that is noticeable from the results obtained from the isomerizations of 38, 70H and 81H is that the selectivity of the circumambulation process appears to be independent of the stability of the proposed intermediates. Moreover, the contrasting behaviour of 38 and 70H is difficult to understand from a single perspective and points to the subtle blend of factors which are at play in these ions in determining the course that they follow.

Conclusions

The foregoing results are the first reported systematic approach to the determination of the activation barriers and possible mechanisms for the isomerization of protonated polymethyl bicyclo[3.1.0]hexenones to protonated phenols. Overall, these results have demonstrated the presence of a remarkable substituent dependence on the rate and mode of isomerization of these protonated bicyclic ketones. In summary, as the substitution pattern at C_1, C_4 and C_5 vary, the mechanism of isomerization changes. Direct ring opening reactions are proposed for cations which are fully substituted at C_1 and C_5 and unsubstituted at C_4. On the other hand a mechanism involving a two step process is proposed for cations with a different substitution pattern at these positions.

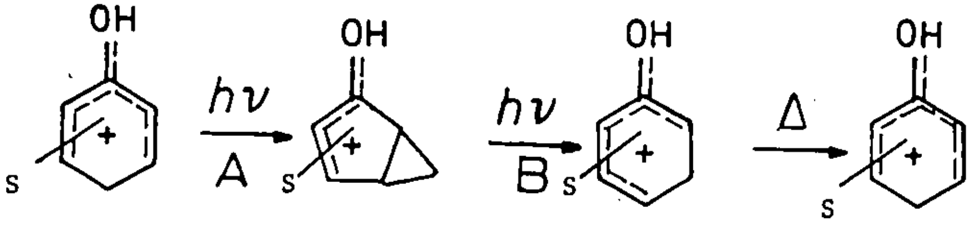
PART IV:

Photochemistry of Protonated Phenols

Qualitative Observations

As is shown by the results summarized in Tables 2.3 and 2.13, direct irradiation of C_4 protonated methyl- and chlorosubstituted phenols at 300 and 254 nm produce protonated bicyclo[3.1.0]hexenones as the major photoproducts. These photoreactions can be understood in terms of the general scheme shown below.[113]

Scheme 23

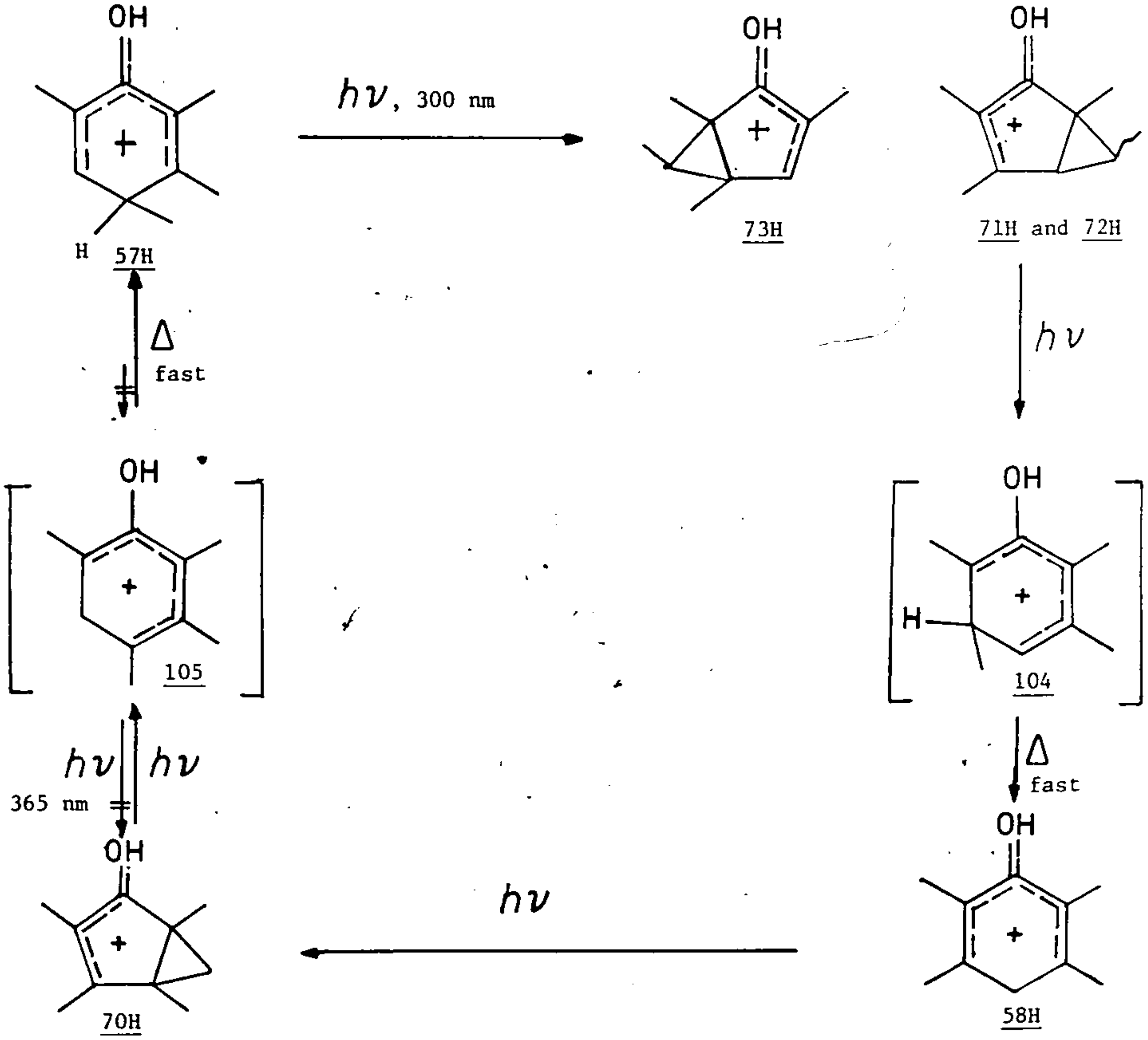


S = Me or Cl

An important feature of this scheme is that the first formed protonated bicyclic ketone can undergo a further photoreaction to give a meta protonated phenol which then isomerizes to the more stable para protonated form. The latter isomer of the starting protonated phenol can potentially undergo further photoreaction. The photorearrangement of protonated isodurenol (<u>57H</u>) well illustrates these steps.

Irradiation of protonated isodurenol in FSO_3H at low temperature leads to the formation of four different isomeric protonated bicyclo-[3.1.0]hexenones and protonated durenol, Scheme 24. Three of these protonated ketones <u>71H</u>, <u>72H</u> and <u>73H</u> have a methyl group at the C_6 and are closely related to the isomerizations mentioned in the introduction of this thesis. They would seem to originate from the para protonated isodurenol, <u>57H</u>, as the photoreactive starting species. The fourth protonated bicyclic ketone, <u>70H</u>, which is present as the major photoproduct, has previously been shown to result from the irradiation of protonated durenol, <u>58H</u>.[126,127]

As can be seen from the results in Table 2.6, bicyclic cations <u>71H</u> and <u>72H</u> exhibit absorption maxima in their UV spectra at ca. 330 nm. Thus under the conditions where broad spectrum light is used for the photoisomerization, the reaction products would also absorb strongly. It is well known that protonated bicyclo[3.1.0]hexenones undergo photo-induced ring opening to give, after a hydride shift, the corresponding para protonated phenol.[103,104,113] Thus the formation of <u>58H</u> can be explained by the photorearrangement of <u>71H</u> and <u>72H</u>. The formation of <u>70H</u> can then result from the photorearrangement of <u>58H</u>. An alternative


OH
57H
H
hν, 300 nm
OH
73H
OH
71H and 72H
hν
Δ
fast
OH
105
OH
H
104
hν
hν
365 nm
Δ
fast
OH
70H
hν
OH
58H

Scheme 24

route to 70H would be the photoisomerization of meta protonated isodurenol, 105. However, the evidence cited below shows that the former route involving the formation of 58H is operative.

Comparable photoisomerizations of 57H occurred when the irradiations were carried out at room temperature in CF_3SO_3H (Table 2.3). In this case the products obtained were the same as to those formed in FSO_3H at low temperature except that the formation of 73H was not observed. This is not unexpected in that 73H is thermally unstable at room temperature and is converted to 57H (equation 66).

The results obtained from following the photorearrangement of 57H as a function of time of irradiation (Figures 10 and 11) provide support for the above sequence of events. It is clear from these figures that the increase in the relative concentration of 70H lags the formation of the other three photoproducts 71H, 72H and 58H. In particular it was noted that the products obtained at very low conversions of 57H (<10%), were exclusively 71H and 72H, (Table 2.7).

The overall mechanism shown in Scheme 24 is further substantiated by the results of the experiment where 57H was irradiated with light of wavelength > 360 nm. Previous work has shown that meta protonated phenols exhibit absorption maxima which are considerably red shifted from those of the para-protonated phenols. Thus meta protonated 2,4,6-trimethylphenol was shown to absorb at 365 nm.[113] In the present case if the formation of 70H from 57H were to involve 105 in equilibrium with 57H, then the use of the longer wavelength light should enhance the formation of 70H as compared to 71H and 72H. This is not the case as only 71H and 72H were formed when 57H was irradiated at 365 nm.

Irradiation of 58H under the same conditions as used for 57H in CF_3SO_3H results in the formation of the same reaction products (Table 2.3 and Figure 12). A photostationary state with the same composition is reached starting either from 57H or 58H.

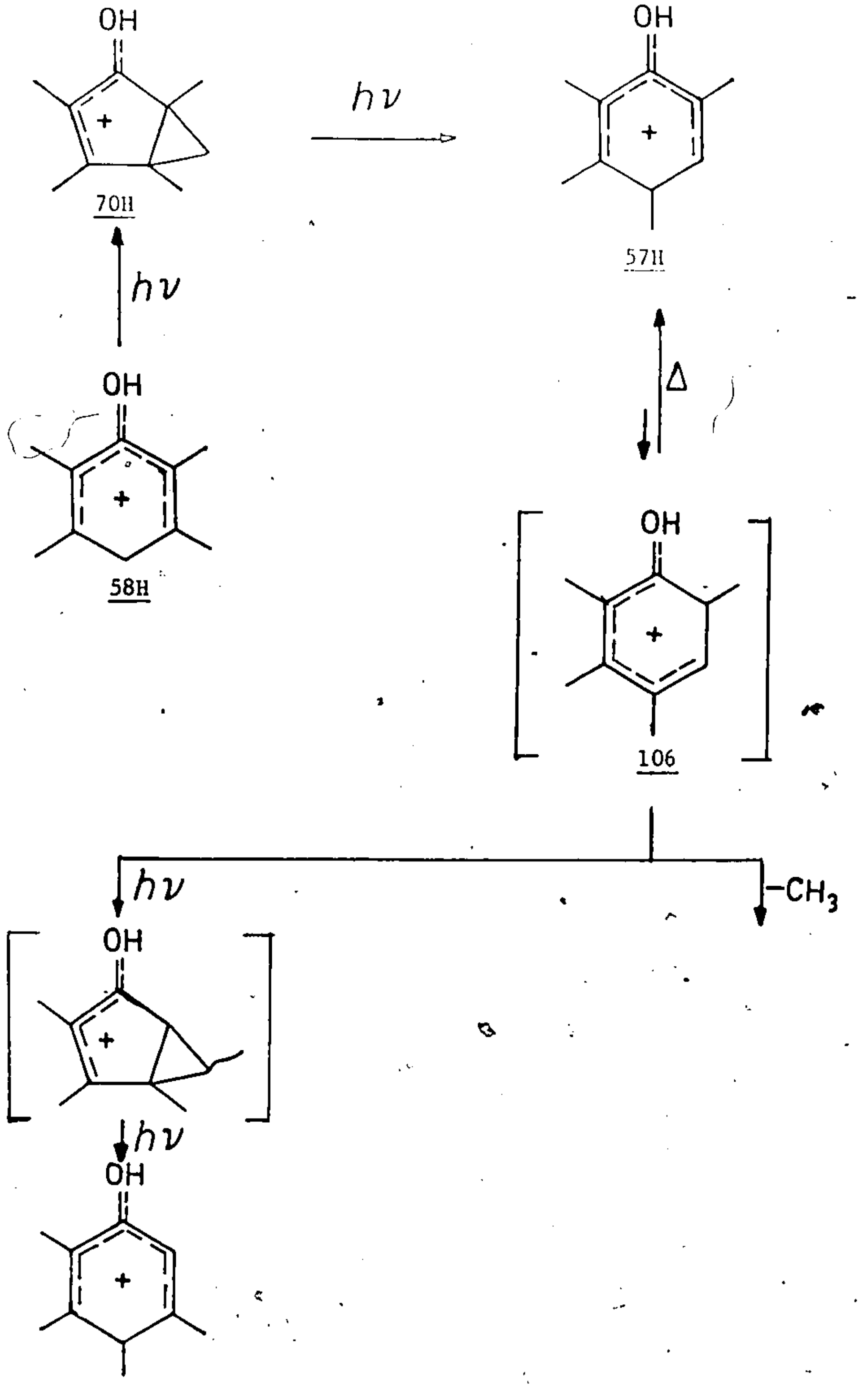
Two points emerge from a consideration of the concentration changes summarized in Figure 12. First, at an early stage of the irradiation (≃ 10 hrs), the rapid increase in the concentration of 70H occurs at the expense of a corresponding decrease in the concentration of the starting material 58H, indicating that the former is a primary photoproduct. Second, the formation of the other photoproducts, 71H, 72H and 57H, is dependent on the initial formation of the bicyclic cation 70H rather than that of the starting material. Overall the photoisomerizations of 58H provides further evidence that strongly supports the overall sequence of events shown earlier in Scheme 24.

Following the completion of this present study on the photoisomerization of protonated durenol 58H in CF_3SO_3H, Baeckström and co-workers reported the formation of some further photoproducts.[127] In addition to 70H (31%); and 57H (16%), they also reported that protonated 2,3,4,5-tetramethylphenol 59H (7%) was present. In addition two unidentified ketones (MW=150, MS) and one dealkylated phenol (MW=136, MS) were detected in 12, 2 and 2% yields, respectively. Baeckström and co-workers suggested that ortho protonated isodurenol 106 is involved in the formation of both 59H and the dealkylated phenol, Scheme 25.

As a result of Baeckström's report, a careful re-examination of the photoproducts arising from the photoisomerization of <u>58H</u> was undertaken. This showed that under the reaction conditions used in this work neither <u>59H</u> nor any dealkylated phenol was present.

The results presented here were entirely reproducible and no additional products could be detected. Indeed the formation of a photostationary state from either <u>57H</u> or <u>58H</u> strongly indicates that there are no irreversible photoisomerization occuring in these systems.

The difference between the results presented here, and those reported by Baeckstrom is disturbing and it is not clear what is the origin of this effect. There could be differences in the nature of the triflic acid, the temperature of the reaction, or the spectral distribution of the light used. It is unlikely that variation in wavelength of the light used is the reason for the difference in products obtained between the two groups. It has been shown here that change of wavelengths in the case of the photoisomerization of the closely related system <u>57H</u> has no effect on the product composition. It would seem unlikely that there would be large differences in temperature in the two reactions and difficult to see how modest temperature changes could so alter the photoinduced pathways. It is known that Lewis acids can compete with a proton for attachment to a phenol, even in strong acid media as are used in this work.[181,182] It is also known that the photoisomerizations of Lewis acid complexes of phenols differs somewhat from those observed with the protonated phenols in strong acids in that products appear to derive from ortho protonated species.[146] It could be that the differences in behaviour between Baeckstrom and our photoisomer-



Scheme 25

ization of 58H arise from the presence of a Lewis acid impurity in the CF_3SO_3H used by Baeckström and co-workers.

It should be pointed out, however, that the failure of Baeckström and co-workers to detect the formation of 71H and 72H is worrying and it raises questions as to the analytical method used by these authors. As was shown in the results section, the separation of all of these isomers by GLC is exceedingly difficult. Baeckström and co-workers have pointed out that all compositions of reaction products formed from irradiation of 58H depend on the length of the irradiation. They suggested that prolonged irradiation of 58H results in an excessive formation of secondary photoproducts which will complicate the inevitable separation procedure. This conclusion does not agree with the present study in which prolonged irradiation of 58H at room temperature does not alter the nature or the composition of the products found at the photostationary state.

One final point that must be stressed is the cleanness of the above photochemical rearrangements of 57H and 58H as well as the rest of the other methyl substituted phenols shown in the results section. This makes them an attractive system for storage of solar energy.

While the overall sequence of events would seem clear, there are a considerable number of details which need to be considered.

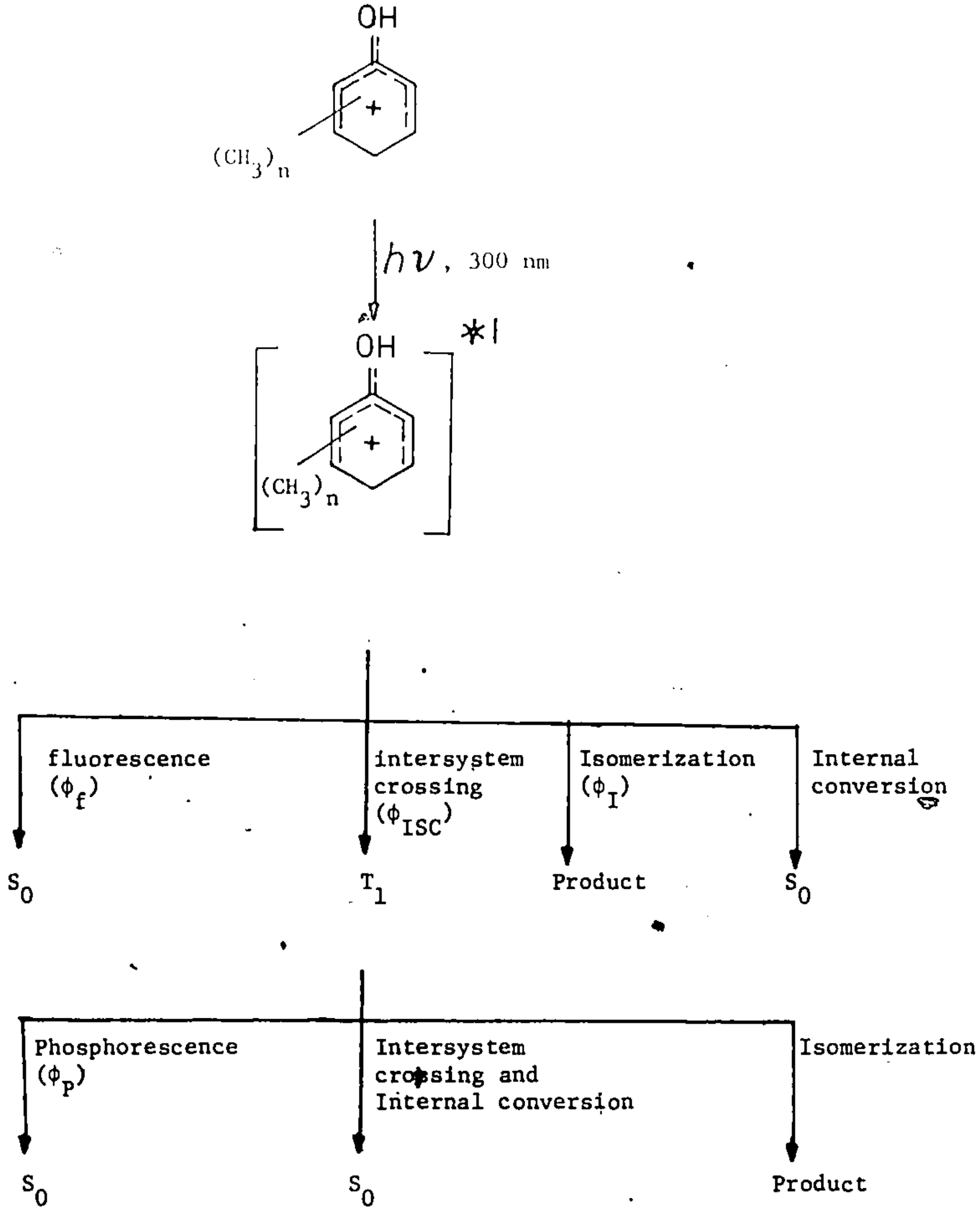
Nature of the Excited State

The absorption spectra of the C_4 protonated methyl- and chloro-substituted phenols exhibit intense absorption maxima in the range 300-330 nm (Tables 2.3 and 2.11, respectively).

Absorption of ultra violet radiation by a protonated phenol will lead to the formation of the lowest excited singlet state (S_1). This state can then lose its energy and return to the ground state by a number of different pathways, Scheme 26. Relaxation can be achieved by the emission of light (fluorescence), a radiationless process such as valence isomerization, intersystem crossing (ISC) to the first excited triplet state (T_1) or internal conversion (IC) to the ground state (S_0). Relaxation from T_1 can also be accomplished by emission (phosphorescence) or radiationless processes such as isomerization and intersystem crossing.

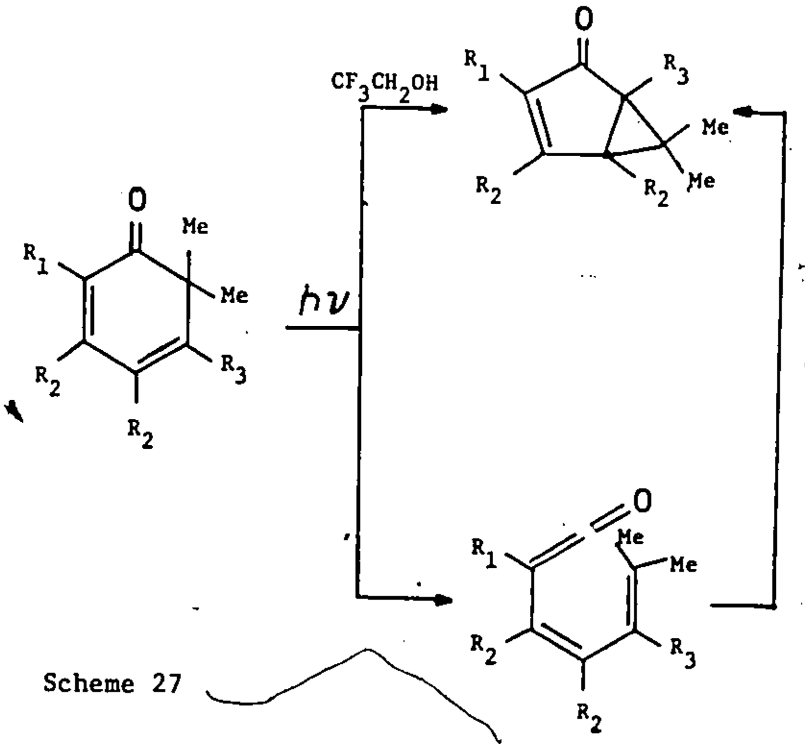
As shown in Table 2.2, all the C_4 protonated phenols (56H-65H) exhibit an intense absorption maxima range from 300 nm to 329 nm depending on the ring substituent. The high intensity of these bands indicates that for all of the C_4 protonated phenols, the transitions are of π,π^* character. This is expected since two of the non bonding n-electrons of the hydroxyl oxygen are bound by protonation, causing the absorption band corresponding to be lowest energy transition to be very intense and of π,π^* character.

For the C_4 protonated phenols discussed in this thesis, photoisomerization to protonated bicyclo[3.1.0]hexenones could be a major dissipative pathway. These photoisomerizations parallel those of the neutral 2,4-cyclohexadienones studied by Hart.[183] One particularly interesting aspect of Hart's work concerns the inversion of the energy of the n,π^* and π,π^* excited states involved in these reactions by the use of trifluoroethanol or a cyclohexane-silica gel slurry as the media for the irradiations. With the more polar solvent systems Hart showed that the tri-, tetra-, and hexamethyl cyclohexa-2,4-dienones isomerized to the


OH
+
(CH3)n
hν, 300 nm
OH
*1
+
(CH3)n
fluorescence
(φf)
intersystem
crossing
(φISC)
Isomerization
(φI)
Internal
conversion
S0
T1
Product
S0
Phosphorescence
(φP)
Intersystem
crossing and
Internal conversion
Isomerization
S0
S0
Product

Scheme 26

corresponding bicyclic ketones without the involvement of a ketene intermediate, Scheme 27. It was also shown that isomerization of these dienones in non polar solvents led to products resulting from a ring opening reaction to the ketene.[184] The ketene intermediate was thought to arise from an n,π^* excited state. With hydrogen bonding or acidic solvents, the relative energy of n,π^* transition is increased while that of π,π^* transition is decreased and in trifluoroethanol or on a silica surface it was suggested that the relative energies of these two states become inverted and that for π,π^* state(s) were of lower energy. The direct formation of the bicyclic ketone was suggested to arise from the π,π^* state. The change in relative energies of n,π^* and π,π^* transitions as a function of the polarity of the solvent has been confirmed by many investigators in studies on the photoisomerizations of unsaturated carbonyl compounds in different solvents.[185-192]



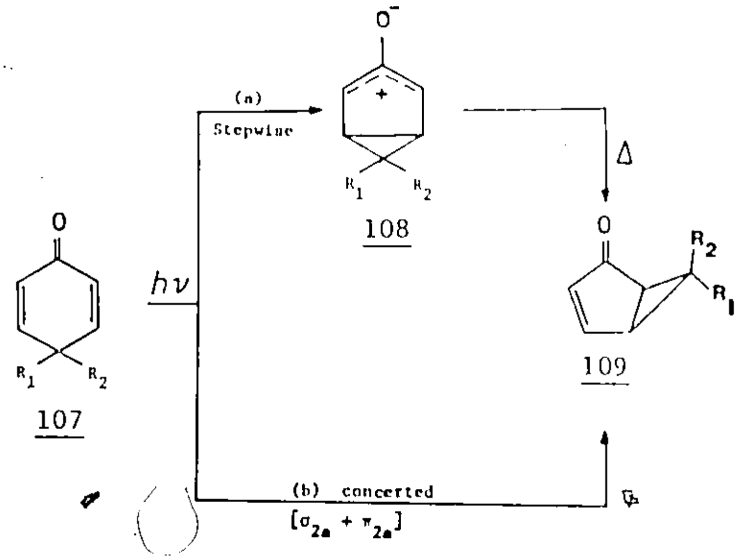
Scheme 27

Previous studies on the photoisomerizations of cross-conjugated dienones have shown in general that these reactions proceed via triplet excited states.[107,109] In the strongly acidic solvents used in this work most of the sensitizers and quenchers used in more conventional media are protonated. This means that their properties will be considerably modified and their adaptation to use in strong acid media is not straightforward. To differentiate bewteen singlet and triplet photochemistry, quenching experiments involving molecular oxygen were carried out. The results given in Table 2.8 indicate that dissolved oxygen has no detectable effect on the efficiencies of these photoisomerizations. While no data are available regarding the solubility of oxygen in CF_3SO_3H or related strong acids, it would seem likely that the photoproducts are formed from singlet or very short lived triplet states.[192]

Possible Isomerization Mechanism

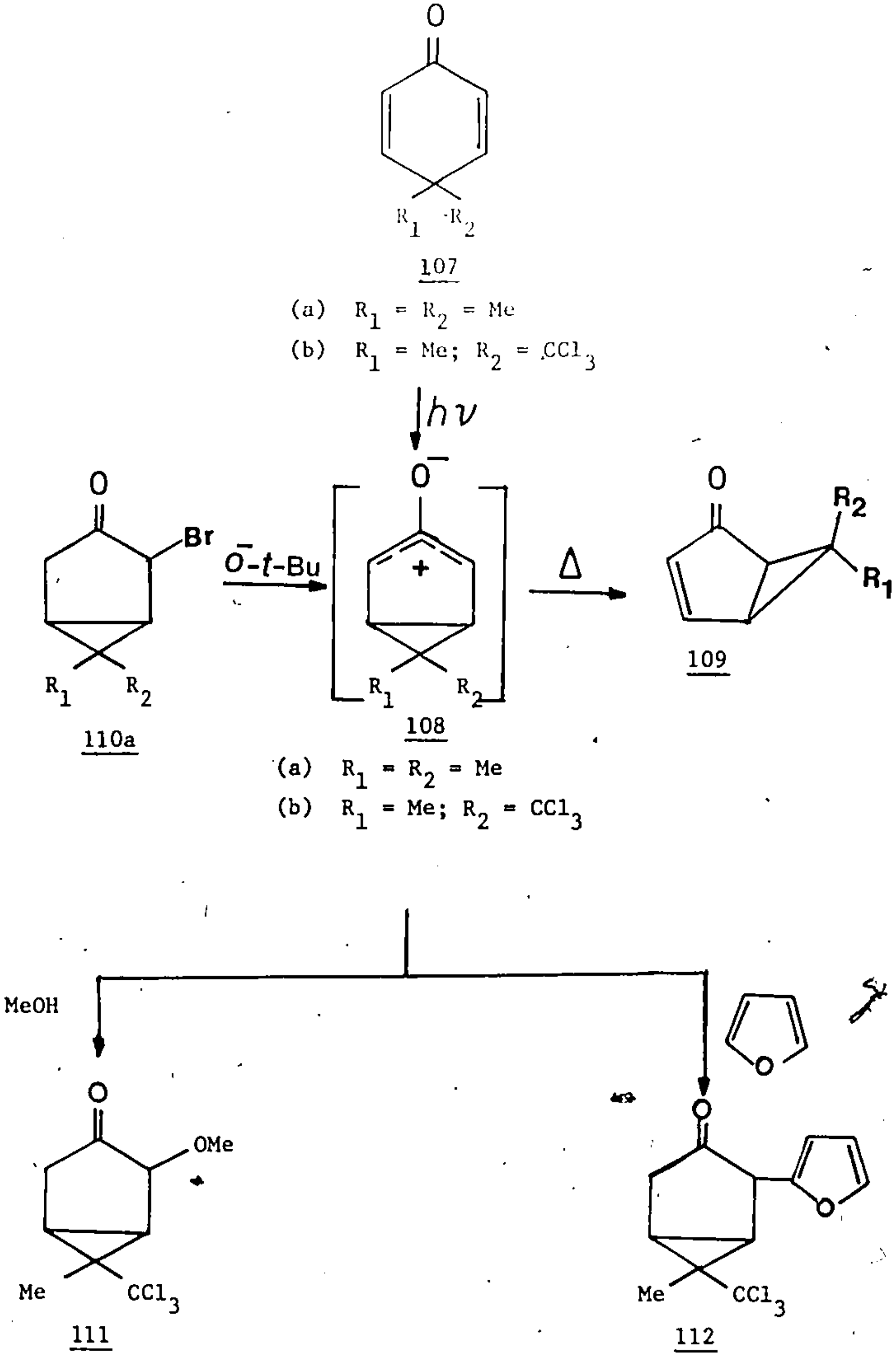
Zimmerman and Schuster[105] have proposed a unifying mechanistic scheme to account for the photorearrangements of cross conjugated dienones to bicyclo[3.1.0]hexenones. This involves a symmetry allowed photochemical disrotatory ring closure in the excited state to form, after electron demotion, the Zwitterionic intermediate <u>108</u> which can then undergo a thermally allowed cyclopropyl migration to give the bicyclic ketone <u>109</u>. Woodward and Hoffmann[91] also have considered the reaction to be formally a [σ2a + π2a] cycloaddition and pointed out that this process is photochemically allowed (Scheme 28).

Scheme 28

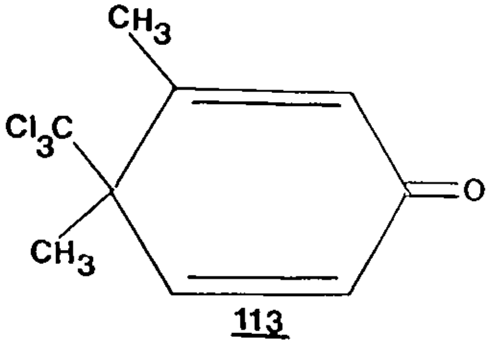


While the Zwitterionic intermediate 108 has not been directly observed in the isomerization of conjugated dienones, there is excellent evidence for its existence.[108,193-197] Zimmerman[194] has reinforced his original suggestion by finding that 110a undergoes an anomolous Favorskii rearrangement to give 109a. Schuster,[196,197] has provided further evidence in his finding that 107 gives the solvent adduct 111 on irradiation of 107b in acidic methanol. More recently, Samuel[108] has obtained evidence which points towards the existence of 108b by trapping using furan, to give the 1:1 adduct of structure 112 (Scheme 29).

The plausibility of the Zwitterion mechanism in the photochemical isomerization of 2,5-cyclohexdienones was further strengthened when Schuster and co-workers have prepared an optically active bicyclic ketones by irradiation of the optically active dienone 113.[198]


O
R_1 R_2
107
(a) $R_1 = R_2 = Me$
(b) $R_1 = Me$; $R_2 = CCl_3$
hν
O
Br
$\bar{O}$-t-Bu
R_1 R_2
110a
O^-
+
R_1 R_2
108
(a) $R_1 = R_2 = Me$
(b) $R_1 = Me$; $R_2 = CCl_3$
Δ
O
R_2
R_1
109
MeOH
O
OMe
Me
CCl_3
111
O
O
O
Me
CCl_3
112

Scheme 29



113

Overall, there is good evidence for the occurrance of a two step mechanism in the photoisomerization of cross-conjugated cyclohexadienones to bicyclo[3.1.0]hexenones.

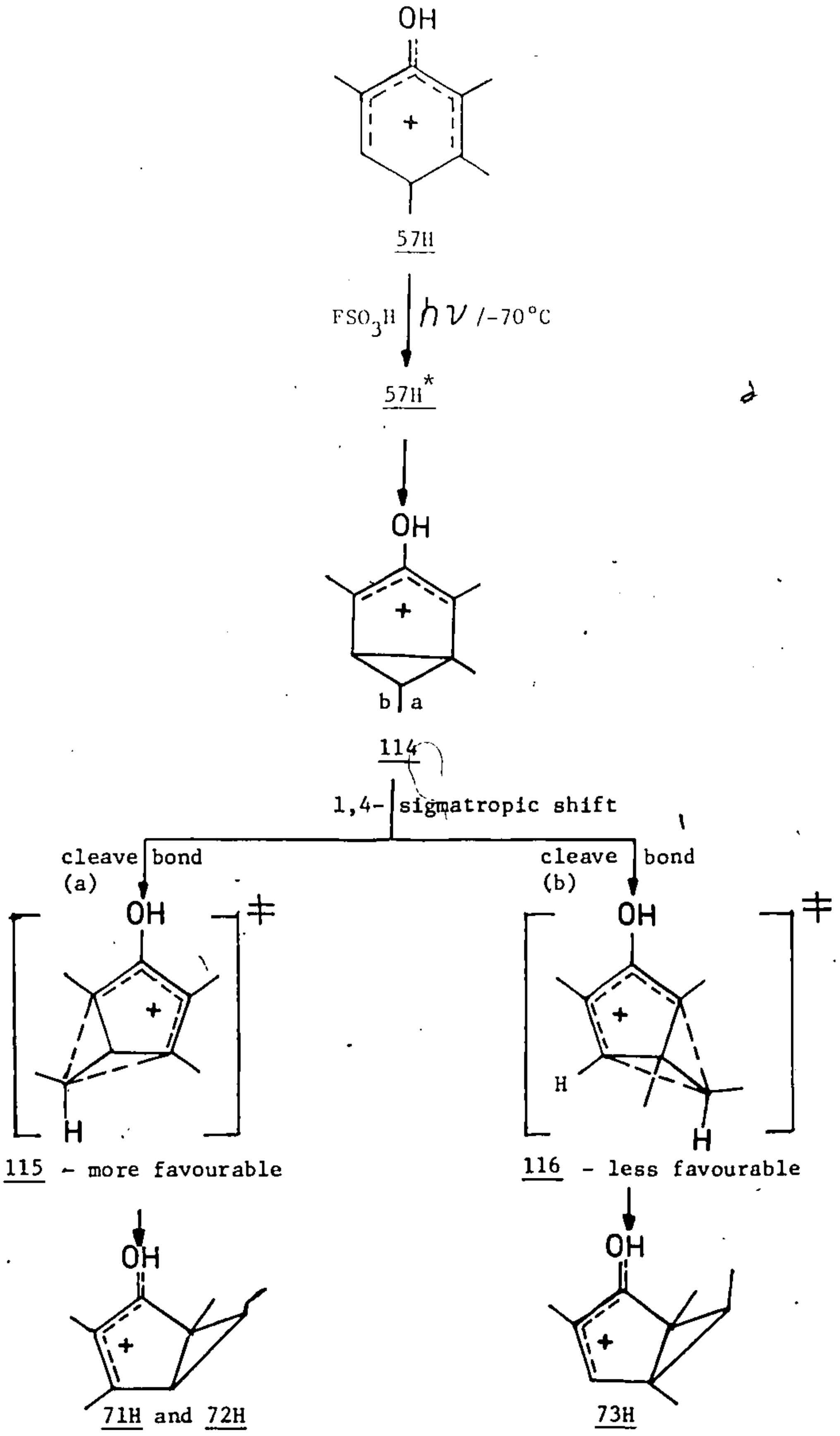
This type of two step rearrangement has also been suggested to take place for the photoisomerizations of protonated cyclohexadienones.[102,104] In support of this it should be noted that the photoisomerization of polymethylbenzenium ions to bicyclo[3.1.0]hexenyl cations has been shown to proceed by a symmetry allowed disrotatory ring closure, a reaction similar to the first step in the two step process, rather than by a [σ2a + π2a] cycloaddition reaction.[93,94]

In the present study, the formation of protonated bicyclo[3.1.0]-hexenones on irradiation of protonated phenols can best be understood in terms of a two step mechanism. This proposal is consistent with all the experimental observations available. For example, it can account for the observed regio- selectivity in the low temperature photoisomerization of the protonated 3-substituted phenols in FSO_3H. As already mentioned, the photoisomerizations of protonated isodurenol <u>57H</u>, 2,3,6-trimethyl <u>60H</u>, 2,3-dimethyl <u>63H</u> and 3-chloro <u>86H</u> phenols in FSO_3H at -70° result in the formation of more than one bicyclic cation. The major cation is the one with the original C_3-substituent (i.e. Me or Cl) on the double bond of the product (Tables 2.4 and 2.12). The reaction scheme that can account for the above regioselectivity is shown for <u>57H</u> in Scheme 30.

This involves the photoexcitation of <u>57H</u> followed by a disrotatory ring closure of the excited cation to give <u>114</u> as an intermediate. There are two possible ways in which this intermediate can undergo a 1,4-sigmatropic shift. As is shown earlier, both the substitution of a cyclopropane bond, and the relative stabilities of the products play an important role in determining the activation barrier for the ring opening reaction of <u>114</u>. The same two effects would seem to be operative in the thermal isomerization of protonated bicyclo[3.1.0]hexenones to protonated phenols. In general, the more highly substituted the bond (i.e. bond a in this case), the lower the activation barrier for its cleavage. Further, the presence of a methyl group at C_4 in <u>71H</u> and <u>72H</u> enhances their thermodynamic stability by ca. 5.0 and 3.0 kcal/mole, respectively, as compared to <u>73H</u>.[199] This suggests that stabilization of the incipient positive charge at C_4 in the transition state <u>115</u> by a methyl group might occur to lower its energy relative to <u>116</u>, which has no methyl group at C_4 (Scheme 30).

Similar observations have also been reported by Pavlik[104] and Childs[113] in the photoisomerization of hydroxycyclohexa- dienyl cations and protonated phenols, respectively.

Scheme 30


OH
+
57H
FSO3H
hν/-70°C
57H*
OH
+
b
a
114
1,4-sigmatropic shift
cleave bond (a)
cleave bond (b)
OH
+
‡
H
115 - more favourable
OH
+
H
H
‡
116 - less favourable
OH
+
71H and 72H
OH
+
73H

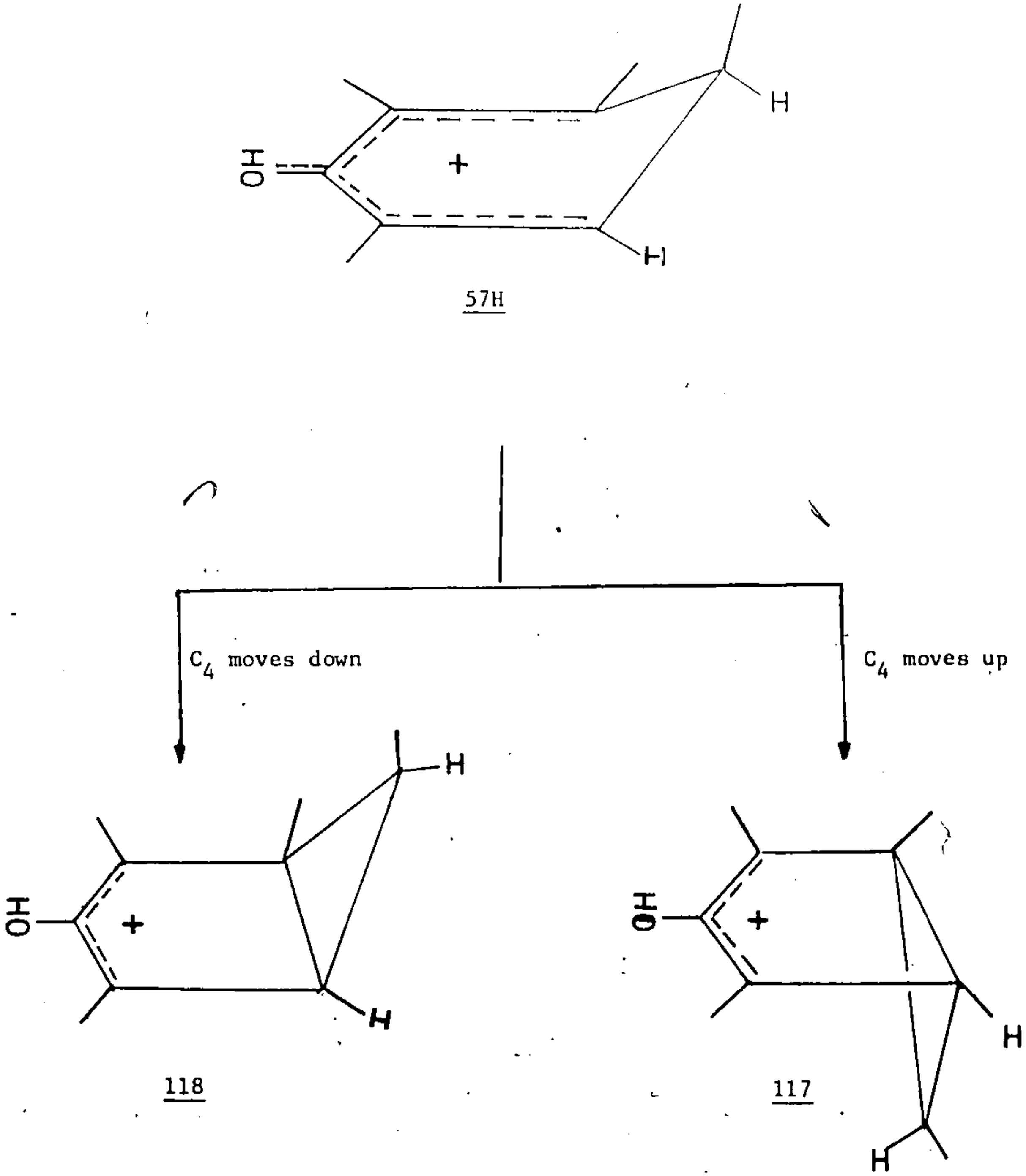
Stereochemistry in the Photoisomerization of Protonated C_4-Methyl Substituted Phenols

The exo-endo isomer ratio

As already mentioned, the photoisomerization of protonated C_4-methyl substituted phenols (i.e. 56H and 57H) results in the formation of protonated endo C_6-methyl substituted bicyclic ketone as the major products. This observation is similar to that previously reported for the photoisomerization of neutral 2,5-cyclohexadienones[88,96,138,139] and benzenium cations.[85,86] In the former case the larger group at C_4 compare to C_6 in the case of benzenium cations preferentially ends up in the endo position at C_6 of the bicyclic ketone.

Previous explanations for the stereoselectivity observed in the photoisomerization of neutral 2,5-cyclohexadienones have dealt with the steric effect of the substituents at C_3 and C_5.[88] However, in this present work the stereoselectivity observed in the photoisomerization of 56H and 57H can be understood in terms of the planarity of the starting cations. Both cations 56H and 57H have been shown earlier to be non planar with the C_4 methyl group adopting a pseudo axial position. This is consistent with the recent experimental and theoretical observations made on cyclohexadienylium ions.[200] On this basis, for example, one would expect that the photochemical ring closure of 57H to yield the endo isomer 117 would be the preferred ring closure pathway (Scheme 31). Closure of 57H to give 117 is an easy process which avoids the much larger molecular motion involved in the formation of 118. This motion to form 117 also avoids the necessity of moving the methyl group at C_4

Scheme 31



57H

118

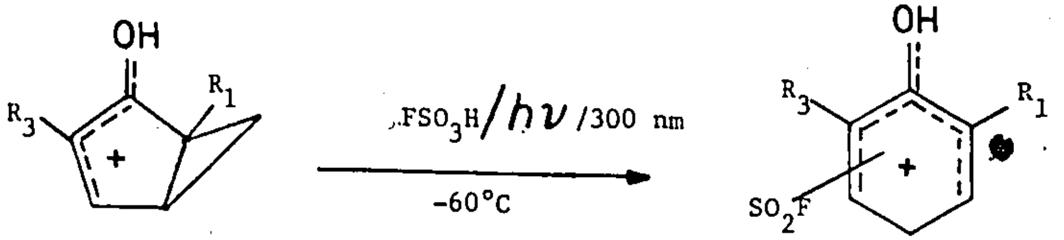
117

through the plane of the buttressed methyl group on C_3 of 57H.[157-159]

Photoisomerization of Protonated Chlorophenols

Two results which are markedly different from those already discussed are the photochemical behaviour of protonated 2-chloro 85H and 3-chloro 86H phenols in FSO_3H at -60oC, Scheme 32. The expected products obtained from these irradiations at 300 nm were protonated bicyclo-[3.1.0]hexenones 91H-94H. However, instead fluorosulfonation of the protonated phenols was observed.

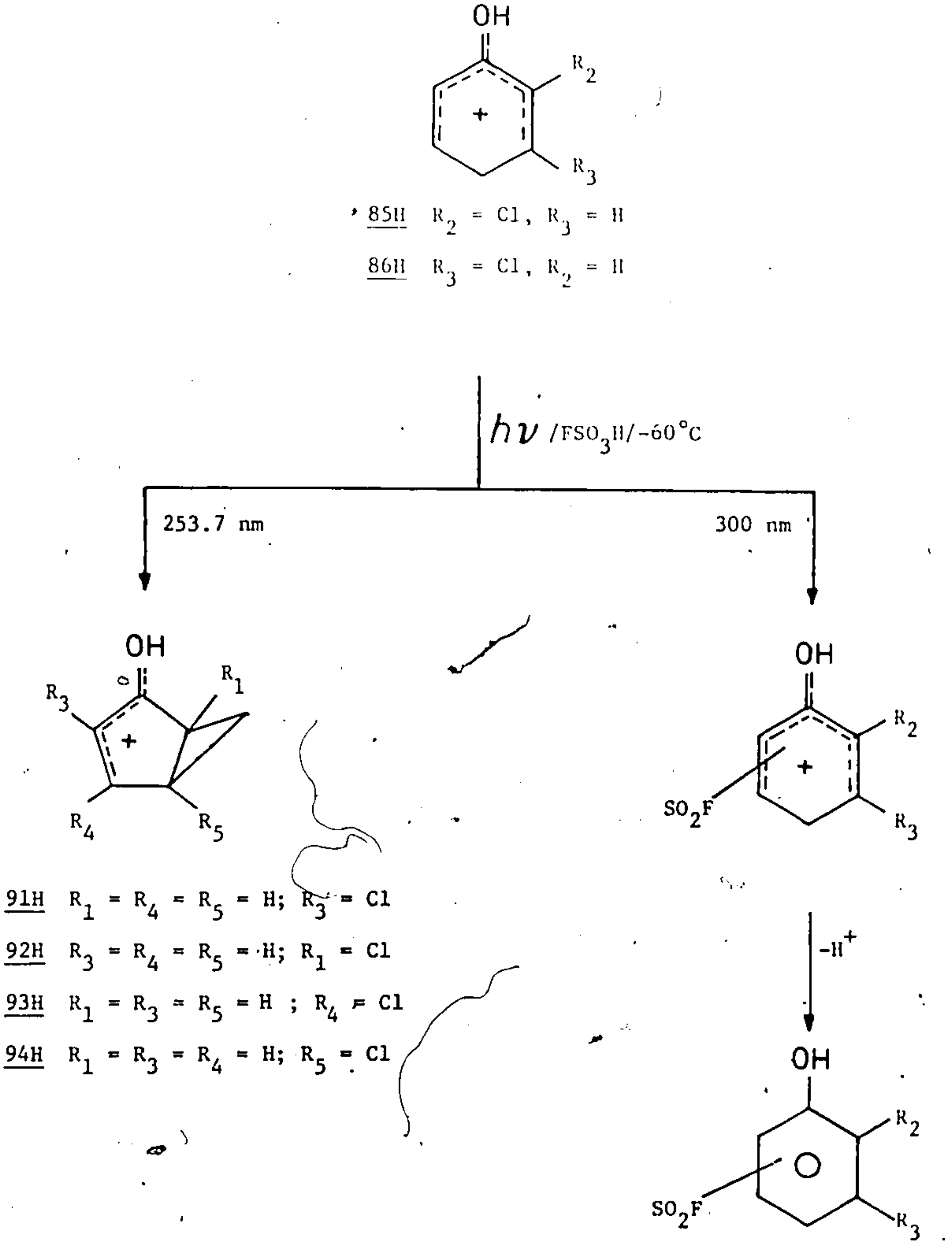
The results obtained from the irradiation at low temperatures (300 nm) of a mixture of 85H, 91H and 92H at different time intervals provides some information that may account for the formation of the fluorosulfonated products. The key point emerging from this study is that the drop in the relative concentration of 91H and 92H is coincides with an increase in the concentration of the fluorosulfonated products. However, during this irradiation the relative concentration of 85H remained unchanged. This would strongly suggest that the fluorosulfonated phenols originate from 91H and 92H, equation 74



(74)

91H R_1 = H, R_3 = Cl

92H R_1 = Cl, R_3 = H



85H R_2 = Cl, R_3 = H

86H R_3 = Cl, R_2 = H

91H $R_1 = R_4 = R_5$ = H; R_3 = Cl

92H $R_3 = R_4 = R_5$ = H; R_1 = Cl

93H $R_1 = R_3 = R_5$ = H ; R_4 = Cl

94H $R_1 = R_3 = R_4$ = H; R_5 = Cl

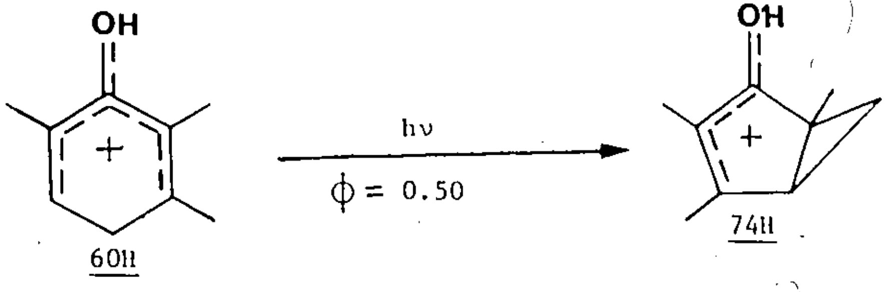
Scheme 32

The mechanisms to account for the formation of these products is not apparent.

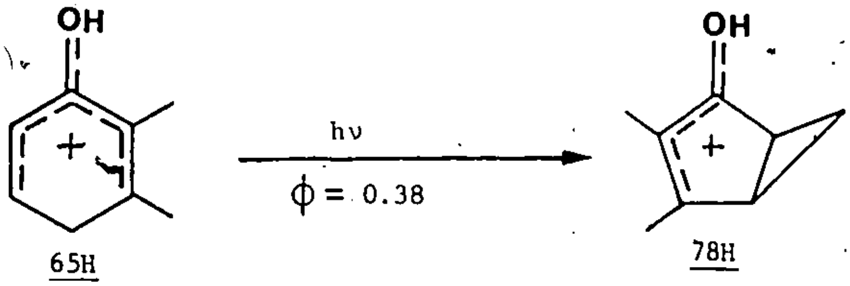
Quantitative Studies

The reported quantum yields are not corrected for the reverse reaction, however, as the measurements were made at low conversions (< 10%) of the starting cation to protonated bicyclic products, this should not alter the results significantly. It should also be noted that the quantum yields for the photorearrangement of the protonated phenols with 3-methyl substituents (i.e. 57H, 60H and 63H) do not take into account the formation of the kinetically unstable minor isomers 73H, 76H and 79H, respectively. As less than 10% of these minor isomers were formed on irradiations at low temperature, neglect of these "hidden" conversions at room temperature will not greatly affect the measured quantum yields.

It is apparent from an examination of the results given in table 2.7 that there is a large structural dependence on the quantum efficiencies for the photoisomerizations of protonated methyl substituted phenols. The measured quantum yields range from 0.018 ± 0.001 to 0.65 ± 0.02. In general, it would seem the presence of methyl substituents at the ortho positions of the phenol enhances the efficiency of the reactions. For example, the photoinduced isomerization of cation 60H shows higher efficiency ($\phi = 0.50 \pm 0.02$) than that of 63H ($\phi = 0.38 \pm 0.02$), equations 75 and 76 respectively.

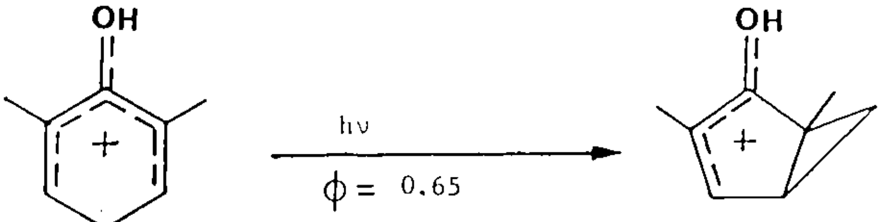


(75)

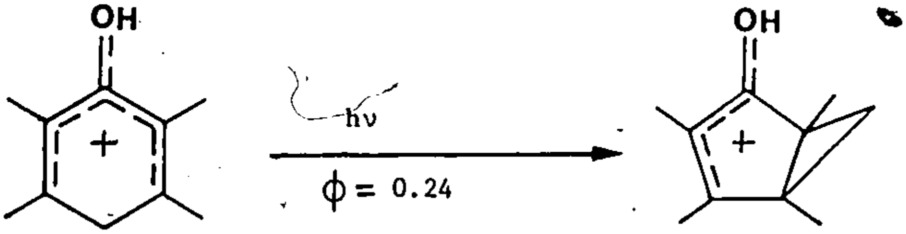


(76)

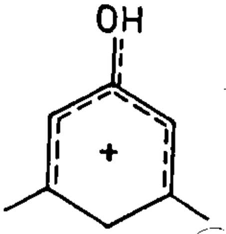
On the other hand the presence of a methyl group at the meta position causes a dramatic drop in the efficiency of these reactions. In the series of reactions shown in equations 77, 75 and 78, a methyl group is successively added to the meta positions of the phenols and as can be seen the quantum yields drops from 0.65 to 0.24. Further evidence to support these results comes from the observation that the photoisomerizations of cations 65H and 87H, which only possess substituents at the meta positions, are highly inefficient. In the case of 87H the results are qualitative and no photoproducts were ever detected under conditions when 85H and 86H were readily photoisomerized.



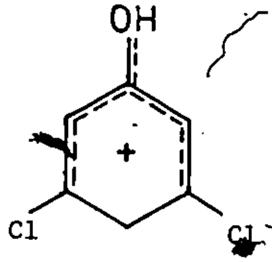
64H 81H (77)



58H 70H (78)



65H



87H

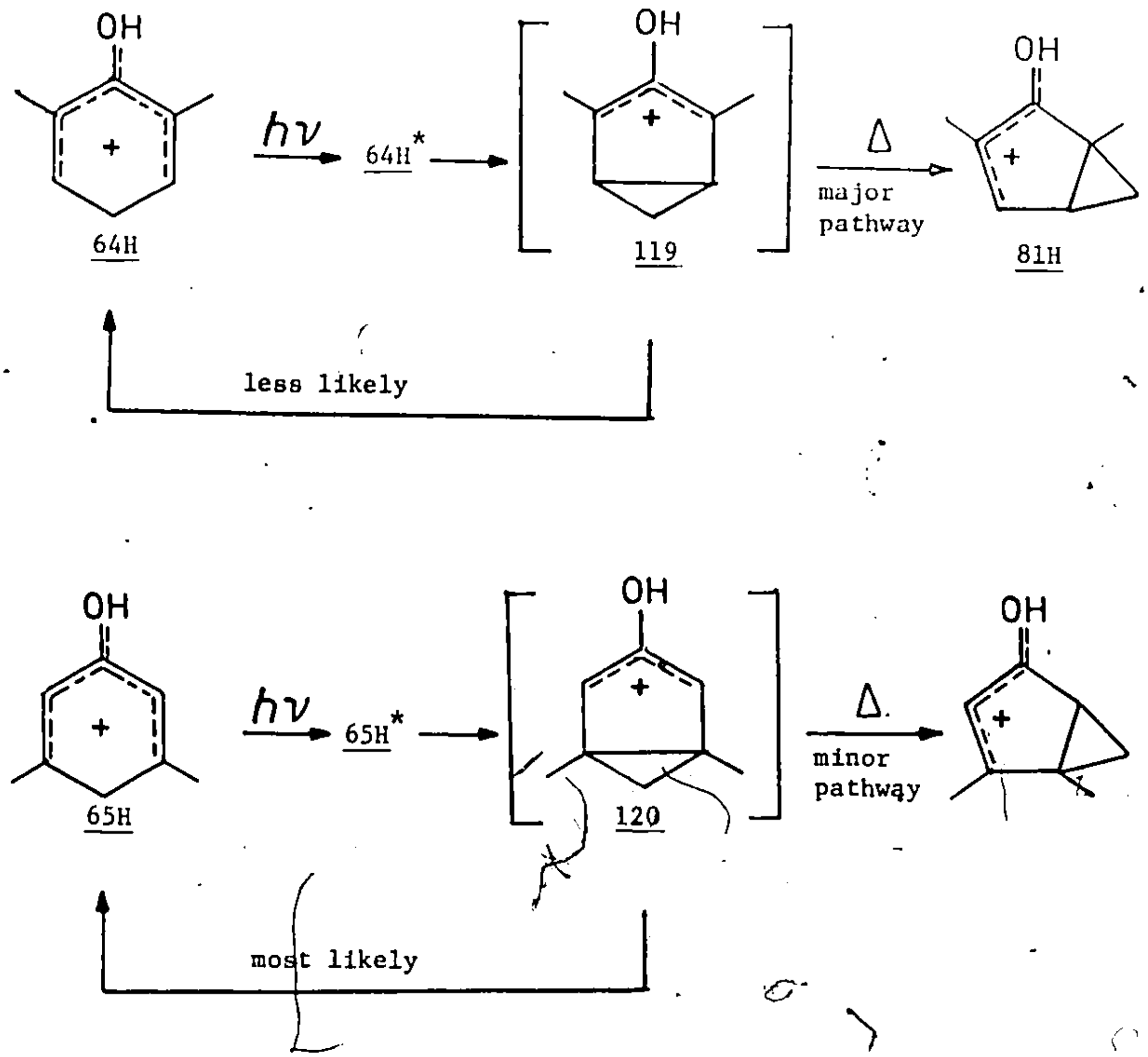
The differences in the quantum efficiencies for the photoisomerization of these protonated phenols can be understood in terms of the two step mechanism proposed for these reactions. In examining the effect of the methyl substituents on the efficiency of these reactions by this pathway, it is useful to consider first the difference in the quantum yields of the two extreme cations, i.e. <u>64H</u> (ϕ = 0.65 ± 0.02) and <u>65H</u> (ϕ = 0.018 ± 0.001).

There are two possible places in the two step process that the methyl groups could influence the efficiency of the reaction. In the first place the quantum efficiency of the actual photochemical ring closure step could depend on the placement of the methyl groups. Second, if it is assumed that the intermediate can either isomerize to the product or revert to starting material, then methyl groups could well be expected to alter the relative rates of these two processes.

In examining the effect of the methyl substituents on the efficiency of the photoinduced ring closure of these reactions, it is important to consider the effect of the methyl groups on the stability of the ground and first excited state. In this regard it is clear that methyl groups at C_3 and C_5 of cation <u>65H</u> tend to stabilize the ground state, whereas methyl groups at C_2 and C_6 in cation <u>64H</u> tend to stabilize the first excited state. Despite the stabilization of <u>64H</u> relative to <u>65H</u>, both cations have very similar UV spectra (Table 2.2) which indicates that there is no difference in the charge distribution at their excited states.

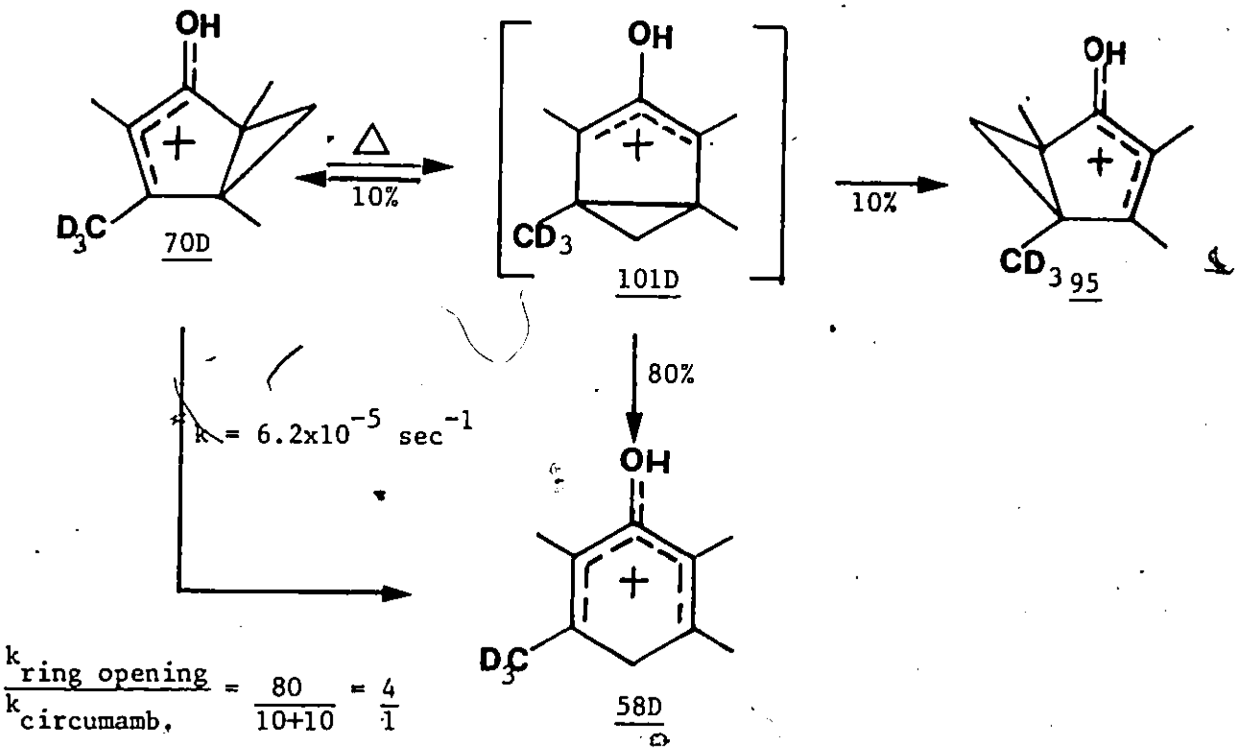
On the other hand the substantial difference in the quantum yields between <u>64H</u> and <u>65H</u> could be due to the difference between the rates of the competing reactions of the two intermediates, <u>119</u> and <u>120</u>. Whether a ring walk or a reverse ring opening of the intermediate is faster might be determined by (a) the positions of the methyl substituents in the intermediates and, (b) the stability of the ring opened product (Scheme 33).

Scheme 33



It should be recalled that methyl substitution at the bridgehead positions of protonated bicyclic ketones greatly enhance their rate of ring opening to give protonated phenols. In the two cases shown in Scheme 33, the two intermediates have quite different substitution patterns at the bridgehead cyclopropyl carbons. In the case of 119, there are no methyls at the bridgehead carbons and this would be expected to raise the barrier to the ring opening reaction relative to that of 120 where there are two methyls. For this difference to be important in determining the overall measured quantum efficiency, the barriers to circumambulation and ring opening must be closely balanced in the case of these ions.

In this regard a more detailed consideration of the isomerization of 58H is interesting in as much as the results of the thermal isomerization of 70D provides some evidence as to the relative rate constants for ring opening versus cyclopropyl circumambulation in the proposed intermediate. In the preceeding section, it was concluded that the splitting ratio for these two relative rate constants is as shown in Scheme 34.



$$\frac{k_{\text{ring opening}}}{k_{\text{circumamb.}}} = \frac{80}{10+10} = \frac{4}{1}$$

Scheme 34

As in the decay of 101D there are two circumambulatory reactions and only one ring opening process, it means that 20% of 101D reverts to the two bicyclic cation, 70D and 95, while 80% ring opens to give 58D.

In the photoisomerization of 58H to 70H, the observed efficiency is 0.24 ± 0.02. Assuming that the photoreaction follows a two step pathway, with the formation of 101D as a relaxed ground state species, then it would be expected that the ratio between the rates of the two competing reactions of the intermediate 101 would stay the same as measured above. This implies that if the quantum yield of the initial photochemical conversion of 58H to 101 is one, the observed maximum efficiency for the formation of 70H must be 0.2. This estimate is very close to the observed value ($\phi = 0.24 \pm 0.02$).

The consistency between the thermal and photochemical results strongly supports the suggestion that cation 101 is an intermediate in the photoisomerization of 58H and confirms the validity of the analysis presented above involving competative ring opening and ring walking of the intermediate bicyclic ions.

Overall it is clear that the barrier for the subsequent reaction of the intermediate formed from the photochemical ring closure of the protonated phenol is largely determined by the substitution pattern at the bridgehead positions. On this basis, it is very likely that the very low quantum yield of 65H is due to fast reverse ring opening of the intermediate 120 to give the ground state starting cation.

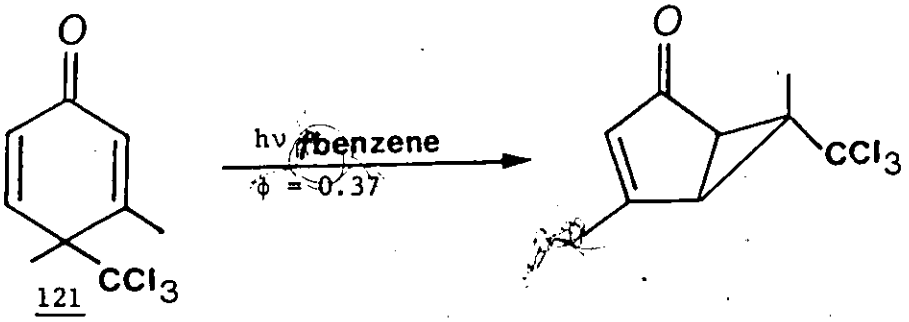
In considering the second effect, that is the relative stabilities of the product, it is clear at least in the case of cations

64H and 65H that this has little or no effect on the efficiency of these reactions.

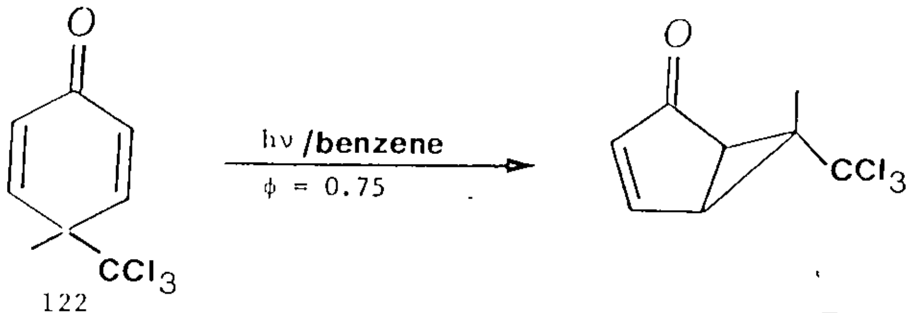
Similar effects to that outlined above for 64H and 65H would seem to be able to account for the other systems.

One further point that must be stressed is the quantum yields of the initial photochemical conversion of the other protonated methyl substituted phenols. On the basis of the above result with 58H if one assumes that the efficiencies of the first photochemical step in these isomerizations of protonated phenols are high and approach unity in each case, then the effect of the placement of methyl substituents can be understood.

It is interesting that the finding of the large structural effect found here for the quantum yields for these photoisomerizations of protonated phenols parallels the behaviour found with the photoisomerization of neutral dienones. For example, Schuster and co-workers[201,202] have reported a marked quantum yield dependence on structure as is shown with the photoisomerization of 3,4-dimethyl-4-trichloro-2,5cyclohexadienone (121)[201] and 4-methyl-4-trichloromethyl-2,5-cyclohexa- dienone (122),[202] equations 79 and 80, respectively.

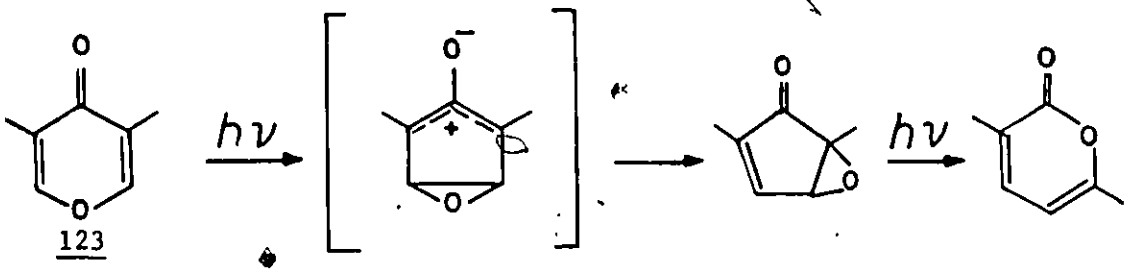


(79)

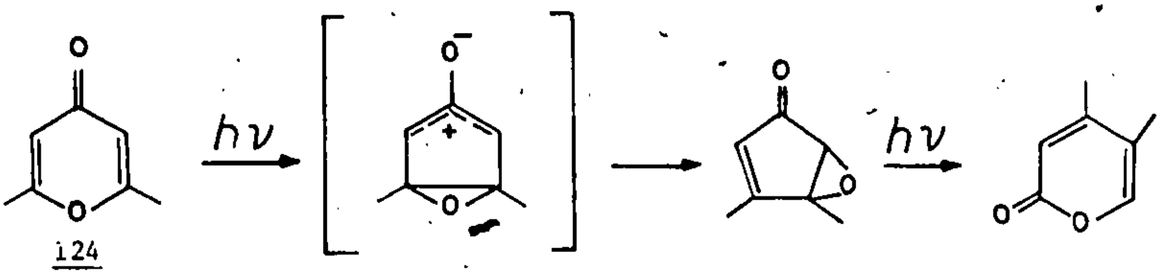


122 (80)

A similar observation has been reported by Barltrop and co-workers[203] in the photoisomerizations of 4-pyrones. Qualitative studies showed that 3,5-dimethyl-4-pyrone (123), undergoes an efficient photoisomerization which is similar to that of the protonated phenols, equation 81. However, the efficiency drops dramatically with 2,6-dimethyl-4-pyrone 124, equation 82.



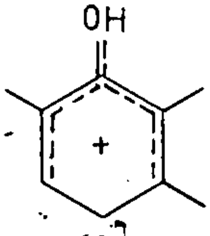
123 (81)



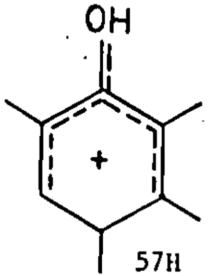
124 (82)

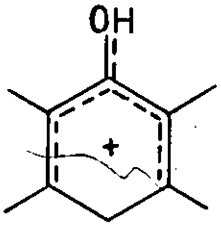
It is conceivable that a similar explanation for the behaviour of these neutral systems holds as that outlined above for the protonated phenols.

In contrast to the substantial effect of both ortho- and meta-methyl substituents on the quantum yields of protonated phenols, there is little or no effect due to the para methyl substituent. This can be seen by comparing the quantum yields of two sets of related protonated phenols, e.g. 60H with 57H and 58H with 56H.

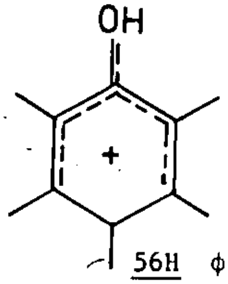

60H

ϕ = 0.50±0.02


57H ϕ = 0.49±0.02

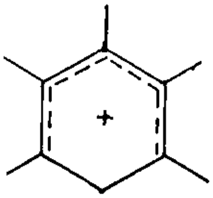

58H

ϕ = 0.24±0.02

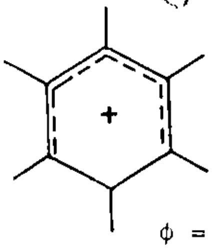

56H ϕ = 0.20±0.02

These results indicate that for at least these two cases, the para methyl substituent has little or no effect on the two competing reactions of the corresponding intermediates. This conclusion is consistent with the argument given in the preceeding chapter that with protonated bicyclo[3.1.0]hexenones in general, an endo methyl group at C_6 has only a small effect on the rate of the circumambulation process.

This small effect of the para-methyl group on the efficiency of these reactions is consistent with the results obtained from the photochemical ring closure of penta- and hexamethylbenzenium ions to the corresponding bicyclo[3.1.0]hexenyl cations 25 and 29 (equations 14 and 16, respectively).[61]



ϕ = 0.23±0.03



ϕ = 0.30±0.05

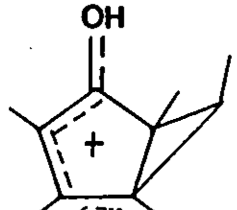
Photoisomerization of Protonated Bicyclo[3.1.0]hexenones

As was pointed out earlier (Scheme 23, Path B), protonated bicyclic ketones photoisomerize to give the corresponding protonated phenols. As can be seen from the data in Table 2.6, the UV spectra of protonated bicyclo[3.1.0]hexeonones are similar to those of protonated phenols (Table 2.2) in that there is a relatively high intensity band which corresponds to the lowest energy transition. As mentioned earlier, for unsaturated ketones in strong acid the excitation energy of n,π^* states is increased substantially, while that of π,π^* states is decreased. It is likely that the low energy absorption for all the protonated bicyclic ketones are of π,π^* character.

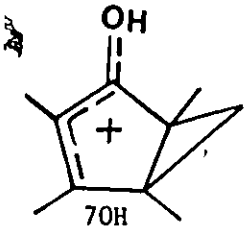
At this point direct evidence about the multiplicity of the excited states involved in these isomerizations is lacking. The absence of any detectable effect of dissolved oxygen suggests that the isomerizations are proceeding via excited singlet states, just as has been suggested for the isomerization of protonated phenols.

Quantitative Studies

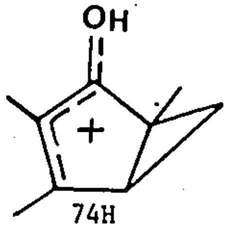
The results in Table 2.8 clearly show that the quantum yields associated with the photoisomerization of protonated bicyclo[3.1.0]-hexenones (67H, 70H, 74H and 78H) to protonated phenols are very similar, ranging from 0.16 ± 0.02 to 0.23 ± 0.02. Clearly the presence of methyl groups at C_1, C_5 and C_6 has very little effect on the quantum yields of these cations.



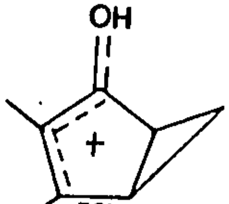
67H
$\phi = 0.20 \pm 0.02$



70H
$\phi = 0.20 \pm 0.02$



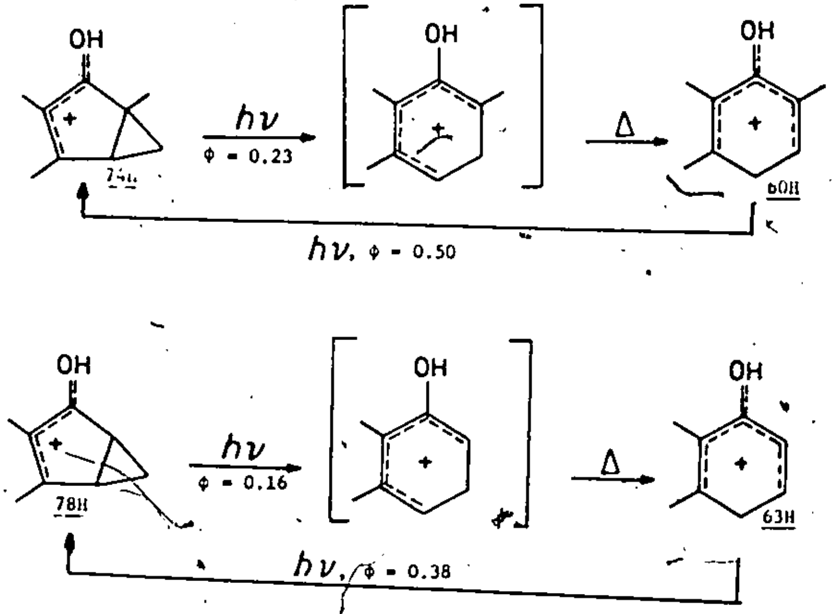
74H
$\phi = 0.23 \pm 0.02$



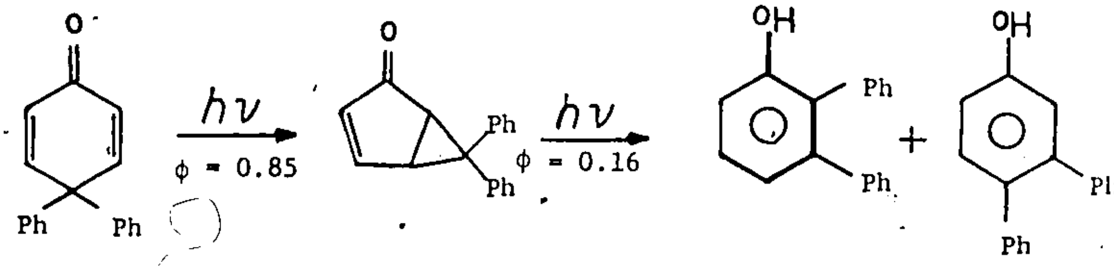
78H
$\phi = 0.16 \pm 0.02$

One interesting point emerges from these results is the relatively low quantum yields for the photoisomerization of bicyclic cations 74H and 81H relative to moderately high quantum yields for their formation from 60H and 63H, respectively, Scheme 35.

Scheme 35



The above observations are similar to that previously reported by Zimmerman and co-workers on the photoisomerization of neutral bicyclo[3.1.0]hexenones[204] (equation 83).



(83)

<u>Conclusion</u>

It is clear from the results presented above that the photo-induced isomerization of protonated phenols to form protonated bicyclo[3.1.0]hexenones can be regarded as a direct extension of the photochemistry of cross conjugated cyclohexadienones.

The quantitative evidence obtained in the present study justifies the designation of the two step mechanism as being the most acceptable pathway for the above isomerizations.

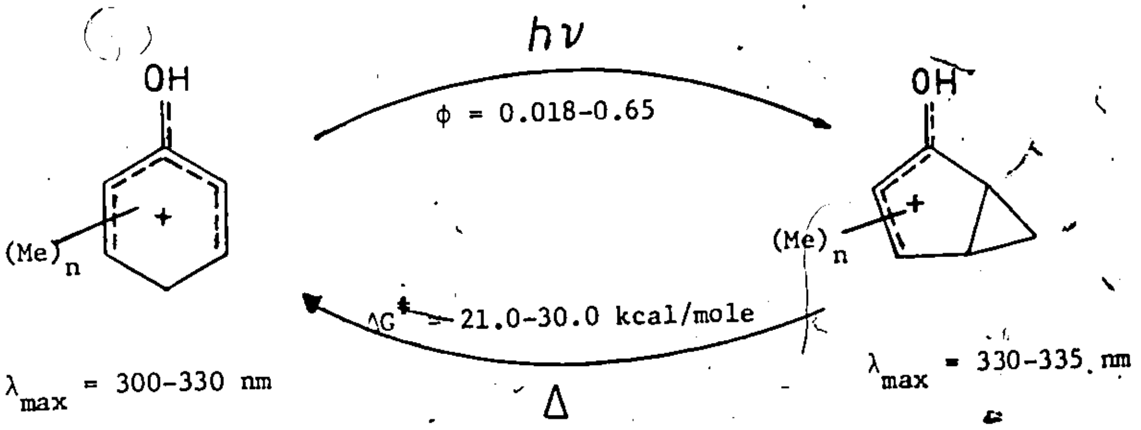
Substituents play an important role in determining the subsequent reactions of the intermediate and hence the efficiency of the reaction. The marked structural dependence of the quantum yields of these reactions agrees very well with the proposed mechanism. In contrast, there is little or no structural dependence of the quantum yields for the photoisomerizations of protonated bicyclo[3.1.0]hexenones.

CHAPTER 4

CONCLUDING REMARKS

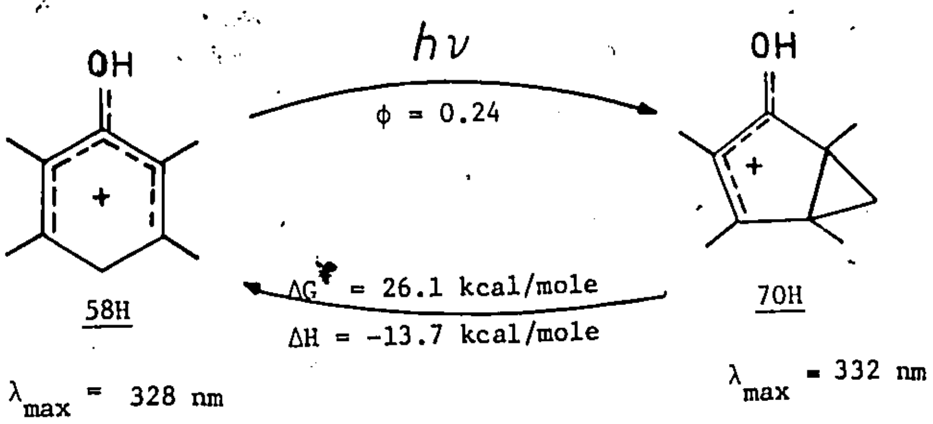
The reason for undertaking the work presented in this thesis was to evaluate the feasibility of using acid catalysed photoreactions to store energy in benzenoid materials. This has been done by examining the individual steps involved in the photochemical and thermal interconversion of protonated phenols and bicyclo[3.1.0]hexenones.

The photochemical and thermal results obtained in this work are summarized in Scheme 36. In addition to the cleaness and the relatively high efficiency of the photochemical step ($\phi \simeq 0.01\text{-}0.65$), the photoproducts undergo a thermally clean isomerization to the starting cations with relatively high activation barriers ($\Delta G^{\ddagger} \simeq 21.0\text{-}30.0$ kcal/mole).



Scheme 36

Preliminary results obtained by another worker in the group at McMaster show that the storage potential of these reactions is very high.[199] One specific example of a storage, energy release cycle is shown in Scheme 37 for protonated durenol 58H and its bicyclic ketone 70H. In this case the difference in enthalpy of 70H and 58H has been found to be -13.7 kcal/mole which corresponds to a potential storage capacity of 91 kcal/kg.



Scheme 37

The potential usefulness of these phenol|bicyclic ketone systems for solar energy storage can be evaluated by comparison with the requirements for such a system outlined on page 4. The first criterion which requires an endothermic photochemical reaction is met in that the bicyclic products are of higher energy than the starting material in all cases. The second condition requiring the system to be cyclic is only partially met as in some cases the bicyclic products rearrange to isomers of the initial protonated phenol, however, in some cases such as the tetramethyl phenols this is not a limiting factor. All of the materials studied showed no evidence for the formation of degredation products upon either photo or thermal isomerization. Thus the third requirement is fulfilled. The fourth criterion which required that only the starting material absorb visible light is not met in this system as both the starting materials and photoproducts absorb UV light in the 300-330 nm range. However, it should be pointed out that photostationary state mixtures contain a substantial proportion of the bicyclic cation (typically up to 60%). The efficiencies of the photoisomerization vary as shown in Table 2.7, however, some of the reactions have high quantum yields thus meeting criterion five. Another advantage of this system is that most of the bicyclic cations are stable at ambient temperature and can be conveniently converted back to protonated phenols upon heating, thus satisfying criterias six and seven.

The final important criterion to be considered is the total cost of such a system. The methyl substituted phenols could be obtained at reasonably low overall cost.

In summary, it is clear that the major disadvantage of the above system is the materials absorb light at 300-330 nm. This means that they are not well matched with the maximum in the solar spectrum.

Of all the materials studied, one can well argue that the tetramethylphenol system is the most efficient photochemical energy storage system. Despite the lower quantum efficiencies of isodurenol and durenol as compared with 2,6-dimethylphenol (Table 2.7), this system would have a considerable storage capacity. This is because all four of the photoproducts eventually thermally revert to durenol with the concomitant liberation of their stored energy.

One possible solution to these problems is modification of the chromophore of the protonated phenol such that it absorbs in the visible region. In fact the use of the chlorophenols represents one such modification. Unfortunately, however, the above results showed that protonated chlorophenols absorb in the same region as protonated polymethylphenols and that their photoisomerization reactions are highly inefficient.

While it is known that irradiation of some neutral benzcyclohexadienones[205,206] and protonated naphthol[126] itself follow different isomerization routes to that of the protonated phenols described here, there are however few reported studies in this area. As protonated naphthalene and its methyl derivatives absorb close to 400 nm[207] it would seem useful to further explore the potential of such systems.

The overall proposed scheme for energy storage involved the conversion of an aromatic system, such as a phenol, to a bicyclic valence tautomer by an acid catalysed reaction. In this present system this raises a problem. While the previous reports show that it is possible to carry out acid-catalysed photoreactions of various compounds, there are some difficulties in using this approach in this particular case.[90,146] The key problems appear to lie in the relative basicities of the bicyclic ketones as compared to the phenols.

However, the present work indicates that cationic systems themselves in acid solution could be used to store solar energy. The photochemical, thermal reactions described in this thesis can be carried out with the concentration of the phenol ranging up to 10% w/v. These are remarkably high concentration for an organic photoreaction to proceed, and this points to the potential use of the system. At this concentration the durenol system shown in Scheme 36 would be capable of storing 9.1 kcal/ℓ of solution.

It is perhaps ironic that with the dramatic fall in the price of oil that research into ways of using and storing solar energy has diminished. This is a short sighted policy in as much as solar energy must inevitably become more widely used and it is only a matter of time until other energy sources become in short supply again. When this happens then it will be appropriate to re-examine this type of system discussed in this thesis.

CHAPTER 5

EXPERIMENTAL METHODS

INSTRUMENTAL TECHNIQUES

^{1}H NMR Spectra

^{1}H NMR spectra were recorded on Varian EM-390 and Bruker WM-250 spectrometers. The probe temperature was measured using a methanol sample for the Varian EM-390 spectrometer and an iron-constantn thermocouple for the Bruker WM-250 spectrometer.

^{13}C NMR Spectra

All spectra were obtained at 62.9 MHz on a Bruker WM-250 spectrometer. Samples were prepared in a microprobe tube using 3-5 mg of the ketones and 0.2 ml of solvent. For the neutral bicyclic ketones, $CDCl_3$, CD_2Cl_2, and CCl_4 were used as solvents and the resonances were referenced to these solvents ($CDCl_3$, δ 77.2, CD_2Cl_2, δ 53.8 and CCl_4, δ 96.7). The spectra of the protonated ketones were obtained in CF_3SO_3H solvent, which was also used as the internal reference (δ 119.2).

Electronic Absorption Spectra

The absorption spectra were obtained on a Tracor Northern DARSS System or Hewlett Packard 845TA. Low temperature UV spectra of the protonated chlorophenols were obtained using the former instrument.

Solutions were prepared by weighing the appropriate amount of the compound in the cell which was then cooled in a dry ice-acetone bath (-78°). FSO_3H, previously cooled to this temperature, was then added and the solution stirred with a cold glass rod. The cell was removed from the low temperature bath and the spectrum obtained immediately. A stream of dry nitrogen was blown on the cell while the spectrum was recorded and condensation of water on the cell did not occur in the short time required for the measurement (2-3 seconds).

Infrared Spectra

The infrared spectra of the compounds were recorded on a Perkin-Elmer model 283 spectrometer using NaCl cells. Calibration of the instrument was carried out using polystyrene film.

Mass Spectrometry

Mass spectra were obtained from a VG 7070F mass spectrometer operating at an ionization potential of 70 eV.

Gas Chromatography

Varian 3700 and Hewlett Packard 5790A (analytical) gas chromatography instruments coupled with Varian CDS III and HP 3390A integrators, respectively, were used. Columns used were a 1/8" x 8' copper column packed with 2% OV17 on Chromosorb W (column A), and a 1/8" x 10' stainless steel column packed with 10% Fluorad FC 431 on Chromosorb W (column B).

An Aerograph model A-90-P_3 gas chromatograph was used for all of the preparative GLC. The column used was a 1/4" x 5' copper column packed with 10% OV17 on Chromosorb W (column C).

Purification of Solvents and Reagents

FSO_3H was purged with dry nitrogen, treated with dry NaF (1 g/100 ml) and distilled. The distillate was redistilled through a 12" glass column and the acid stored in small quantities (0.5 ml) in sealed glass ampoules.

CF_3SO_3H was distilled prior to use.

The acids used in the fluorescence measurements were checked for the presence of emitting impuriti~~es~~ prior to use.

Cyclohexane was refluxed over $LiAlH_4$ and distilled. Pyridine was refluxed over solid KOH and distilled.

Most of the phenols employed are commercially available. They were routinely purified by sublimation before use. Preparation of other phenols is described below.

SYNTHESIS

2,3,4,6-tetramethylphenol, 57

This was prepared using the procedure of Finn and Musty.[208]

2,3,4,5-tetramehtylphenol, 59

The title compound 59 was prepared from 2,3,5-trimethylphenol by the procedure described by Dakshinamurty and Santappa.[209]

Pentamethylphenol, 56

This was prepared from either isodurenol, 57, or durenol, 58, using the three step procedure decribed by Finn and Musty.[208]

METHOD I

2,3,4,6-tetramethyl-5-chloromethylphenol, 125 was obtained from the chloromethylation of isodurenol, 57.[208] Yield: 65%. M.P.: 123-124°C. ^{1}H NMR ($CDCl_3$) δ: 4.70 (s, 2H, CH_2); 4.55 (b, OH); 2.25 (s, 6H, $2CH_3$); 2.17 (s, 6H, $2CH_3$) ppm. IR $(CHCl_3)_3$ ν: 3610, 2920 cm^{-1}. M.S. m/e (rel. abund. %): 198 (M^+, 30); 163 (100); 149 (5); 119 (7); 105 (4); 91 (6); 77 (5); 65 (3); 51 (3). High res. M.S. (m/e): M^+ obsd: 198.0812, M^+ calcd: 198.0812

1-acetoxy-2,3,4,6-tetramethyl-5-chloromethylbenzene, 126 was prepared by the acetylation of 125 according to the procedure of Finn and Musty.[208] Yield: 62%. M.P.: 90-92°C. ^{1}H NMR ($CDCl_3$) δ: 4.70 (s, 2H, CH_2); 2.35 (s, 3H, CH_3); 2.25 (s, 6H, $2CH_3$); 2.17 (s, 6H, $2CH_3$). IR ($CHCl_3$) ν: 2940, 1765 cm^{-1}. M.S. m/e (rel. abund. %): 240 (M^+, 1); 222 (35); 198 (4); 180 (95); 162 (100); 148 (10); 133 (18); 119 (37); 105 (15); 91 (23); 77 (18); 65 (10); 53 (10). High res. M.S. (m/e): M^+ obsd: 240.0936, M^+ calcd: 240.0917.

Pentamethylphenol, 56 was prepared in 50% yield from the reduction of 126.[208] M.P.: 126-127° (lit.[210] 125°).

METHOD II

Starting with durenol 58, pentamethylphenol was prepared using the same route that is followed in Method I.

2,3,5,6-tetramethyl-4-chloromethylphenol, 127 was prepared in 46% yield by the chloromethylation of durenol.[208] M.P.: 140-141°C. ^{1}H NMR ($CDCl_3$) δ: 4.72 (s, 2H, CH_2); 4.69 (s, OH); 2.35 (s, 6H, $2CH_3$); 2.20 (s, 6H, $2CH_3$) ppm. IR ($CHCl_3$) ν: 3605, 2910 cm^{-1}. M.S. m/e (rel. abund. %): 198 (M^+, 14); 163 (100); 162 (31); 119 (56); 91 (13); 77 (11); 63 (4); 51 (9). High res. M.S. (m/e): M^+ obsd: 198.0810, M^+ calcd: 198,0811.

1-acetoxy-2,3,5,6-tetramethyl-4-chloromethylbenzene, 128 was prepared in 50% yield from 127 by similar procedure to that used for the preparation of 126.[208] M.P.: 113-114°C. ^{1}H NMR ($CDCl_3$) δ: 4.70 (s, 2H, CH_2); 2.25 (s, 9H, $3CH_3$); 2.10 (s, 6H, $2CH_3$) ppm. IR ($CHCl_3$) ν: 2920, 1735 cm^{-1}. M.S. m/e (rel. abund. %): 240 (M^+, 8); 198 (34); 163 (100); 162 (38); 119 (7); 91 (12); 77 (8); 65 (5); 53 (6). High res. M.S. (m/e): M^+ obsd: 240.0888, M^+ cald: 240.0916.

Pentamethylphenol, 56

128 was converted to 56 by reduction using Zn/HCl.[208] Yield: 42%. M.P.: 126-127°C (lit.[210] 125°).

The spectroscopic properties of the phenol obtained by method I and II are identical.

1,3,5-trimethyl-4-methyl-d_3-bicyclo[3.1.0]hexenone, 129. This compound was prepared from 1,3,4,5-tetramethylbicyclo[3.1.0]hexenone 70 using a procedure similar to that outlined by Hart and co-workers.[111] The bicyclic ketone 70 (50 mg) was dissolved in $NaOCD_3/CD_3OD$ (0.5 ml CD_3OD/50 mg Na). The solution was left at 25°C and its ^1H NMR spectrum examined periodically. After 1 h the methyl signal at δ 1.96 had disappeared and no further change in the NMR spectrum was observed after several hours. The trideuterio ketone was isolated by pouring the solution into 5 ml of CH_2Cl_2 and washing with ice water (3x5 ml). After drying ($MgSO_4$), the solvent was evaporated slowly through a 7 cm Vigreux column to give 5 as an oil. ^1H NMR ($CDCl_3$) δ: 1.47 (s, 3H, CH_3); 1.33 (s, 3H, CH_3); 1.20 (s, 3H, CH_3); 1.16 (d, 1H, J=3 Hz); 0.83 (d, 1H, J=3 Hz) ppm.

GENERAL TECHNIQUES AND PROCEDURES

Protonation of Phenols and bicyclo[3.1.0]hexenones

(i) FSO_3H

The cation precursor, ca. 15-20 mg, was placed in a clean dry medium walled 5 mm NMR tube and cooled to -78°C. Precooled (-78°C) FSO_3H acid (0.5 ml) was transferred to the NMR tube. Complete solution was achieved by agitation of the acid with a 2 mm diameter glass rod.

(ii) CF_3SO_3H

The cation precursor ca. 15-20 mg in an NMR tube was cooled in an ice bath (0°C). CF_3SO_3H acid (0.5 ml), cooled previously to 0°, was added by dropper. Dissolution of the base was achieved as the solution was slowly brought to ambient temperature.

PHOTOCHEMICAL PROCEDURES

Low temperature irradiations were carried out using a partially silvered quartz Dewar which was surrounded by ten lamps. The lamps used were Southern New England Ultraviolet Company RPR 2537 A° or RPR 3000 A° depending on the wavelength desired. The Dewar was filled with methanol and held at -70°C with an FTS Systems Flexicool Unit, FS-2084 PI. The cooling probe of this refrigeration unit was inserted directly into the center of the quartz Dewar. Samples were contained in tubes placed around the central cooling unit.

Samples in CF_3SO_3H or CF_3SO_3H-SbF_5 were irradiated at 35°C in a Rayonet Photoreactor (Southern New England Ultraviolet Co.) with 16 lamps. The lamps used were again either RPR 2537 A° or RPR 3000 A° depending on the wavelength desired.

For both systems, the samples were prepared in 5 mm, clear, medium-walled nmr tubes. The samples were not degassed, and the tubes were sealed with plastic caps. Quartz tubes were used with 2537 A° lamps.

Preparative scale irradiations were carried out using 2 g of phenol dissolved in 10 ml of CF_3SO_3H. The reaction mixtures were stirred with a magnetic stirrer during irradiation. Aliquots were withdrawn periodically to check the progress of the reaction using ^1H NMR spectroscopy. When the desired conversion had been achieved, the solution was carefully quenched as shown below.

Isolation of the Photoproducts

The FSO_3H acid solution added dropwise to a rapidly stirred mixture of sodium bicarbonate in ether kept at -78°. The dry ice-acetone bath was removed and the mixture was allowed to warm to 0°. Ice water was added and stirring maintained as the flask was allowed to warm to room temperature. The ether layer was washed twice with saturated $NaHCO_3$ solution and then water and dried ($MgSO_4$). Ether was removed carefully by evaporation through a 7 cm Vigreux column using a steam bath.

In the case of CF_3SO_3H and CF_3SO_3H-SbF_5-solutions neutralization was achieved by pouring the acid solution slowly into a saturated solution of $NaHCO_3$. The organic materials extracted into ether (3x20 ml) and the combined extracts washed with water (2x20 ml) and dried over $MgSO_4$. The solvent was removed as above.

The products were analysed quantitatively by analytical GLC. Preparative GLC was normally used to isolate the products.

The GLC conditions for the separation of the bicyclic ketones together with their high resolution mass spectra were given in Table 4.1. Other physical properties of these ketones are given in full in Chapter 2.

Trimethylsilylation of Phenols 57 and 58

Acid solutions resulting from the irradiation of 57H and 58H were neutralized and the products recovered as outlined above. The resulting crude photoproducts were examined by analytical GLC using column B. The bicyclic ketones were evaporated on a steam bath and the off-white solid

Table 4.1. GC and Mass Spectral Data of the Bicyclic Ketones

	Analytical GLC^a			M.S. (m/e)	
Column (Temp. °C)	Ketone^b (R_T min)	Phenol (R_T min)	Ketone	obs.	calcd.
B(190)	67(3.22)	56(27.40)	67	164.1210	164.1201
B(180)	70(4.61)	58(21.45)	71	150.1030	150.1016
B(180)	71(3.76)	57(21.84)	72	150.1047	150.1043
B(180)	72(5.22)	-	73	150.1070	150.1096
B(180)	73(2.71)	-	74	136.0867	130.0888
B(190)	74(3.29)	60(10.17)	77	122.0699	122.0731
B(190)	77(2.49)	62(13.56)	91	128.0028	128.0029
B(190)	79(2.44)	63(13.09)	92	128.0038	128.0029
A(100)	91(15.57)	84(9.08)		C = 56.10%	C = 56.03%
A(100)	92(11.66)	-	93	H = 4.00%	H = 3.89%
A(100)	93(18.84)	85(16.74)	94	128.0060	128.0029
A(100)	94(14.73)	-			

[a] Nitrogen gas flow rate of 20 ml/min was maintained throughout the analysis.

[b] All bicyclic Ketones are liquids.

products (ca. 10 mg) was dissolved in 1 ml of dry pyridine. 10 μl of the pyridine solution was then diluted with 100 μl of dry cyclohexane. Trimethylsilyl aryl ethers were prepared by mixing equal volumes (ca. 100 μl) of the cyclohexane solution and bis(trimethylsilyl)trifluoroacetamide (BSTFA) in a screw cap septum reacti-vial. The reaction was allowed to stand at room temperature for 1/2 h to obtain the silyl ethers.

GLC analysis of the products (column B, 190°C) showed two peaks to be present: retention times 5.78 and 6.64 minutes. These were identified by comparison with derivatives of authentic samples as the two silyl derivatives of durenol <u>69</u> and isodurenol <u>68</u> respectively, equation 38.

Control experiments were run by taking a mixture of phenols <u>57</u> and <u>58</u> and bicyclic ketones <u>70</u> and <u>71</u> of known composition in order to ensure that the assay method was reliable. The resultant mixture was analysed by GLC (column B) to ensure about the exact composition of the mixture. Evaporation of the bicyclic ketones on steam bath gave a white residue which was silylated as outlined above. GLC analysis of the products (column B) showed that the amount of each silyl derivative obtained are equivalent to the amount of the corresponding phenol in the starting mixture. Quantitative determination of the two silyl derivatives was carried out by GLC using the calibration curve obtained from silylation of a mixture of <u>57</u> and <u>58</u> of known composition. It was shown that the silylation was quantitative and that the two silyl derivatives had identical detector response.

Fluorescence Measurements

Fluorescence studies were performed at room temperature with a Perkin-Elmer LS-5 fluorescence spectrophotometer using 10^{-4} M solutions of durenol in purified triflic acid at room temperature. An excitation wavelength of 313 nm was employed and the sample emission was monitored from 320 nm to 600 nm. There was no detectable emission observed at room temperature.

Quantum Yield Measurements

The light source used in this work was an Osram HBO 200W super-pressure mercury lamp coupled with a Kratos LPS 25T power supply. Wavelength selection (313 nm) was achieved using a Kratos GM100 grating monochromator with entrance and exit slits set for a 24 nm bandwidth. The filter used was an Optikon filter no. 313FS10-25 with a high wavelength cut off at 325 nm. The parallel beam from the monochromator was split by a quartz plate (7.5 cm square, 1.5 mm thick), fixed at 45° to the beam inside a light tight box. A typical splitting ratio was 10 to 1. This was monitored after every run using an electronic actinometer and every other run using potassium ferrioxalate actinometry.[145]

Samples were contained in 22 nm o.d. x 2 mm quartz "Lollipop cells", and 22 nm o.d. x 10 mm and 22 mm o.d. x 20 mm quartz actinometer cell were employed. The samples were prepared by weighing the phenol or ketone (5-10 mg) into the sample container and adding CF_3SO_3H (0.5 ml).

The quantum yield was measured at 313 nm using potassium ferrioxalate[145] as the primary standard to calibrate the electronic actinometers. The percent conversion, in all cases, was less than 10% and the quantum yields were not corrected for back reaction.

After irradiation the neutral photoproducts were recovered by an analogous procedure to that described above. The degree of conversion of the starting material was determined by analytical GLC using column B. The detector response of the GLC was calibrated using standard solutions of isomeric phenols and bicyclic ketones and in all cases the isomers exhibited an identical detector response. Peak areas measured with the Hewlett Packard integrator were well within the errors reported.

Data for the above measurements are given in Tables 4.2 and 4.3 and the final calculated values of the quantum yields are summarized in Tables 2.7 and 2.8.

Some of the quantum yields were measured in both degassed and stirred solutions. This was achieved by bubbling dry argon through the sample before and during the time of irradiation. Data for these experiments are included in Tables 2.7, 2.8, 4.2 and 4.3.

The quantum yield for the conversion of each protonated phenol to the corresponding protonated bicyclo[3.1.0]hexenone was measured for at least three times, Table 4.2. The mean of the ϕ values and the errors (standard deviation of the ϕ values from the mean) are reproted in Table 2.7.

Quantum yields for the conversion of protonated bicyclo[3.1.0]-hexenones to protonated phenols were measured twice, Table 4.3. The two values averaged to give the quantity reported in Table 2.8. The error was estimated at ± 10%.

Table 4.2. Quantum Yield Data for the Photoisomerization of Protonated Phenols

Reaction	Wgt (g) $\times 10^{-3}$	Moles $\times 10^{-5}$	% Conversion	Moles Conv. $\times 10^{-6}$	Einstein of Light $\times 10^{-6}$	Φ
56H → 67H	20.0	12.20	1.83	2.23	11.2	0.199
"	9.0	5.48	1.65	0.90	4.0	0.225
"	5.0	3.05	1.70	0.50	2.77	0.188
"	3.85	2.35	5.90	1.38	7.52	0.184
"[a]	3.70	2.26	3.50	0.79	4.02	0.197
"[b]	4.40	2.69	4.70	1.26	5.85	0.216
57H → 71H + 72H	7.6	5.07	6.1	3.04	6.00	0.507
"	4.7	3.13	5.1	1.59	3.40	0.469
"	6.1	4.06	4.4	1.79	3.72	0.481
58H → 70H	9.7	6.47	1.50	0.97	4.16	0.233
"	9.9	6.60	2.0	1.32	5.65	0.234
"	4.7	3.13	5.2	1.63	6.24	0.261
"[a]	5.0	3.33	4.43	1.47	6.18	0.239
"[b]	10	6.66	3.16	2.10	9.03	0.233
60H → 74H	14.8	10.91	3.20	3.49	7.02	0.497
"	11.1	8.07	5.80	4.68	8.99	0.521
"	5.3	3.89	9.6	3.73	7.70	0.485

Table 4.2. Quantum Yield Data for the Photoisomerization of Protonated Phenols (continued)

Reaction	Wgt (g) $\times 10^{-3}$	Moles $\times 10^{-5}$	% Conversion	Moles Conv. $\times 10^{-6}$	Einstein of Light $\times 10^{-6}$	Φ
63H → 78H	9.16	7.50	2.40	1.80	5.07	0.355
"	5.50	4.50	4.0	1.8	4.71	0.382
"	3.70	3.03	4.34	1.31	3.23	0.407
"[a]	6.0	4.91	3.20	1.57	4.48	0.351
64H → 81H	7.40	6.06	7.70	4.66	7.31	0.638
"	5.90	4.83	8.50	4.10	6.16	0.666
"	4.70	3.85	6.40	2.46	3.85	0.640
65H → Product	4.85	3.97	0.52	0.21	11.45	0.018
"	4.90	4.01	0.65	0.26	15.0	0.017
"	2.20	1.80	0.85	0.153	7.86	0.019

[a] degassed.

[b] check for layering.

Table 4.3. Quantum Yield Measurements for the Photoisomerization of Protonated Bicyclic Ketones

Reaction	Wgt (g) x10^{-3}	Moles x10^{-5}	% Conversion	Moles Conv. x10^{-6}	Einstein of Light x10^{-6}	Φ
67H → 56H	4.95	3.02	6.5	1.96	9.13	0.215
"	4.80	2.93	5.3	1.55	7.95	0.195
70H → 57H	4.35	2.90	4.1	1.19	5.99	0.198
"	5.15	3.43	4.8	1.65	8.66	0.190
74H → 60H	5.85	4.30	3.70	1.59	7.50	0.212
"	6.0	4.40	4.2	1.85	7.44	0.248
78H → 63H	4.70	3.85	3.20	1.23	8.42	0.146
"	4.01	3.27	4.40	1.44	8.42	0.171

THERMAL EXPERIMENTS

Thermal rearrangement of bicyclo[3.1.0]hexenones in CF_3SO_3H

Each ketone (ca. 10 mg) was dissolved in CF_3SO_3H according to the method described above. The resultant solutions were examined by ^1H NMR at various temperatures between ~ +34° (probe temperature) and 100°C for cations 67H, 70D, 71H, 72H, 74H, 78H and 81H and between 0° and 30°C for cations 73H and 76H. Normally, the bath or probe temperature was increased from the lowest value by increments of 10° until an isomerization took place. Isomerization was followed, as mentioned earlier, by ^1H NMR spectroscopy. Products were identified as described in the results section (2-III).

Isomerization Rate Constants

The rate constants for the conversion of the protonated bicyclic ketones 67H, 70H, 70D, 71H, 72H, 74H and 81H to their isomeric phenols at 60°C were determined as follows. The ketone (~ 10 mg) in an NMR tube was dissolved in CF_3SO_3H (0.40 ml) according to the method described above. A small amount of $(CH_3)_4N^+BF_4^-$ was added as an internal standard. A ^1H NMR spectrum of this mixture was recorded at room temperature. The peak heights of the methyl signals in the starting cations were measured relative to the peak height of the singlet at δ 3.10 of the internal standard (peak half-widths were the same). This ratio was used as a dimensionless concentration function.

The sample was heated in a Haake A81 constant temperature bath (T = 60 ± 0.5°C) and at the various time intervals the sample was cooled quickly to 25°C and its ^1H NMR spectrum obtained. The relative concentration of the starting cation was determined from this spectrum by comparison with the signal due to the internal standard. The first order rate constant was calculated using the formula

$$k = \frac{1}{t} \ln \frac{C_o}{C_t}$$

where C_o = relative concentration at time t_o

C_t = relative concentration at time t

t = time

The rate constant for the reaction k, was calculated as shown in equation

$$k = \frac{\Sigma k_i}{n}$$

where n = number of determinations of k_i.

Except <u>70D</u>, the reactions were followed in all cases until they were greater than 90% complete. In the case of <u>70D</u> the reaction was monitored until 45% conversion. The average deviation (d) of the individual rate constants in each set of isomerizations was calculated as

$$d = \frac{\Sigma|k_i - k|}{n}$$

where d = average deviation

k_i = individual rate constant

k = average rate constant

n = number of determination of k_i

A plot of $\ln C_o/C_t$ vs time in each case gave a good straight line.

This procedure was repeated for the conversions 67H to 56H, 70H to 58H, 74H to 60H, 78H to 63H and 81H to 64H. The sample was heated in a refluxing water bath (T = 100 ± 0.5°C) and the results are included in Table 2.14.

The rate constants for the thermal rearrangement of 73H to 57H and 76H to 75H were obtained at 20° and 30°C, respectively, using a Bruker WM-250 NMR spectrometer. The probe temperature was measured using an iron-constantn thermocouple and digital thermometer. The progress of the thermal isomerization was followed by observing the appropriate changes in the ^{1}H NMR spectrum with time. Similar calculations to that outlined above were performed and the results are reported in Table 2.14.

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