PHOTOCHEMISTRY OF BENZENONIUM CATIONS

PHOTOCHEMISTRY

OF

# POLYMETHYL AND HYDROXY-POLYMETHYL

CYCLOHEXADIENYL CATIONS

#### By-

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# A Thesis

Submitted to the School of Graduate Studies in Partial Fulfilment of the Requirements

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M<sup>C</sup>Master University

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to my parents

and to life

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#### ABSTRACT OF THE DISSERTATION

Photochemistry of Cyclohexadienyl Cations

by

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Fluorosulphonic acid has been employed to generate cyclohexadienyl cations by protonation of weak bases in order to study the affect of uv light on such systems which are variably substituted. Differing substitution has been obtained by selecting polymethylbenzenes, cyclohexadienones and polymethylphenols as cation precursors.

The photoisomerization of the 1,2,4,5-tetramethylcyclohexadienyl cation to the 1,2,4,5-tetramethylbicyclo-[3.1.0] hexenyl cation has been studied by nmr methods and is discussed mechanistically in terms of competitive electrocyclic and  $[\sigma 2_a + \pi 2_a]$  mechanisms of ring closure. Investigations of a similar 1,2,3,5-tetramethylcyclohexadienyl cation failed to uncover an analogous photoisomerization. This result is briefly discussed in relation to the demonstrated instability of the supposed photo-product which has been produced by a non photo-

ix

chemical route.

Both the 1-hydroxy-6,6-dimethyl- and 1-hydroxy-4,4-dimethylcyclohexadienyl cations have been generated from the corresponding cyclohexadienones by low temperature protonation in FSO<sub>3</sub>H. Photoisomerization of these systems produced the same 2-hydroxy-6,6-dimethylbicyclo-[3.1.0] hexenyl cation which underwent further photorearrangement to various protonated phenols, the nature of which depended upon the frequency of irradiation.

A number of protonated polymethylphenols have been investigated with respect to their site(s) of protonation in fluorosulphonic acid and their tendency to undergo photochemical reaction. Several members of this series have been shown to rearrange photochemically to isomeric phenols through a bicyclo [3.1.0] hexenyl cation intermediate. A necessary criterion for this reaction has been established as protonation of a methyl bearing ring carbon.

An exceptional example of the phenol photoisomerization was the photo-conversion of protonated 2,4,6-trimethylphenol to protonated 1,3,5-trimethylbicyclo 3.1.0 hex-3-en-2-one. This, as well as additional evidence led to the conclusion that a significant amount of meta protonation occurred with this phenol.

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#### GENERAL INTRODUCTION

Although the carbonium ion in its many and varied ground state reactions has formed an integral part of chemistry for decades <sup>1</sup> there have been few and then only recent reports concerning excited state reactions of this widely discussed intermediate. In contrast, the photochemical reactions of numerous neutral molecules have been studied in the gas, <sup>2</sup> liquid<sup>3,4</sup> and solid <sup>5</sup> phases. A few photochemical reactions of carbanions are known <sup>6</sup> but the underlying rational is not, as yet, strongly established.

When considering the development of cation photochemistry in the late 1960's one is compelled to acknowledge a previous lack of interest and/or substrate as paramount factors in its slow start. Early experiments <sup>7</sup> (ca. 1900-1930) established the ionic nature of several diphenyl and triphenyl methane derivatives in various solvents but a lapse of 35 years occurred till the stable carbonium ions, tropenium (tropylium) <sup>8</sup> and triphenylcyclopropenium,<sup>9</sup> were observed. The "aromatic" <sup>10</sup> nature of these ions and particularly the large resonance stabilization of the latter account for their presence in solutions which are only mildly acidic. Lacking such structural stabilization the carbonium ions so often implicated as

transient intermediates in thermal reactions eluded observation and thus the interest of photochemists.

Though the fact of carbonium ion existence has been long unchallenged the structure and reactions of these compounds have recently undergone intensive investigation. Most prominent in these studies are the strong or so-called "super" acids which form distinctive proton complexes with weak organic bases. Since the development of these strong acid systems weaves an inextricable thread into the fabric from which many cation photochemical reactions are tailored a consideration of the progress in this area is highly relevant. As several publications <sup>11,12</sup> well delineate various aspects of carbonium ions an exhaustive survey would be superfluous.

#### Strong Acids --- A Brief History of Carbonium Ion Formation

Perhaps of most general interest is the alkyl carbonium ion, a traditionally ephemeral species whose true nature must have tormented the soul of many a sturdy chemist. To obtain this previous whisp as a stable and observable species  $Olah^{13}$  has reacted several alkyl fluorides with the strong Lewis acid, antimony pentafluoride (SbF<sub>5</sub>).

 $\frac{37}{\text{SbF}_{5}} \rightarrow CH_{3}CH_{2}CH_{2}CH_{2}SbF_{6}$ 

An alternate procedure, employed later in this thesis, involved the action of fluorosulphonic acid on appropriate alcohols at temperatures sufficiently low to preclude side reactions.<sup>14</sup> Several such previously unobserved cations proved very stable while others have undergone rearrangement.

$$\begin{array}{ccc} Me & Me \\ I & FSO_3H & I \\ Me-C-OH & & & \\ Me & SbF_5 & Me-C+ \\ Me & & & Me \end{array}$$

More pertinent to the work of this thesis are the initial observations by M<sup>C</sup>Clean and co-workers with weak aromatic bases in strong protic media. The O bond nature of the proton-base complex had been previously disputed by at least one author.<sup>15</sup>

COMPLEX

AROMATIC BASE

T COMPLEX

However, strong evidence in favour of the  $\sigma$  complex appeared in the uv spectral observations of systems reported initially by Gold and Tye.<sup>16</sup> Fully supporting this postulate was the unambiguous demonstration by nmr that a paraffinic -CH<sub>2</sub>- group indeed existed in several aromatic systems disolved in hydrogen fluoride (HF) saturated with boron trifluoride (BF<sub>3</sub>).<sup>17</sup> Thus MacClean provided the first indisputable example of carbonium ion formation by proton addition to an aromatic system. The somewhat surprising ease of formation and stability of these cations at ambient temperatures is more appreciated if one recognizes the simultaneous loss in aromatic character experienced by the base.<sup>\*</sup>

A number of acids have proven sufficiently strong to produce stable cations but each has its own advantages and limitations. Despite the wide temperature range afforded by the HF/BF<sub>3</sub> system the highly corrosive nature of the hydrogen fluoride imposes a definite material limitation thereby reducing its desirability for general use. Fluorosulphonic acid or admixtures with  $SbF_5$ , advanced by

\* Unless otherwise stated the ortho, meto, para designation strictly employed for aromatic systems will be used, where applicable, for the benzenonium cations with reference to a prime ring substituent rather than the site of protonation. Gillespie,<sup>18</sup> do not have this drawback although the upper operating temperature may be necessarily low because of fluorosulphination reactions.<sup>19</sup> Its high mobility at low temperatures (mp -89.0°) and high acidity  $(H_{\circ} \sim -15)^{20}$  of neat FSO<sub>3</sub>H make it an ideal solvent for generating and preserving cations at low temperatures. Diluents such as sulphuryl fluoride chloride  $(SO_2ClF, mp -124.7°)$  and sulphuryl fluoride  $(SO_2F_2, mp -136.7°)$  allow temperature reduction without appreciably decreasing acid strength.<sup>21</sup>

# Previous Examples of Organic Cation Photo-rearrangements

Although the literature contains a number of early references to possible cation photochemical reactions (figure 1) no thorough or even preliminary investigations were forthcoming from such observations. For example, Reid<sup>22</sup> in 1954 noted that following irradiation of pyrene in HF/BF, a significant change in the uv spectrum occurred yet no product identification was attempted despite the suggestion that chemical reaction may have taken place. Another instance involved the recovery of 9-phenylfluorene from crystalline trityl perchlorate which had inadvertantly been exposed to sunlight for several weeks. Incidentally, this was one of the products of trityl perchlorate irradiation in acetic acid identified in a later investigation by van Tamelen.<sup>24</sup> Harmon and co-workers reported the light sensitivity of tropylium chloride. 25 However, the true origin of the three unidentified "products of photolysis" is unclear as the authors claim these products are identical

5

Possible early photo-transformations of organic cations







-----H



23





hγ conc. H,SO

hγ

26

25

REF.

to those of thermal decomposition of tropylium bromide. Most recent was the possibility of photoracemization of the optically active trans pentamethylcyclopentenyl cation offered by Sorenson.<sup>26</sup>

However, van Tamelen's publication<sup>24</sup> in 1968 represents the first systematic investigation of carbonium ion excited state chemistry. In this study the photochemistry of the highly stabilized triphenyl methyl carbonium ion, as well as the triphenylcyclopropenium and tropylium cationic systems were investigated under conditions mildly acidic in comparison with the strong acids mentioned earlier. Photochemical reaction of tropylium fluoroborate (1) in dilute aqueous acid afforded the bicyclo [3.2.0.] hepta-3,6-dien-2-ol (3) together with the corresponding ether (4) presumably through the intermediacy of the bicyclo [3.2.0.] heptadienyl cation (2).



Photocyclization of the triphenylmethyl carbonium ion (5) in 96%  $H_2SO_4$  gave only 9-phenylfluoren-9-cl (10) but irradiation in other solvents gave various products.

7.



However, photolysis of the triphenylcyclopropenium system led to products consistent with a radical mechanism. Photoproducts 3 and 10 were suggestive of cationic collapse with solvent but that solvent incorporation was a photochemically induced step could not be dismissed. Thus the greatest limitation of this exploratory work was the lack of primary photoproduct observation. Removal of this impasse required a solvent system which would stabilize the primary photocation\* by preventing collapse with nucleophiles.

Such a course was followed by Childs and Winstein<sup>27</sup> when they irradiated protonated pentamethylbenzene (11) in  $SO_2ClF/FSO_3H$  solution. That this polymethylbenzene formed a stable cation in strong acid had been shown previously.<sup>28,17</sup> Figure 2 illustrates the photoisomerization of protonated pentamethylbenzene to the bicyclo [3.1.0.] \* Photocation will henceforth refer to any cation observed as a photoproduct of a cationic precursor.

Photolysis of polymethyl benzenonium cations in FSO<sub>3</sub>H at -80°









13













hexamethyl and heptamethyl analogues of the bicyclic system arose from irradiation of the corresponding hexamethyl<sup>30</sup> and heptamethyl<sup>31</sup> benzenonium cations in  $FSO_3H$ .

Furthering the use of strong acid media Childs<sup>32</sup> has re-examined the photoreactions of tropylium fluoroborate with fluorosulphonic acid as solvent. In contrast to van Tamelen's result the singular photolysis product in FSO<sub>3</sub>H was the 7-norbornadienyl cation (17a). A Wagner-Meerwein rearrangement of the photo-bicyclo [3.2.0.]heptadienyl cation(2a) accounted for the observed product but noted was the likeliehood that this reaction would be slow relative to capture of nucleophilic solvent such as that used by van Tamelen.



Methyl substitution of the tropylium cation (1b) did not alter the reaction course as the 2-methyl-7-norbornadienyl cation (17b) appeared as the photoproduct. However, methoxy and hydroxy substitution significantly altered the nature of the observable products. Indeed, the postulated photocation intermediate was stabilized to such an extent by these substituents that both the 1-methoxy and 1-hydroxy bicyclo [3.2.0] heptadienyl cations (2c) and (2d) were observed along with a norbornenone derivative (18c) and (18d).



18 c 18 d

As an extension of benzenonium cation photoreactions Childs<sup>33</sup> has explored the excited state rearrangements of the protonated hexamethylcyclohexadienones. Irradiation of the protonated forms of the cross conjugated and linear conjugated dienones gave rise to one photoproduct identified as the 2-hydroxy-hexamethylbicyclo [3.1.0.] hexenyl cation. A more detailed account appears later along with a consideration of a similar system studied by Filipescu and Pavlik.<sup>34</sup>

Inquiries  $^{35,36}$  by Koptyug and co-workers involved the preparation of bicyclo [3.1.0.] hexenyl cations in a manner analogous to that of Childs and Winstein.<sup>27</sup>

Very recently the photorearrangements of protonated eucarvone were outlined by Childs and Hine.<sup>37</sup> Furthering earlier work<sup>38</sup> in other solvents these authors report the reaction of 19 to 20 which is unique to eucarvone irradiation in strong acid (FSO<sub>2</sub>H). An open chain



intermediate (19a) which could re-cyclize was suggested.



19a

# SECTION 1 PHOTOCHEMISTRY OF POLYMETHYL BENZENONIUM CATIONS

# Formation of Polymethyl Benzenonium Cations

Aromatic hydrocarbons have long been known to disolve in strong acid, principally concentrated H<sub>2</sub>SO<sub>4</sub>, with simultaneous colour formation. Though often used as a qualitative test in organic chemistry,<sup>39</sup> studies of the nature of these reactions were often fruitless. Relative basicities of the polymethylbenzenes were first investigated by M<sup>c</sup>Cauley and Lien<sup>40</sup> in 1950. Subsequent workers<sup>41</sup> employed a similar HF/BF<sub>3</sub> acid system to embrace all the members of this series. A modern review of this field is available.<sup>42</sup>

The uv spectra of various unsubstituted aromatics in strong acid media had been reported by Gold and Tye<sup>16</sup> but spectra of the methyl substituted benzenonium cations (mesitylene and toluene) in HF/BF<sub>3</sub> were presented by Reid.<sup>22</sup> More recently Perkampus<sup>43</sup> has reported the infared spectra of the complexes formed from the methyl benzenes and HX/AlX<sub>3</sub> to be consisent with the  $\sigma$  bond nature of the system.

In the area of benzenonium cation observation nmr spectroscopy has been most useful. Thus the cations of the pentamethyl and hexamethylbenzenes 44 in HF/BF, have been

recorded as have those of m-xylene, mesitylene, and the three tetramethylbenzenes.<sup>45</sup> Shortly thereafter fluorosulphonic acid served to generate the cations of mesitylene, durene, pentamethyl and hexamethylbenzene while those of m- and p-xylene have been observed in a FSO<sub>3</sub>H/SbF<sub>5</sub> medium.<sup>28</sup>

## History of Polyalkyl Benzenonium Cation Photochemistry

Despite the fact that the  $\sigma$  complex nature of the polymethyl benzenonium cations had been firmly established a period of ten years lapsed before the photochemical properties of these systems became apparent. Until this present series of investigations the only examples involved the photoisomerisation of the penta-, hexa-, and heptamethyl benzenonium cations.<sup>27</sup> Figure 3 illustrates not only the photoproducts of these isomerisations but also the covalent precursors of the initial cations. Of the three products only 14 entailed the possibility of stereoisomer formation but in fact only the endo-methyl isomer shown in figure 3 was observed. The non-planar<sup>46</sup> hexamethyl benzenonium cation has the geometry of 26 which is less sterically strained than the planar species.



Since the methyl group is predisposed above the cyclopentadienyl cation moiety it is not surprising that photoclosure leads to the endo-methyl isomer. Furthermore, during transformation of 13 to 14 either the methyl or the hydrogen of the methine moiety must pass through the plane of the ring. Preferential passage of the smaller hydrogen atom through this plane, congested by the methyl groups on adjacent carbons would give rise to the isomer with the methyl in the endo position.

Recently two similar phototransformations were effected by Koptyug and co-workers.<sup>35</sup> Both the ethylhexamethyl (27) and chloromethyl-hexamethyl (28) hexadienyl cations isomerised upon irradiation to the expected bicyclic cations (29) and (30) respectively, shown below.

h~,90% (+)



30a

21



30b

hγ,87%

29a

29b

28

Again the steriochemistry is in favour of the larger group occurring in the endo position.

Structural Evidence for the Bicyclo 3.1.0. hexenyl Cation

Protonation of 31 in FSO<sub>3</sub>H at low temperatures gave a cation 12 whose nmr spectrum and rate of thermal ring opening to 11 were identical to those of the photo-



product of protonated pentamethylbenzene.2

The non-photchemical synthesis of 14 via the action of  $AlCl_3$  on halide 32 has been reported by Koptyug<sup>47</sup> to give a material identical to the photoproduct of 13.



32

Further work by this group involved the preparation of a  $C^{13}$  enriched species 14, the spin-spin coupling constant  $J_C^{13}_{-H}$  of which, was characteristic of R-C-H fragments in cyclo-propanes.<sup>48</sup>

With the skeletal structure of 12 and 14 established there remained the problem of the most appropriate electronic representation. There can be no doubt that a significant degree of charge delocalization into the cyclopropyl ring occurs. The cyclopropane hydrogens of 12 are deshielded some 2-3 ppm relative to those of the hydrocarbon 31. Since a direct field dffect failed<sup>27</sup> to account for these shifts delocalization of cyclopropyl bonds  $C_1-C_6$  and  $C_5-C_6$  was invoked as shown in 33.



Noteworthy is the intact  $C_5-C_6$  bond, delocalization of which would correspond to incipient opening of 33 to the cyclo-hexadienyl cation.

# Mechanism of Cyclohexadienyl Cation Photochemical Ring Closure

A known thermal reaction of substituted pentadienyl cations is rearrangement to the corresponding cyclopentenyl cations.<sup>49</sup> The suggestion by Woodward and Hoffmann<sup>50</sup> that a concerted electrocyclic ground state closure would



proceed in a conrotatory manner was experimentally confirmed 26 by Sorenson and co-workers. In contrast is the inertness of the ground state cyclohexadienyl cation which may be viewed, at least electronically, as a pentadienyl cation whose ends are joined by a -CR2- bridge. This structural difference prohibits the conrotatory closure found in the pentadienyl system since analogous closure of the cyclohexadienyl cation leads to a highly strained trans cyclopropyl ring which, even if formed, would likely open to give the starting cation. However, photochemical closure of the cyclohexadienyl cation to the corresponding bicyclo 3.1.0. hexenyl cation is a very facile process. In general terms the photo-induced promotion of an electron of 11 (shown below) produces an excited state 34 which can rearrange to 12.





The exact nature of the excited state is unknown but it seems reasonable that the reaction involves the lowest previously unoccupied molecular orbital of 11. Whether this remains as the singlet or intersystem crosses to the triplet is open to question. Viewing this reaction as a concerted process one is restricted to the singlet form which allows interpretation in terms of the orbital symmetry of the first excited state. In the following discussion of this mechanism the symmetry of the excited state is assumed to be +---+ for the pentadienyl cation moiety illustrated in figures 4 and 5. Depicted therein are the familiar electrocyclic ring closure and the somewhat more esoteric  $\left[\sigma_{2} + \pi_{2}\right]$  cycloaddition mode recently invoked to account for photoreactions of cyclohexadienones and cyclohexenones. <sup>52</sup>As evaluation of the results of this section require an understanding of the details of these mechanisms a short discussion of their major features is appropriate. Considering the electrocyclic mechanism (figure 4) first we find that disrotatory closure results in effective overlap of the p orbitals of like symmetry on carbons 1 and 5. Not only does this  $C_1 - C_5$  bond formation lead directly to the observed product but such disrotatory closure in the excited state is predicted by considerations advanced by Woodward and Hoffman. 51

The alternate  $\begin{bmatrix} \sigma_{2}^{2} + \pi_{2}^{2} \end{bmatrix}$  cycloaddition mechanism (figure 5) formally involves addition of the 2  $\sigma$  electrons of the  $C_{1}-C_{6}$  bond to the 2 $\pi$  electrons of the  $C_{4}-C_{5}$  bond in a very precise manner. Antara (a) participation of the  $\sigma$  bond

cation



FIGURE 4

FIGURE 5  $\begin{bmatrix} \sigma_{2_{a}} + \pi_{2_{a}} \end{bmatrix}$  closure of the excited state cyclohexa-

dienyl cation



involves configurational inversion at one terminus (ie  $C_6$ ) with retention at the other  $(C_1)$  whereas antara (a) involvement of the  $\pi$  bond engenders addition of the  $\sigma$ electrons to opposite sides of the  $\pi$  system. The overall reaction may be considered as addition of electron density from the highest occupied molecular orbital of the pentadienyl system to the lowest unoccupied molecular orbital associated with the  $\sigma$  bond.

## Experimental Differentiation of Mechanism

Since cations which had been irradiated previously were not amenable to differentiating these mechanisms a scheme was devised which would do so. In view of the fact that the  $\left| \mathbf{O}^{2}_{a} + \mathbf{\Pi}^{2}_{a} \right|$  mode involved ring skeletal rearrangement but the electrocyclic one did not, a ring labelling approach or variant thereof was attractive. The cations selected for study were those of protonated durene (1,2,4,5tetramethylbenzene) (35) and isodurene (1,2,3,5-tetramethylbenzene) (36) both of which were reported earlier and were readily characterized by low temperature nmr with FSO,H as solvent (figure 6). Figure 7 outlines the likely photoproducts of these two cations by the alternative mechanisms. 37 occurs as product of electrocyclic closure of 35 whereas the  $\sigma_{2}^{2} + \pi_{2}^{2}$  process would generate 38 or its thermal product of rearrangement (36). Alternatively the  $\sigma_{2a} + \pi_{2a}$  process may lead to 39 which could further rearrange thermally to protonated 1,2,3,4-tetramethylbenzene (40), Electrocyclic

FIGURE 6 nmr chemical shifts of several cyclohexadienyl and bicylo 3.1.0. hexenyl cations




closure of 36 leads to 38 in contrast to the  $\begin{bmatrix} \sigma & 2 \\ a & \end{bmatrix}$  mechanism which produces 37.

Irradiation (pyrex filter, -80°) of the long wavelength absorption of protonated durene (35) in FSO<sub>3</sub>H effected an 80% conversion to the tetramethylbicyclo 3.1.0. hexenyl cation (37) identified by its nmr spectral similarity to the analogous pentamethyl system (12) and the consistency between expected and observed spectra. The non-equivalence of the cyclopropyl protons, the symmetry implied by the 2 methyl peaks, and the characteristic<sup>53</sup> absorption of the vinylic hydrogen are in good agreement with the proposed structure. As continued, short irradiation did not significantly alter the relative concentrations a photostationary state occurred involving photo-reversion of 37 to 35. This result is in accord with simple electrocyclic closure. Extended exposure of an equilibrium solution of 35 and 37 did however yield increasing concentrations of 36. After a 2 hour irradiation of 20 mg of durene, which equilibrated with its bicyclic isomer in 60 minutes, approximately 5% of 36 was detected by nmr.

An inefficient  $\begin{bmatrix} \sigma 2_a + \pi 2_a \end{bmatrix}$  reaction would produce 38 which, in view of its methyl substitution pattern, may be expected to ring open thermally to protonated isodurene.

\* Toshiba 125 watt Hg light source, no filter.

38 could also be formed from 37 by a thermal  $\begin{bmatrix} 1,4 \end{bmatrix}$  sigmatropic rearrangement of the cyclopropyl ring. However, such a process is unlikely at -80° since 37 exhibits thermal ring opening to 35 with a first order rate constant k=1.6x10<sup>-3</sup> at -32° and no detectable formation of 36. A photochemically induced  $\begin{bmatrix} 1,4 \end{bmatrix}$  sigmatropic reaction with configurational retention at the migrating centre is not attractive since no such retention is found when either the exc- or endo-methyl isomers of the hexamethylbicyclo  $\begin{bmatrix} 3,1,0 \end{bmatrix}$  hexenyl cation is irradiated.

During short (1 hour) irradiations protonated isodurene failed to undergo observable change. Since the product (37) expected from 36 by the  $\left[\sigma 2_a + \pi 2_a\right]$  mechanism was previously extablished as a stable entity under the reaction conditions the  $\left[\sigma 2_a + \pi 2_a\right]$  mode was ruled out as an efficient process for isodurene as well. Extensive irradiation of 36 gave small amounts of 35 and 37 again consistent with a slow  $\left[\sigma 2_a + \pi 2_a\right]$  reaction.

That no product was observed upon short irradiation of protonated isodurene (36) could be explained in terms of the substituent pattern of the expected product of electrocyclic closure (38). Cation 37 is advantageously methyl substituted at positions 1 and 3 of the allylic cation. moiety whereas the methyl substitution at carbons 2 and 3 in the corresponding cation 38 does not permit such charge stabilization. Thus 38 may ring open thermally at -70° to protonated isodurene(36). The mechanism of ring opening

although consistent with symmetry forbidden disrotatory opening of the  $C_1-C_5$  bond is open to question.

ant.

## Thermal Lability of the 1,2,3,5-tetramethylbicyclo [3.1.0.] Hexenyl Cation---A Test of Hypothesis

However convincing the previous argument appeared there remained the possibility that because of its particular methyl substitution pattern protonated isodurene failed to photo-cyclize. The assumption that, if formed, the photocation (38) would rearrange to 36 at low temperature appeared open to investigation. Non-photochemical generation of 38 under the irradiation conditions was necessary to validate the point in question.

To do so we relied upon the technique, extended by Olah,<sup>14</sup> for producing stable cations from alcohols. The alcohol (41) shown in figure 8 was synthesized by a methyl Grignard addition to the ketone (42) which became available through a concurrent research program. Both nmr and ir spectral data for the alcohol appear in table 1. Within three minutes of disolving alcohol (41) in fluorosulphonic acid at -78° the nmr spectrum at -75° showed only peaks attributable to protonated isodurene (36). Thermal instability of cation 38 was thus confirmed and a lower limit for the associated rate constant established\* as  $k > 1.0 \times 10^{-2} \text{ sec}^{-1}$  at -75° which corresponds to a free energy of activation of  $\Delta G \ll 13.1$ kcal/mol.

Thus it was demonstrated that the unobserved bicyclic cation 38 arising from electrocyclic closure of protonated

FIGURE 8

Synthetic method for the

cation 38







36

FIGURE 9

Expected photo-product of

protonated prehnitene irradiation



40







nmr and ir data for 2-hydroxy-1,2,3,5-tetramethylbicyclo [3.1.0.] hex-3-ene



mar absorpcions in cs_ (cecian	le chy isi iane as	Incernal Scandardy
absorption		proton
9.81 (1H, $dJ^{AB}=4$ cps)		A
9.59 (1H, dJ <sup>AB</sup> =4 cps)		В
8.87 (6H, sbroadened)	<b>a</b>	
8.82 (3H, ssharp)	-	E,F,G
8.52 (3H, dJ <sup>CD</sup> =2 cps)		c c
4.66 (1H, $qJ^{CD}=2 cps$ )		D
5.37 (lHvery diffuse)		H
• • • • • • • • • • • • • • • • • • •		•

#### ir with carbon tetrachloride as solvent



s--singlet, d--doublet, q--quartet

isodurene would undergo rapid thermal reversal to starting material. This result also reinforces the earlier contention that the cation 38, derived from 35 by a slow  $\left[\sigma_{2a}^{2} + \pi_{2a}^{2}\right]$ process would ring open to give the observed product isodurene.

#### Irradiation of Mesitylene and Prehnitene in FSO,H

If indeed stabilization of the allylic portion of the bicyclo [3.1.0] hexenyl cation is the crucial factor in product preservation then cation 40 (figure 9) derived from the protonation of prehnitene (1,2,3,4-tetramethylbenzene) would be expected upon irradiation to yield the thermally stable cation 39.

Following a procedure identical to that used for the other protonated tetramethylbenzenes cation 40 was irradiated for periods in excess of that necessary to isomerize an equal amount of protonated durene. Nevertheless, no observable photochemical reaction occurred. In view of the apparently satisfactory argument presented to account for previous results involving durene and isodurene the lack of product formation was totally unexpected. Seemingly the stability of a bicyclic cation is largely affected by bridgehead substitution as well as substitution on  $C_6$ , previous examples of which are known.<sup>27</sup>

One interpretation of this bridgehead substitution dependance is that a significant degree of charge delocalization exists on the cyclopropyl ring and with no methyl stabilization at the  $C_c$  position the substituents at the bridgehead position have an increased role in stabilizing the delocalized charge.

Mechanism of Thermal Ring Opening in Bicyclo 3.1.0. Hexenyl Cations

Inherent in the discussion so far is the assumption that one undefined mechanism pertains to all examples of bicyclo 3.1.0 hexenyl cation thermal ring opening. There may indeed be competitive ring opening mechanisms dependent upon not only the extent but also position of methyl substitution. That such a situation exists is supported by the recent observation of the bicyclo 3.1.0 hexenyl cation 43 bearing only hydrogens.<sup>55</sup> The thermal stability of this cation has been shown to be greater than that of previously mentioned systems except for the fully methylated cation which possesses an approximately equal stability.

Consistent with the thermal products of ring opening exhibited by these systems is  $C_1 - C_5$  bond scission. If this process is concerted a conrotatory mode of ring opening is 51 predicted. However, this avenue leads to an energetically prohibitive trans double bond in the product while the alternative disrotatory opening is expected to occur only in the first excited state. Thus we are faced with accepting one of the following possibilities:

- a) A non-concerted route for C<sub>1</sub>-C<sub>5</sub> bond rupture
  (ie diradical)
- b) A symmetry forbidden concerted pathway with
  C<sub>1</sub>-C<sub>5</sub> bond opening which would contravene the
  Woodward-Hoffmann rules

#### c) An alternate course

Speculation on several alternate mechanisms was possible. One, which has been suggested by Baldwin<sup>56</sup> to account for the 1-methylcyclopentadiene product (44) in the thermal rearrangement of 2-methylbicyclo [2.1.0.] pent-2-ene (45) is the  $[\sigma_{a}^{2}+\sigma_{s}^{2}]$  process.



Figure 10 illustrates the application of this mechanism to the 1,2,4,5-tetramethylbicyclo [3.1.0.] hexenyl cation (37). Regection of this mechanism is necessitated by the lack of agreement between the predicted (isodurene) and known product (durene) of thermal ring opening. Similar opening of cation 38 would give protonated durene (35) and not the observed protonated isodurene (36).

Also discussed previously<sup>57</sup> in terms of the bicyclo-  $\begin{bmatrix} 2.1.0 \end{bmatrix}$  pent-2-ene system is the retro-ene reaction.<sup>58</sup> Shown in figure 11 for the now familiar cation 37 this process is expected to exhibit a large primary kinetic isotope effect  $(7-12)^{59}$  since a hydrogen is transferred from C<sub>6</sub> to C<sub>2</sub> in the rate determining step. Thus a probe of this mechanism would

## FIGURE 10

 $\begin{bmatrix} \sigma 2_{a} + \sigma 2_{s} \end{bmatrix}$  Ring opening of the 1,2,4,5-tetramethylbicyclo [3.1.0] hexenyl cation





37

36

## FIGURE 11

Retro-ene opening of the bicyclic cation 37



be the relative rates of thermal isomerization of 37 and 37-D.

At -85° protonated durene appears as a slightly broadened singlet in the nmr spectrum indicating that a very rapid proton exchange process averages the methyls even at this low temperature. Dissolution of durene in  $FSO_3D$  results in formation of cation 35-D in which the 3 ring hydrogens are replaced by deuterium. That such a species does occur is evidenced by the appearance at -85° of distinct methyl singlets observable now only because of the decreased exchange rate in  $FSO_3D$ .

35-D photo-isomerized to the corresponding bicyclic



cation 37-D which showed methyl absorptions identical to those of 37-H and the expected absence of methylene and allylic peaks. Measurement of 37-D's thermal rate of rearrangement to 35-D indicated a first order rate process with a rate constant  $k=1.6\times10^{-3}$  at  $-32^{\circ}$ . Similar measurement of the 37-H system gave  $k=1.7\times10^{-3}$  at  $-31^{\circ}$  which is identical to that of 37-D within the estimated 10% error range. The lack of any observable isotope effect necessitates the dismissal of the retro-ene reaction. That such a mechanism is untenable is not surprising in that hydrogen transfer must, in this case, be to a relatively non-basic methyl-bearing carbon which would give species 46. Such a mode however may pertain to bicyclic cations which are unsubstituted in the 2 and/or 5 positions, an example of which is the bicyclic cation derived from protonated isodurene. This perplexing problem may yield to solution by non-photochemical production of a series of cations which involves independent variation of methyl substitution at both the bridgehead and  $C_6$  positions.

#### SECTION 2 PHOTOCHEMISTRY OF HYDROXY BENZENONIUM CATIONS

This section involves the extension of polymethylbenzenonium cation photochemistry to include excited state reactions of hydroxy substituted cations. Ealier references have been made to work in this area.

Depending on one's inclination this field may be viewed as a variant of cyclohexadienone photochemistry in the special circumstance of a strongly protic solvent or alternatively as that of stable hydroxy-benzenonium cations. However, there is little advantage to be gained by any strong distinction since comparisons between these two fields of research are valid and conducive to recognition of common types. For convenience this topic will be divided into two parts consisting of (A) protonated cyclohexadienone and (B) protonated phenol photochemistry.

#### Part A --- Photochemistry of Protonated Cyclohexadienones

In retrospect the general type of reaction exhibited by protonated cyclohexadienones should not have been unexpected as analogous reactions of the neutral molecules are numerous. With this in mind the reader should take note of the reaction types which follow in the very limited review of cyclohexadienone photochemistry. Because of the vastness of this field only those examples which have special relevance to the present work are presented. Anyone wishing to explore

the field in depth is invited to read several reviews and recent publications. 61

#### A-i Photochemistry of 2,5-cyclohexadienones

The light sensitivity of 2,5-cyclohexadienones was discovered long ago but only recently have the products been identified and received mechanistic interpretation, 63 Santonin (47) is an excellent example of this recent progress as numerous photochemical changes of this system have been studied. Of particular interest was its conversion to lumisantonin (48) reported by Barton.<sup>63</sup>



47

In general the 2,5-cyclohexadienones undergo two types of photo-reactions in neutral media. Skeletal rearrangement with consequent lumiketone formation, as in the case of santonin, is the most common. However, in certain cases phenolic products may follow expulsion of a substituent at the 4 position. Recent examples of this reaction have been provided by several workers.<sup>64</sup>

Both structural<sup>65</sup> and solvent<sup>66</sup> dependencies have been demonstrated for this system. Indeed the latter dependence proved great enough to allow selective generation of several complex products such as the spiro-ketone (49) which



otherwise would be a difficult synthetic problem.

A structurally simplified system, 4,4-diphenyl cyclohexadienone, has been rigorously studied by Zimmerman and 67,68 co-workers. Initial investigations showed that the photoproducts of 50 were those shown in figure 12. 'Zwitterionic' species were used in the mechanistic scheme outlined in figure 13 to account for the formation of the bicyclic ketone 53. A similar electronic transition-bond alteration mechanism was proposed to rationalize the conversion of the bicyclic ketone to phenols 51 and 52. The photo-acid (54) was considered to arise from a ketene intermediate which derived from homolytic cleavage of bond b of the cyclopropyl ketone (53).<sup>68</sup>

Although the conversion of 50 to 53 proceeds by way of a triplet state  $^{69}$  the subsequent reactions of the latter to 51, 52 and 54 is somewhat more complex. The ketene preFIGURE 12

Photolysis products of 4,4-diphenylcyclohexa-

2,5-diehone





54

ω

FIGURE 13

Suggested mechanisms for the photo-rearrangement

of 4,4-diphenylcyclohexa-2,5-dienone



desessor of 54 has been considered to arise from both singlet and triplet states shown in figure 12. A triplet pathway has also been proposed to account for formation of 51 and 52 from 53.

This mechanistic interpretation in terms of the zwiterionic intermediate has received wide acceptance<sup>60</sup> principally because such migrations have been observed only in electron defficient species such as 55 which results from  $\Upsilon^*$ --n demotion. The electronic structure of 55 should be noted since it resembles, at least formally, the structure proposed as an intermediate in the present work.

Of special significance was Zimmerman's discovery that the phenol isomer ratio of the previous reaction was highly dependent on the medium acidity. Molecular orbital calculations<sup>70</sup> on the protonated and unprotonated zwitterionic species supported the experimental preference for the 3,4-diphenyl phenol formation with increasing acid strength (3,4-/2,3-=1.80 at pH=0). Furthermore the photophenol (51+52) to photo-acid (54) ratio proved to be pH independent thereby suggesting that cyclopropyl ketone (53)which is the common precursor had minimal interaction with the solvent protons prior to excitation.

There are a priori two stereochemical courses for the rearrangement of the cyclopropyl ring involving either retention or loss of configuration at the migrating center. To investigate this aspect of 2,5-dienone photochemistry Zimmer-

man<sup>71°</sup> ingeniously synthesized both the exo and endo isomers of 2-bromo-6-phenyl-6-p-bromophenylbicyclo [3.1.0.] hexan-3-one (56) of figure 13a. Subsequent treatment of 56 (exo or endo) with base gave 6-phenyl-6-p-bromophenylbicyclo [3.1.0.]hex-3-en-2-one (57), through the intermediate 58. The beauty of this experiment appears in the non-photochemical generation of a model zwiterionic compound (58) to approximate the hypothesized intermediate (55 of figure 13) of the photochemical transformation. Observed retention of exo or endo stereochemistry during the transition of 56 to 57 required configurational inversion at the migrating center which is characteristic of Zimmerman's 'slither' mechanism.

Very similar concurrent work was reported to give the same stereochemical result.  $^{72}$  .

Following this impressive work a publication<sup>73</sup> by one of Zimmerman's former associates appeared suggesting that although the bicyclic ketone may open to phenolic products by a polar mechanism the 4,4-diphenyl cyclohexa-2,5-dienone need not isomerize through such an ionic species. Based on the lack of phenol formation from photolysis of the 2,5dienone in the gas phase or non-polar media as opposed to its appearance in a polar solvent these results somewhat tempered the ionic mechanism. A recent suggestion by Woodward and Hoffmann<sup>52</sup> concerning the  $\left[ \sigma 2_a + \pi 2_a \right]$  mechanism, discussed earlier, also favours a non-ionic pathway. 132 Stereochemistry of the 1,4 sigmatropic rearrangement of the zwitterionic species suggested by Zimmerman



FIGURE

#### A-ii Photochemistry of 2,4-cyclohexadienones

Although discovered later the light induced isomerizations of linearly conjugated cyclohexa-2,4-dienones proved to be as facile as those of the cross-conjugated 2,5-dienones. The former class of dienone has been observed to undergo four general types of photoreaction two of which follow:

- a) Ring fission to a cis ketene followed by photochemical conversion to the trans ketene which may react with nucleophiles.
- b) Cyclopropyl ketone formation via two distinct mechanisms.

The ketene reaction has received by far the most attention in the literature. Special consideration of the cyclopropyl ketone formation is also warranted since a strong analogy exists with the similar cationic species.

Hart<sup>74</sup> first reported the latter reaction for the hexamethyl system. Labelling experiments indicated that an obvious mechanism of photo-induced methyl shift followed by closure did not apply and the novel 'bond-crossing' mechanism shown below was suggested.



Later Hart<sup>75</sup> observed ketene formation by low temperature ir studies with the same dienone and proposed that the only photochemical step in the 2,4-dienone rearrangement was ketene formation and that all other steps were thermal.



Subsequent recyclization of the ketene gave the observed cyclopropyl ketone. Shortly before this Chapman<sup>76</sup> described the production and observation of a cis-ketene from a 2,4cyclohexadienone by a similar method but he did not investigate the characteristics of the ketene. Hart, however did so and showed that a strong solvent dependence existed for ketene formation and subsequent recyclization. Previously a marked dependence on the ring substitution pattern had been demonstrated for the photo-rearrangements of pentamethylcyclohexa-2,4-dienones but no account of this structural dependence has been presented in light of the apparent necessity of a ketene intermediate.

As with the 2,5-dienones dipolar intermediates have been employed to represent excited states in 2,4-dienones. Though experimental evidence is lacking to confirm such

species in the isomerization to bicyclic ketones supportive evidence has been presented for such an ionic species following the photochemical opening of the cyclopropyl ketone 59. 76a Photolysis of 59 in MeOH leads to the isolable product 61. Intermediate 60 can theoretically undergo methyl migration to either  $C_4$  or  $C_6$  or alternatively capture solvent through



60a to 61, the only observable product.

This result is somewhat reminiscent of the 4,4diphenylcyclohexa-2,5-dienone photolysis discussed earlier in which the authors suggested the bicyclic ketone may proceed to phenolic products through an ionic intermediate 73similar to 60b and 60c.

### A-iii<sup>®</sup> <u>Previous Photochemistry of Hydroxy-polymethyl Benzenonium</u> <u>Cations</u>

During the course of the present endeavour several closely related photochemical reactions of alkylated hydroxybenzenonium cations have been reported. Although alluded to earlier these investigations follow in a more detailed account.

The first example of a hydroxy-polymethyl benzenonium cation photorearrangement was reported by Childs. 77 Shown in figure 14 are the photo-isomerizations of cations 62 and 63, obtained by disolving the corresponding dienones 78 in FSO<sub>2</sub>H, to the hexamethylbicyclo [3.1.0.] hexenyl cation 64. Essentially 100% conversion of 62 to 64 occurred whereas continued irradiation of 63 brought about a photostationary state consisting of a 50/50 mixture of 63 and 64, a ratio also reached by irradiation of 64 alone. The degree of isomerization of 62 and 63 has been rationalized in terms of the differing wavelength absorptions of the various species. Cation 62 ( $\lambda^{max}$ =400 nm) was irradiated with  $\lambda$ >380 nm so that the product cation 64 ( $\lambda^{\text{max}}$ =340 nm) failed to absorb light and rearrange. However, to excite cation 63 ( $\lambda^{max}$ =341 nm) the necessary irradiation also promoted cation 64 to an excited state from which it isomerized.

A further example involves cations 65 and 66 of figure 15 which photo-rearranged in 96%  $H_2SO_4$  at ambient temperature to the same 1-methyl-4-hydroxybenzaldehyde (67). Filipescu and Pavlik, having alternated irradiation and uv analysis,

# FIGURE 14

## Photolysis of the hexamethyldienones in $FSO_3H$ at $-80^{\circ}$ °



# FIGURE 15

Mechanism proposed by Filipescu and Pavlik to account for the photoisomerization of 65 and 66



suggested that the 2-hydroxy-6-methyl-6-dichloromethylbicyclo [3,1.0] hexenyl cation (68) acted as an intermediate which itself being photo-labile further rearranged to the unstable cation 69. Subsequent methyl migration exclusively to the 4 position reflected an earlier observation<sup>70</sup> of isomer dependence on medium acidity.

Although implicit in the structure of cation 68 the stereochemistry of this cation received no mention since uv analysis would fail to differentiate any exo-endo isomers of 68. Concurrent work in this laboratory on this particular photo-isomerization allowed such a distinction to be made. nmr spectra of the photo-products indicated that both exo and endo isomers were present. The results of this study are reported later.

#### A-iv Possible Mechanisms

As in the case of the polymethyl benzenonium cations there are a number of a priori mechanisms for these rearrangements, several of which are illustrated in figure 16 for the 1-hydroxy-6,6-hexamethylcyclohexadienyl cation (62). Path A depicts a photo-induced alkyl shift which if occurring by a concerted process predictably<sup>51</sup> involves antarafacial [1,6] sigmatropic migration. Despite the severe stereochemicl restraint of such a step the symmetry allowed photochemical disrotatory electrocyclic closure of the resulting  $4\pi$  cyclohexadienyl system (70) would be very favourable in light of similar reactions<sup>27, 35</sup> discussed earlier. This argument

FIGURE 16

Possible cyclization mechanisms for the hydroxy-<sup>\$</sup> polymethyl benzenonium cation



pertains as well to the latter step of path B which is preceded by a symmetry-allowed suprafacial methyl migration in the ground state.

Mechanism C entails a symmetry allowed electrocyclic closure between  $C_1$  and  $C_5$  in the excited state to give 71 followed by a ground state [1,4] sigmatropic migration of the cyclopropyl group. Not only does this route involve an intermediate species 71 previously recognized in a similar reaction <sup>80</sup> but the sigmatropic rearrangement also has precedent in the heptamethyl benzenonium cation.<sup>27</sup>

A  $\left[\sigma^2_a + \Pi^2_a\right]$  mechanism was a possibility but the results of the previous section suggested the cyclohexadienyl cation did not isomerize efficiently by this route. Interstingly an alternate  $\left[\sigma^2_a + \Pi^2_a\right]$  cycloaddition can be visualized which involves the addition of the  $\sigma$  electrons of the  $C_6^{--}$  methyl bond to the  $C_4^{-}C_5 \Pi$  bond.

Out of hand rejection of scheme B was necessitated by the demonstrated stability of cation 62 (k=1.10x10<sup>-3</sup> at 61°)<sup>81</sup> at operating temperatures (-80°). Paths A and C differed in that the latter conserved the integrity of the dimethyl group of cation 62 whereas the former did not. With this latter point in mind I undertook the irradiation of protonated 6,6-dimethylcyclohexa-2,4-dienone.

## A-V <u>Photolysis of Protonated 6,6-dimethylcyclohexa-2,4-dienone</u> 6,6-dimethylcyclohexa-2,4-dienone<sup>82</sup> was disolved in FSO<sub>3</sub>H at -78° to give the corresponding cation 73 (figure 17).



 сл сл Low temperature  $(-45^{\circ})$  uv spectral absorptions at 363 nm and 243 nm were very similar to those at 370 nm and 251 nm reported for model cation 74.<sup>83</sup> Furthermore the nmr spectrum



of 73 agreed very well with that of 74.

Cation 73 appeared suitable for resolving the mechanistic question since paths A and C would each give the characteristic products also shown in figure 17. Subsequent irradiation of the long wavelength absorption of 73 at -80° brought about conversion to three photo-products, the conccentrations of which varied with time. Graph 1 shows the relative proportions of reactant and photo-products obtained during photolysis by intermittent nmr analysis. Identified on the basis of their spectral agreement with authentic protonated material two of the products were found to be protonated 2,3-dimethylphenol (75) and 3,4-dimethylphenol (76). The third and most informative was assigned the structure of cation 77 both because of the excellent agreement between the observed and predicted nmr spectra and concordance with model compounds. Figure 18 illustrates the nmr chemical shifts of the 1-hydroxy-6,6-dimethylbicyclo-



[3.1.0.] hexenyl cation (77).  $H^{A}$  and  $H^{B}$  are both characteristically positioned and exhibit spin-spin coupling with  $J^{AB}=5$  cps.  $H^{B}$  is somewhat broadened by a small coupling with  $H^{C}$  ( $J^{BC}$  l cps) which along with  $H^{D}$  appear at typical bridgehead positions.<sup>84</sup> Two distinct absorptions at 78.33 and 78.55 are indicative of the 2 non-equivalent methyls at  $C_{6}$ . On the basis of previous work <sup>27a,b</sup> the lower field absorption is assigned to the exo methyl.



FIGURE 18

Several points may be obtained from graph 1. The rapid increase of cation 77 coupled with a corresponding decrease in starting material 73 indicated that the former was the primary observable photo-product. Since the conccentration of protonated phenols 75 and 76 more closely reflects the change in bicyclic cation (77) concentration than that of the starting material, the bicyclo [3.1.0] hexenyl cation is implicated as the origin of the phenols.

The photochemical nature of this dependence was demonstrated by the inertness in the absence of light of a partially irradiated solution. Furthermore, the ratio of the two isomeric phenols remains constant which reinforces the contention that the phenols derive from a common intermediate. With a ratio of approximately 3/1 in favour of the protonated 3,4-dimethylphenol these results are consistent with preferential migration to the 4 position reported for similar photo-rearrangements.<sup>34,68</sup> On this basis an extension of scheme 2 (figure 19) is proposed to account for the observed products.

Graph 2 illustrates a similar study with a 500 watt high pressure mercury light source instead of the 100 watt low pressure lamp used previously. The marked retardation in rate of reactant loss, decrease in bicyclic cation concentration and increase in phenol concentration all point to the differing wavelength-intensity distributions of the two lamps. In general low pressure lamps were found to be superior for producing high concentrations of bicyclic cations despite the necessary increase in irradiation time.

#### A-Vi <u>n-- $\pi^*$ versus $\pi$ -- $\pi^*$ Excitation</u>

Selective irradiation of the  $n--\pi^*$  or  $\pi--\pi^*$  bands of 2,4-cyclohexadienones has been shown by Hart<sup>85</sup> to cause their photochemical rearrangements to proceed by different mechanisms. One particularly interesting aspect of this work concerns the inversion of the relative energy differences



Photolysis mechanism of 73 to 77, 76 and 75 in FSO<sub>3</sub>H at -80°













OH

(+)

НН

75









OH



time

involved in these excitations with the use of trifluoroethanol or a cyclohexane-silica-gel slurry. With these solvent systems Hart has isomerized the tri-, tetra-, and hexamethyl cyclohexa-2,4-dienones to the corresponding bicyclic ketones. Previously it had been demonstrated that isomerizations of these dienones had occurred through the ketene which arose efficiently from the lower energy  $n--\pi^*$  transition. But with these two particular solvents the ketene mechanism was experimentally ruled out and a  $\pi--\pi^*$  excitation invoked to account for the photo-reactions which occurred through the 'bond-crossing' mechanism.

An exception encountered in Hart's work was the 6,6dimethylcyclohexa-2,4-dienone which gave products in accord with a ketene mechanism arising from  $n - -\pi^*$  excitation. In contrast I have isomerized this dienone to the corresponding protonated bicyclic ketone with FSO<sub>3</sub>H as solvent. Not only does this confirm Hart's  $\pi - -\pi^*$  postulate, since the n electrons on oxygen are bound up with the proton but also points out the advantage of FSO<sub>3</sub>H as a solvent for investigating the transitions involved in such reactions.

### A-VII Photochemistry of the 1-hydroxy-4,4-dimethylcyclohexadienyl Cation

To ascertain whether a photoisomerization analogous to that exhibited by protonated hexamethylcyclohexa-2,5dienone would occur in the dimethyl series cation 80 was
prepared by protonation of the corresponding 2,5-dienone (81).



Both low temperature nmr and uv spectra were consistent with the assigned structure (figure 20). Irradiation ( $\lambda$ >290 nm) of this cation gave at least 3 identifiable products, two of which were identical to those obtained from photolysis of the 1-hydroxy-6,6-dimethylcyclohexadienyl cation. These were protonated 3,4-dimethlyphenol and the 2-hydroxy-6,6-dimethylbicyclo[3.1.0] hexenyl cation. A third, which exhibited nmr absorptions similar but not identical to those of protonated 2,3-dimethylphenol, was identified as protonated 3,5-dimethylphenol by comparison with an authentic sample protonated under similar conditions. Remarkable was the low (~10%) concentration of the protonated bicyclic ketone which appeared in concentrations as high as 65% during the photolysis of the isomeric cation.

Accounting for a portion of these results is photochemical closure between  $C_3$  and  $C_5$  of cation 80 shown in figure 21 folowed by a [1,4] sigmatropic migration of the cyclopropyl ring to give cation 77. Presumably 77 opens as suggested previously but the protonated 2,3-dimethylphenol

nmr and uv spectral data for 4,4dimethyl and 4-methyl-4-dichloromethylcyclohexa-2,5-dienones in strong acids





Solvent FSO3H





FIGURE 21





83

λ<sup>max</sup> 310, £ (5370) 260, (13,000)



84

λ<sup>max</sup> 360, **ξ**(6340) 252, (6930) peaks were obscurred by those of the 3,5 isomer. Since the only difference in irradiating the two dimethyl isomeric cations was the wavelength of light required to effect isomerization it seemed likely that a previously unexcited molecule was now undergoing a photochemical reaction. Separate irradiations of both the protonated 2,3- and 3,4dimethylphenols under the conditions used for 80 indicated that the latter photoisomerized to the 3,5 isomer which resisted further change .

As the nature of this isomerization appeared somewhat unique a systematic investigation of other methylated phenols appeared worthwhile especially since only scanty reports of phenol photo-rerrangements are to be found in the literature.<sup>87</sup> Both the results of this investigation and a mechanistic interpretation of the 3,4-dimethylphenol isomerization are presented later.

## A-Viii Irradiation of the 1-hydroxy-6-methyl-6-dichloromethylcyclohexadienyl Cation

The photochemical rearrangement of the cation 65 as outlined by Filipescu and Pavlik was discussed earlier.



65

However the question of stereochemical consequence of the photo-induced ring closure was unanswered by their investigations. To confirm this earlier work and further, to probe the possibility of stereoisomer formation, 65, derived from the dissolution of the corresponding dienone 82 in HFSO<sub>3</sub>, was irradiated with  $\lambda$ >320 nm at -60°. 65 isomerized to cations 69a and 68b identified on the basis of their nmr



68a  $R_1 = CH_3$ ,  $R_2 = CHCl_2$ 68b  $R_2 = CH_3$ ,  $R_1 = CHCl_2$ 

spectra (table 2) as the two isomeric 2-hydroxy-6-methyl-6dichloromethylbicyclo [3.1.0] hexenyl cations and a small amount of unidentified phenolic material derived from the photo-rearrangement of 68a and 68b. Excellent agreement between the mnr chemical shifts of 68a and 68b and those of cation 77 (page 56) reinforced the proposed structure of both of these systems. Stereoisomer assignents have been made for 68a and 68b under the assumption that substituents  $R_1$  and  $R_2$  absorb at a lower field in the nmr spectrum when

# TABLE 2

nmr chemical shifts of 2-hydroxy-6-methyl-6-dichloromethylbicyclo [3.1.0] hexenyl cations 68a and 68b

Cation	Vinyl H's	Bridgehead H's	Methyl H's	ссі <sub>2</sub> н
6 8a.	1.13 (q)	5.88 (broad)	8,12	4.15
	2.87 (d)	6.36 (broad)		
68b	1.13 (q)	5.76 (broad)		
	2.87 (d)	6.20 (broad)	8,38	4.33
	J <sup>AB</sup> = 5	cps, $J^{BC} = 1.3 \text{ cps}$		L

66

e

they are exo.<sup>27,35</sup> Thus cation 68b (methyl-endo) was found to predominate over 68a by a factor of 3.6 to 1. Such a ratio is consistent with the argument, presented earlier (page 16), to account for the photoisomerization of the hexamethylcyclohexadienyl cation to a single product which bore the larger group (Me) in the endo position. Cation 68b similarly bears the larger group (-CHCl<sub>2</sub>-) in the endo position.

Akin to this reaction is the isomerization of cation 28 (page 16) to 2 isomeric products of which the one with the larger group endo appears in slight excess. One must remember however, when comparing systems of which only one has an intermediate thermal step that migration may not proceed with 100% inversion of configuration about the migrating center. If such is the case the final isomer ratio would not accurately reflect the initial photochemical closure.

An interesting side-light of the photochemical reaction is the apparent rate enhancement obtained with increasing temperature. Although only a highly qualitative mention of this aspect is possible at this stage further variable temperature studies would hopefully establish this point. Such a dependence would strongly support the existence of the proposed intermediate ground state reaction.

#### PART B PHOTOCHEMISTRY OF PROTONATED POLYMETHYL PHENOLS

The initial difficulty encountered in formulating a mechanism for the photochemical conversion of 3,4-dimethylphenol in FSO<sub>3</sub>H to its 3,5-dimethyl isomer led to an exploration of the nature of 3,4-dimethylphenol protonated at low temperatures. With the aid of both nmr and uv spectroscopy we have studied the protonation of not only the latter system but also other alkylated phenols. Results of this study and various photoisomerizations of protonated phenols are reported in the following pages.

#### B-1 Structure of Protonated 3,4-dimethylphenol

As phenols would be expected to protonate either ortho or para to the hydroxy function a suitable method was required which would differentiate these isomers. The electronic spectral properties of various cationic species have been reported<sup>22</sup> and although not as effective as nmr for structural assignments it has been quite helpful in some cases.<sup>16</sup> Fortunately the uv spectra of species such as 83 and 84 (figure 22) are quite distinct and suitable for characterization<sup>83</sup> (see page 63).

The low temperature  $(-85^{\circ})$  uv spectrum of protonated 3,4-dimethylphenol was obtained by disolving the phenol in cold  $(-78^{\circ})$  FSO<sub>2</sub>H. Observed absorption maxima at 361 nm

and 255 nm agreed very well with an ortho protonated structure. Distinction between isomers 76 and 85 however was not possible



by this method. Further investigation by low temperature  $(-50^{\circ})$  nmr supported ortho protonation and in particular, species 76; the chemical shifts are shown in table 3. The broadening of the lowest field proton was attributed to coupling with an adjacent methylene group possible in 76 but not 85. Moreover, closer examination of the spectrum revealed a small but discernable doublet at  $\mathcal{T}$  8.38 (J=7.5 cps) which is typical of the H-C-CH<sub>3</sub> moiety in the cyclohexadienyl cation.<sup>28</sup> The most likely structure seems to be 86. A small absorption at  $\mathcal{T}$  7.41 could account for the other methyl





86



nmr chemical shifts of 3,4-

dimethylphenol in FSO3H at -45°

Protonation	Ring H's	Methylene or	Methyl H's
Site		Methine H's	
A) 5% para 2.64	(m, J=10 cps)	unobserved	7.41
	others unobserved		8.38 (d, J=7.5 cps)
B) 95% ortho	2.67	5,80	7.33
•	2.93		7.76

FIGURE 23

3.0

nmr spectrum of 3,4-dimethylphenol in FSO<sub>3</sub>H at -45°

I

8.0

group. A very small and diffuse doublet at  $\tau$  2.64 (J=10 cps) is tentatively assigned to H<sup>2</sup> of 86 which is in good agreement with H<sup>7</sup> of 66. On this basis then a 5% concentration of 86 is proposed.

#### B ii Mechanism of 3,4-dimethylphenol Photoisomerization

Once the existence of the para protonated species was established the difficulty in proposing an acceptable mechanism was greatly diminished. The structural similarity of such a species and the 1-hydroxy-4,4-dimethyl benzenonium cation is striking. The structural analogy made quite attractive the possibility of  $C_3-C_5$  bond formation in cation 86 followed by cyclopropyl migration to 89 via 88 shown in figure 24. Photochemical opening of the protonated bicyclic ketone (89) followed by proton rearrangement would give the observed product 91.

The overall mechanism accounts nicely for the photoisomerization but there are several criticisms. Although the photo-cyclization of 86 to 87 is highly reasonable the following thermal step is not so sound. Indeed, migration of a cyclopropyl ring bearing hydrogen and methyl substituents at C<sub>6</sub> has been observed<sup>27</sup> but at a significantly higher temperature. For the endo-methyl-hexamethylbicyclo [3.1.0]hexenyl cation the reported free energy of activation for the sigmatropic rearrangement is 15.3 kcal/mol which corresponds to a half life of 10 hours at -80°. As the observed isomerization of cation 86 was significantly faster

Photolysis of 3,4-dimethylphenol in FSO<sub>3</sub>H at -60 FIGURE 24



 $(t_{1/2}=1 hr)$  the activation barrier must be much lower especially since 87 can also be expected to undergo a competative photo-reversion to 86. Such a decrease in the activation parameter is not unreasonable when one considers the relative allylic stabilization in cations 87 and 89. The former likely incurred a destabilization effect from the hydroxy group at the 2 position whereas the latter would have the combined stabilizing effect of both the hydroxy and the methyl at the 1 and 3 positions.

A second point of contention is the lack of definitive observation of the intermediate ketone 89. However, such a quest may be predisposed to failure for several reasons most important of which is the photo-lability of Of necessity cation 89 is excited during irradiation 89. of 86 so that accumulation of 89 will be minimal. Further reducing the chance of 89 accruing is the nature of the migrating center. If cation 88 represents the transition state for the transformation of 87 to 89 then the extent of methyl substitution at the migrating center should affect the rate; it being faster for a tertiary than a secondary carbonium ion. Thus the secondary center of cation 88 inherently migrates slower than the tertiary center of the 1-hydroxy-4,4-dimethylcyclohexadienyl cation for which the maximum bicyclic cation concentration observed was 10%.

A priori, cation 88 can undergo cyclopropyl migration in two directions of which the one leading to the observed

product appeared in figure 24. Migration in the other direction followed by photochemical ring opening leads to an overall degenerate reaction since the product is 3,4-dimethylphenol. Such a consideration poses the intriguing question of what factors, if any, control the course of such rearrangements.

#### B iii Structure of Various Polymethyl Phenols in FSO,H

Since it appeared that the photo-rearrangements of methylated phenols in FSO<sub>3</sub>H required the presence of a very particular structural entity (ie para protonation on a methyl bearing carbon) an investigation of the protonation site(s) of the polymethyl phenols appeared in order. Previous reports of phenol protonation studies<sup>88</sup> were few and since they were concerned with only the lower homologues further incentive was added to the study.

A similar technique was employed to obtain observations on all these systems. Low temperature ( $-50^{\circ}$ ) nmr studies followed the disolution of the particular phenol in cold ( $-78^{\circ}$ ) FSO<sub>H</sub>; table 4 records the protonation sites and nmr data thereby derived.

Several general conclusions about the relative basicities of various ring positions can be drawn. Most impressive was the high basicity of the unsubstituted para position relative to the corresponding ortho site (see the 2,3- and 2,4-dimethylphenols). The basicity of the para



Protonation site(s) and chemical shift data of polymethyl-

phenols in  $FSO_3H$  at -50

Phenol	Protonation Site	Ring H's	Methylene or Methine H's	Methyl H's
2,3-dimethyl-	100 % para	2.82 (d, J=9 cps) 1.74 (d, J=9 cps)	5.83	7.46 7.80
2,4-dimethyl-	A) 13 % para	obscurred by B	5,96	7.45 8.42 (d, J=7.5 cps)
	B) 87 % ortho	1.64 (bs) 2.80 (ss)	5,66	7.64 7.75
2,5-dimethyl-	100 % para	1.94 (bs) 2.93	5,93	7.43 7.77
2,6-dimethyl-	100 % para	1.68	5.83	7.67
3,4-dimethyl-	A) 5 % para	2.64 (m, J≅10 cps)	unobserved	7.41
· ·				8,38 (d, J=7,5 cps)
	B) 95 % ortho	2.67 (bs)	5,80	7.33 7.76
		2.93 (ss)		
3,5-dimethyl-	100 % para	3.06	6.01	7.48

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table 4 continued

Phenol	Protonation	Ring H's	Methylene or	Methyl H's
·	Site	з <b>с</b>	Methine H's	ę
2,3,4-trimethyl-	A) 23% para	1.74 (d, J=8 cps)	6.30 (m)	7.47
•				8.42 (d, J=7 cps)
				other obscurred
	B) 77% ortho	2,81	5,83	7.36, 7.75, 7.78
2,3,5-trimethyl-	100% para	3,02	5,98	6.53 (6H)
				6.74 (3H)
2,3,6-trimethyl-	100% para	1,98	5.89	7.75 (6H)
				7.47 (3H)
2,4,5-trimethyl-	A) 15% ortho	1.73	5,79	7.73 (3H)
		e e e e e e e e e e e e e e e e e e e		others obscurred
	B) 85% para	2.02 (bs)	6.30	7.51, 7.84
		3.02 (ss)	(d) 1=1.2 cbs)	8.47 (d, J=7.5 cps)
2,4,6-trimethyl-	A) 53% oxygen	2,98		7.65 (very broad)
	B) 47% para	1.79	6.12 (q, J=7 cps)	7.65 (very broad)
				8.45 (d, J=7.5 cps)

.

table 4 continued

	•			
Phenol	Protonation Site	Ring H's	Methylene or Methine H's	Methyl H'ş
3,4,5-trimethyl-	A) 60% ortho B) 40% para	3.12 3.12	5.84 6.32 (q, J=7.5 cps)	7.35, 7.62, 7.83 7.48 (6H) 8.37 (d, J=7.5 cps)
2,3,5,6-tetramethy	1- 100% para	erra dara dara tina	5,95	7.54, 7.80
2,3,4,6-tetramethy	1- 100% para	1.98	6.27 (m)	7.50, 7.73, 7.77 8.44 (d, J-7.5 cps)
pentamethy1-	100% para		6.38 (q, J=7.5 cps)	7.58, 7.84 8.48 (d, J=7.5 cps)

\* s-singlet, d-doublet, q-quartet, m-multiplet, bs-broad singlet, ss-sharp sinlet All chemical shifts reported in 7 values as measured relative to internal tetramethylammonium chloride

position bearing a methyl group exhibited such a basicity decrease relative to the unsubstituted site that the ortho position became competetive for the available proton (contrast 2,3- and 2.4-dimethylphenol). In line with the superior stabilizing effect of the hydroxy group relative to methyl was the apparent dearth of meta substitution.

Only 2,4,6-trimethylphenol protonated on the oxygen of the hydroxy function to any observable extent (47%). Such oxygen protonated species are characterized by high field ring protons and low field ring methyl groups with respect to those of ring protonated phenols. The former protons exhibited very similar nmr absorptions to those of protonated 2,4,6-trimethylanisole which protonates only on the oxygen. The exceptional behaviour of this phenol is attributable to the unique substitution pattern. Reduced basicity of the ortho and para sites, due to their methyl substitution, is compounded by a lack of such substitution at the meta positions which could stabilize any ortho or para protonated species. Such stabilization is afforded by the hydroxy group alone making the para position of 2,4,6-trimethylphenol much like that of para-cresol which protonates solely on oxygen. With such diminished ring basicity the weakly basic n-electrons of oxygen compete effectively with the para ring position for the proton.

#### B iv Photoisomerization of Various Protonated Phenols

Following the investigation of its structure in FSO<sub>3</sub>H each of the phenols was exposed to ultra-violet light at -80°. Only those exhibiting protonation of a methyl bearing carbon isomerized, thereby confirming the earlier suggestion that such proclivity necessitated this type of functionality. However, no protonation of an ortho methyl bearing carbon was detected. If it had the intermediate bicyclic material, if indeed such existed, could have been observed in a manner analogous to that of cation 64 derived from 62 (page 47).

Identification of the photo-product was, in most cases, effected by comparison with the nmr spectra of protonated authentic material obtained from the structural study. In the particular case of 2,4,6-trimethylphenol the isomeric phenol was isolated by quenching the cold acid solution in aqueous bicarbonate solution and extraction with ether. Separation by vpc (A)<sup>\*</sup> afforded a compound with the following characteristics. Mass sprectrum gave m/e=136 which is consistent with the mass of a trimethylphenol (136). An OH stretch of 3740 cm<sup>-1</sup> in the infared characterized the product as a phenol. nmr spectra with CCl<sub>4</sub> and FSO<sub>3</sub>H (-60°) were identical to those of authentic 2,3,5-trimethylphenol in these solvents.

\* For code see experimental section

Figure 25 outlines the results of these irradiations and depicts both the migrational mode leading to the observed product and the alternate hypothetical path when such is not degenerate. In each case the apparent isomerization involved transfer of a para methyl group to an unsubstituted meta position. Notably both 3,4,5-trimethylphenol and pentamethylphenol failed to isomerize despite their para protonation. By the proposed mechanism such a result would be predicted since the only possible reactions are degenerate.

In the case where cyclopropyl migration can theoretically occur in two different directions to give two unique products one is struck by the appearance of a single product. Such is the case for the 2,4-dimethylphenol. In this reaction the product phenol corresponds to the protonated bicyclic ketone intermediate with the greater stabilization of its allylic cation portion. That a single methyl group could so strongly direct the reaction course was very surprising, especially since the methyl group is in the 2 position where its affect would be minimal.

No change was observed for those phenols which protonated ortho or para at an unsubstituted position. Photo-closure likely occurs in these cases but the barrier to thermal migration of the primary carbonium ion (93) precludes such a step, thus allowing cation 92 to re-open

Photolysis of protonated polymethylphenols in FSO<sub>3</sub>H at -60<sup>e</sup>



\* continued on the following page

FIGURE

25













photochemically. Such a large migrational barrier has been reported for similar systems.<sup>27</sup>

#### B-V 2,4,6-trimethylphenol --- A Special Case

Not only was 2,4,6-trimethylphenol anomolous in that it exhibited oxygen protonation but it also photoisomerized to two products in contrast to the single observable product of the other phenols. This second product, at first thought to be the bicyclic intermediate of the phenol rearrangement to protonated 2,3,6-trimethylphenol, was shown to have the structure of 42. An infared spectral absorption at 1690 cm<sup>-1</sup>



42

characterized 42 as a bicyclo 3.1.0. hex-3-ene-2-one.

Consistent with this structure is the nmr spectrum with  $CS_2$ as solvent shown in table 5. The absorptions at  $\mathcal{T}$  9.15 and  $\mathcal{T}$  8.69 are assigned to the H<sup>A</sup> and H<sup>B</sup> hydrogens which are at low field compared to cyclopropane ( $\mathcal{T}$  9.78) because of the carbonyl deshielding effect. Reduction of the carbonyl group to the alcohol (page 29) shifted these signals to  $\mathcal{T}$  9.81 and  $\mathcal{T}$  9.59 which are in good agreeement with the cyclopropane model. The lowest field methyl group at  $\mathcal{T}$  8.44 appears as a doublet (J=1.3 cps) due to coupling with the vinyl proton (H<sup>C</sup>) at  $\mathcal{T}$  3.05 (J=1.3 cps).

Disolution of 42 in FSO<sub>3</sub>H at -78° yielded a pale yellow solution which had the nmr spectrum also shown in table 5. The vinyl proton ( $\gamma$  1.75) exhibited a downfield shift of 1.30 ppm relative to its position in the neutral molecule because of formal chage concentration on the 3 position of the allylic cation. As expected the methyl groups showed a significantly smaller shift. More interesting though are the very large downfield shifts of the cyclopropyl hydrogens which were 1.30 ppm for the endo (T 7.81) and 1.90 ppm for the exo (T 6.75) protons. These positions are very similar to those of the bicyclic cation 12 (page 23) which appear at  $\mathcal{T}$  7.40 and  $\mathcal{T}$  6.47. Thus the 2 methylene protons on C, are affected by the positive charge to a greater extent than the allylic hydrogen. This result supports the earlier contention that, in such systems, the cyclopropyl bonds are significantly delocalized.

TABLE 5

nmr chemical shifts of 1,3,5-trimethylbicyclo [3.1.0]hex-3-en-2-one (42) in CS<sub>2</sub> and FSO<sub>3</sub>H

Solvent	Vinyl H's and CH <sub>3</sub>	Bridgehead CH <sub>3</sub>	C <sub>6</sub> H⁵s
cs <sub>2</sub>	3.05 (1H, q, J=1.3 cps)	8.65 (3H, s)	8.69 (1H, d, J=3 cps)
	8.44 (3H, d, J=1.3 cps)	8.76 (3H, s)	9.15 (1H, d, J=3 cps)
FS0 <sub>3</sub> H	1.75 (1H, m, J 1 cps)	8.29 (3H, s)	6.75 (1H, d, J=4 cps)
-40°	8.18 (3H, d, J=1 cps)	8.32 (3H, s)	7.81 (1H, d, J=4 cps)

A 2 mg sample of 42 obtained by preparative vpc (A) was analysed by high resolution mass spectrometry. A computer technique (see experimental section) was employed to determine precisely the molecular weights and calculate the difference between the theoretical and found weights. Excellent agreement was obtained for the parent peak P  $C_{9}H_{12}O$  (observed mass 136.0891429, calculated mass 136.0888093 error .00035), P-1  $C_{9}H_{11}O$  (obs. mass 135.0815692, calc. mass 135.0809847, error .00033), P+1  $C_{8}^{13}C_{1}H_{12}O$  (obs. mass 137.0927967, calc. mass 137.0921647, error .00063).

The nmr spectrum of 42 in FSO H appeared identical to that of the observed photo-product. Moreover, irradiation or 42 in this solvent  $(-30^{\circ}, \lambda)$  340 nm) quickly established a photostationary state consisting of 2,4,6-trimethylphenol and 42 in a ratio similar to that obtained by irradiating the phenol alone under the same conditions.<sup>\*</sup> The maximum observed conversion was 43% of total material with  $\lambda > 360$  nm.

Individual low temperature uv spectra in FSO<sub>3</sub>H were obtained for both 2,4,6-trimethyl and ketone 42. The latter exhibited a broadened peak at 351 nm which gradually trailed off to  $\lambda \cong 450$  nm and a much sharper peak at 253 nm. Comparison with the hydroxy-hexamethyl [3.1.0.] hexenyl cation gave good agreement in general shape but the long

\*This ratio is highly dependent on the light source and even the extent to which the particular lamp has been used. wavelength absorption of 42 (351 nm) was at a somewhat lower energy than that of the model cation (340 nm).

Of the several maxima exhibited by 2,4,6-trimethylphenol the most outstanding despite its lack of intensity was that at 385 nm. Such a low energy transition is quite similar to that exhibited by protonated mesitylene ( $\lambda^{max} = 390 \text{ nm}$ )<sup>26</sup> which suggested meta protonation of the phenol had occurred to a small extent. Chloro-mesitylene, which is known to protonate in the meta position,<sup>89</sup> was selected as a second model compound to discover if an electronegative substituent would significantly alter the absorption spectrum. Disolved in FSO<sub>H</sub> chloro-mesitylene gave a low temperature uv spectrum with maxima at 381 nm and 271 nm which suggested such substitution had little affect

These factors in combination with the demonstrated structure of 42 suggested that protonated 42 arose from the photo-induced electrocyclic closure of the meta protonated form of 2,4,6-trimethylphenol. Although such protonation of a phenol has previously escaped detection the methyl substitution pattern of this particular phenol makes it the one most likely to do so. With the same arguments outlined earlier to account for the increase in basicity of the oxygen n electrons relative to the para ring carbon one can appreciate the similar increase in relative basicity of the meta position.

# B-Vi Interaction of Phenols and SbF<sub>5</sub> in FSO<sub>3</sub>H

If meta protonation did indeed occur then an increase in medium acidity would be expected to increase the relative proportion of such a species since the medium would become less discriminating in which site was protonated. Since the addition of  $SbF_5$  to  $FSO_3H$  enhances acidity<sup>90</sup> low temperature uv and nmr spectra were obtained with an  $SbF_5/FSO_3H$ (v/v--1/5) system. The change in the nmr spectrum was far greater than anticipated as it suggested only species 94 existed in this medium. Such a result however seemed





95

96

94

inconsistent with a simple increase in acidity as a mixture of protonated species was expected. More appealing was 95 which engenders strong interaction between the phenol oxygen and Lewis acid  $(SbF_5)$ . Such co-ordination would greatly reduce the 'electron donating' potential of the oxygen and allow the remaining methyl groups to control the protonation site. Such a result is guite similar to observations made recently by Childs.<sup>81</sup> In FSO<sub>3</sub>H containing 30% SO<sub>3</sub> both the hexamethylcyclohexadienones form only a single species 97.



97

Co-ordination of SO<sub>3</sub> with the hydroxy group inhibited its directing effect to such an extent that the position of the sixth methyl group was determined by the remaining methyls.

B vii Interaction of SbF<sub>5</sub> and the Hexamethylcyclohexadienones

To investigate the complexing power of  $\text{SbF}_5$  the two hexamethylcyclohexadienones <sup>78</sup> were disolved in solutions of  $\text{SbF}_5/\text{SO}_2$ . Preliminary results suggest that a similar situation occurs with  $\text{SbF}_5$  as with  $\text{SO}_3$  since a small concentration of 98 was observed (identified by its nmr spectral similarity to 97).



However, the interaction is by no means simple as various concentrations of 98 were found depending on temperature of complexation and other factors. Further work is required before definitive results will be available.

### B VILL Observation of the Bicyclic Intermediate in the 2,4,5-trimethylphenol Fhotoisomerization

During the course of the irradiation of 2,4,5-trimethylphenol in FSO<sub>A</sub> several small peaks (~2%) were noted in the nmr spectrum. That these appeared at the positions expected for peaks of the bicyclic intermediate led to the expectation that under suitable irradiation conditions the intermediate might be increased to concentrations high enough to suitably characterize it. Figure 26 simulates and superimposes the low temperature uv absorptions of the para protonated form of the reactant phenol and hypothesized bicyclic intermediate in the former's photo-rearrangement to 2,3,5-trimethylphenol. If the long wavelength absorption of the reactant ( $\lambda$  = 300 nm) could be irradiated without appreciably affecting the similar absorption of the bicyclic intermediate ( $\lambda$ =340 nm) then the latter should accumulate to a level which would allow observation.

In this pursuit 2,4,5-trimethylphenol, disolved in FSO H at  $-78^{\circ}$ , was irradiated at  $-70^{\circ}$  with a narrow wavelength band of light (~30 nm) centered at 300 nm obtained from a Bausch and Lomb grating monochromator (lamp D). Low temperature nmr spectra showed an accumulated product (~40%) which was not the 2,3,5-trimethylphenol observed in earlier experiments. (a 15-20% concentration of this



phenol was also noted after 18 hours irradiation). Of particular interest were the high field absorptions at **7**8.30 and **7**8.56. The former appears as a doublet with  $J^{AB} = 6.6$  cps while the latter is a doublet of doublets with  $J^{AB} = 6.6$  cps and  $J^{BC} = 1.1$  cps. That these absorptions are characteristic of cyclopropyl methyl groups can be seen by comparison with the exo and endo methyls of the 1-hydroxy-6,6-dimethylbicyclo [3.1.0] hexenyl cation (77-page 56) which appear at **7**8.33 and **7**8.55 respectively. The doublet nature of these absorptions suggests that they are coupled with a proton. These results alone suggest that perhaps two stereoisomeric intermediates, 99 and 100, occurred in approximately equal amounts. A secondary



99

100

coupling of the endo methyl of 99 with  $H^C$  tentatively accounts for the doublet of doublets nature of the  $\tau$  8.56 absorption. Further evidence for this was obtained from an nmr decoupling experiment. Irradiation of a small peak at  $\Upsilon$  6.65 destroyed the secondary coupling (J= 1.1 cps). That this absorption represents the H<sup>C</sup> proton is supported by anology with the similarly located proton in cation 77 which absorbs at  $\Upsilon$  6.48.

A sharp singlet at 78.11 is indicative of a bridgehead methyl group and compares favourably with a similar methyl group at 78.29 found in the product of 2,4,6-trimethylphenol photolysis in FSO<sub>3</sub>H.

A downfield absorption at  $\tau$  3.85 can be argued to represent the H<sup>D</sup> proton.

Quenching of this solution in the usual manner afforded a product mixture which was analysed by nmr with CCl as solvent. The following methyl absorptions were  $_4$  observed:  $\Upsilon$  8.41 (d, J= 1.4 cps),  $\Upsilon$  8.60 (s),  $\Upsilon$ 8.68 (s). From table 5 (page 85) it can be seen that the 8.41 absorption above compares well with that of the vinyl methyl  $\Upsilon$ 8.44 (d, J= 1.3 cps) therein. Although the peaks at  $\Upsilon$ 8.60 and  $\Upsilon$ 8.68 appear at positions typical of bridgehead methyls the ratios defy interpretation in terms of the two isomers.

vpc analysis (col A) indicated that the product mixture consisted of at least 4 compounds. The first 3 which came off much sooner than the phenols had retention times very similar to 1,3,5-trimethylbicyclo [3.1.0.] hex-3-en-2-one and appeared in an approximate 1/9/9 ratio. Collection of the latter two (1/1 ratio) gave sufficient material for an ir analysis which showed a strong carbonyl absorption at 1690 cm<sup>-1</sup> which characterized them as bicyclo-[3.1.0] hex-3-en-2-ones.

This preliminary work led to the conclusion that bicyclic 3.1.0, hex-3-en-2-ones are photochemically derived from 2,4,5-trimethylphenol in FSO<sub>3</sub>H and that these are indeed the intermediates promulgated for the over-all photochemical conversion to 2,3,5-trimethylphenol. To establish that these compounds are actually intermediates requires irradiating the isolated materials in FSO<sub>3</sub>H and demonstrating that they lead to 2,3,5-trimethylphenol.

Both nmr and vpc analysis suggest that the endo and exo methyl isomers are present in approximately equal amounts. This result was unexpected since the hexamethyl benzenonium cation photoisomerizes to a single bicyclic product. Moreover, Koptyug has also shown that the larger group preferentially appears in the endo position. If indeed these results have been correctly interpreted they provide the first example of cyclohexadienyl cation photo-cyclization which proceeds with no apparent regard for product stereochemistry. However we must exercise restraint in accepting such a precarious conclusion at this stage.

#### EXPERIMENTAL

#### SYNTHESIS AND PREPARATIONS

#### A) <u>Pentamethylphenol</u>

Following the method of Francis<sup>91</sup> 1-nitro-2,3,4,5,6pentamethylbenzene was prepared by the action of benzoyl nitrate on pentamethylbenzene. Standard reduction of the nitro group with  $SnCl_2/HCl$  afforded the tin double-salt of the corresponding amine which was subsequently decomposed by bubbling H<sub>2</sub>S through its aqueous solution. The resulting white salt was reacted in the usual manner with  $NaNO_2$  in dilute aqueous sulphuric acid to give a white solid with mp 123°-124° (pentamethylphenol mp 125°)<sup>91</sup>

#### B) 2,4,6-trimethylanisole

This compound was prepared by Dr. R.F.Childs in the following manner. Approximately 10 g of 2,4,6-trimethylphenol were disolved in an aqueous solution of NaOH (slight molar excess). To this was slowly added a similar excess of dimethylsulphate. Ether extraction of this solution followed by solvent removal and vacuum distillation afforded about 8 g of 2,4,6-trimethylanisole.

C) 2,3,4-trimethylphenol

2,3-dimethylphenol was converted to **its** methyl ether as described for 2,4,6-trimethylphenol. This was then converted to the 2,3,4-trimethylphenol by published procedures.<sup>92</sup>
# D) Chloro-mesitylene (1-chloro-2,4,6-trimethylbenzene)

Chloro-mesitylene was prepared from 1-amino-2,4,6trimethylbenzene via the Sandmeyer reaction. Interestingly the diazonium-cupric chloride complex did not decompose until heated to 55.

# E) 2-hydroxy-1,2,3,5-tetramethylbicyclo 3.1.0. hex-3-ene

20 mg of 1,3,5-trimethylbicyclo[3.1.0] hex-3-en-2-one were added to a 10 fold excess of methyl magnesium iodide (in dry ether) obtained by reacting 48 mg of magnesium with a 2 fold excess of methyl iodide under a nitrogen atmosphere. After several hours, addition of a saturated aqueous solution of ammonium chloride caused a gaseous evolution. Following salt disolution more ether was added and this layer drown off,dried with anhydrous magnesium sulphate, filtered and evaporated to give the strong smelling alcohol (about 12 mg).

# F) Deuterated Fluorosulphonic Acid (FSO,D)

Two equivalents (1 mol) of deuterosulphuric acid  $(D_2SO_4)$  were added to 1 g of potassium fluorosulphate (KFSO<sub>3</sub>). Bulb to bulb distillation under vacuum of the magnetically stirred and heated (159°) mixture effected a slow transfer of FSO<sub>3</sub>D. A few small solid particles, assumed to be  $D_2SO_4$ , were detected in the receptacle liquid upon cooling to  $-78^\circ$ .

## G) 2,3,4,6-tetramethylphenol

l g of isodurene (contaminated with durene) was reacted at 0° with fuming sulphuric acid. Neutralization with NaOH followed by evaporation of water yielded a slightly water soluble sodium salt. Addition to molten KOH, contained in a **a** nickel crucible, accompanied by continued stirring and prolonged heating gave a white solid upon dilution of the pot mixture in water and neutralization with HCL. Ether extraction followed by MgSO<sub>4</sub> drying and solvent removal afforded the desired product contaminated with the expected amount of 1-hydroxy-2,3,5,6-tetramethylbenzene.

This method was inneffective in preparing pentamethylphenol from pentamethylbenzene.

## H) 4,4-dimethylcyclohexa-2,5-dienone

4,4-dimethylcyclohex-2-enone was prepared by Miss T.K. Ho from the condensation of isobutyraldehyde and methyl vinyl ketone. This compound was disolved along with an equi-molar amount of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (D.D.Q.) in a minimum volume of benzene which was then refluxed for 30 hours. Several partionings of the reaction mixture between aqueous base and benzene removed the phenolic products. Drying of the benzene layer followed by solvent evaporation gave the 4,4-dimethylcyclohexa-2,5-dienone.

### I) 6,6-dimethylcyclohexa-2,4-dienone

One mole of freshly distilled cyclopentadiene was

disolved in 1 mole of acetone and slowly added to 24 g of sodium disolved in 300 ml of absolute ethanol at such a rate that the temperature never exceeded 40°. Steam distillation of the product gave the yellowish-orange 6,6-dimethylfulvene which was then converted to the desired cyclohexadienone by established procedures.

# J) <u>Preparation of Fluorosulphonic Acid (FSO<sub>3</sub>H)</u>

Fluorosulphonic acid was obtained in 28 oz bottles from Allied Chemical. Preceding the distillation of the acid was addition of about 1 g of NaF which combines with any sulphur trioxide which is present. The crude acid was distilled through a 10 inch Vigreaux column and collected in a round bottom flask. To prevent excess atmospheric water entering a CaCl<sub>2</sub> drying tube was added. From a 125 ml batch distillation only the middle 75 mls were kept and preserved in sealed glass ampoules each containing enough acid for 1 or 2 protonations.

# K) Preparation of Antimony Pentafluoride (SbF<sub>5</sub>)

Crude  $SbF_5$  was obtained from the Ozark-Mahoning Co. in a 2 lb metal cylinder. The blue syrupy liquid was subjected to distillation in a manner similar to  $FSO_3H$ . Generally the  $SbF_5$  was used immediately after distillation with no special precautions taken to exclude moisture despite its deliquescent properties. Criteria of purity are the viscosity and transparency of the liquid. When kept for extended periods white, chunky particles of dihydrate consistently formed even though initially the high viscosity indicated relatively high purity.

#### GENERAL TECHNIQUES AND PROCEDURES

#### L) <u>A Typical Carbonium Ion Preparation</u>

To a clean, dry nmr tube was added the desired amount of carbonium ion precursor (ie--a phenol or cyclohexadienone). Both the nmr tube and an opened ampoule of fluorosulphonic acid were then cooled in a dry ice-acetone bath (-79°). The thin-walled capillary dropper used for introducing the acid to the nmr tube was cooled by alternately withdrawing the cold FSO<sub>2</sub>H from the ampoule into the dropper and expelling it back into the ampoule. After several repetitions the acid was introduced to the cold nmr tube by slow expulsion onto the walls. Manual stirring with a thin (~2 mm) glass rod completed the disolution. In cases where the cation stability was low the glass rod was previously cooled in liquid nitrogen and very rapidly plunged from the latter into the acid solution. During this procedure water is invariably introduced. With materials very slow to disolve in the acid slight warming of the nmr tube with the finger-tips aided this process considerably.

# M) Quenching of Cations

An effective mode of quenching cations was the rapid addition of the nmr tube contents to a cold (-78°) rapidly stirred mixture of ether and potassium carbonate contained in a small round-bottomed flask. Washings from the nmr tubes, obtained by slow introduction of cold (-78°) ether, were added to the former solution. Water was then added to the cold ether and stirring maintained as the flask was allowed to warm to room temperature. Various products of the quench were then separated by vpc.

## N) Vapour Phase Chromatography (vpc)

Although generally used for separating various quench products this technique was also employed to prepare pure samples of synthesized materials. The machine used was an Aerograph model A-700 in conjunction with the followin columns:

- (A) 10' x 1/4" (copper) 20% carbowax on chromosorb 60/80
- (B) 10' a 1/4" (copper) 15% carbowax, 5% KOH on chromosorb 60/80

#### 0) Nuclear Magnetic Reonance (nmr)

Routine analysis of compounds was carried out on Varian machines-models T-60 and A-60. The latter was equipped with a variable temperature probe with a practical range of  $-80^{\circ}$  to  $+200^{\circ}$ . This facility was usually employed to observe cations in the range  $-80^{\circ}$  to  $-40^{\circ}$  but also used to perform kinetic runs on cation rearrangements occurring at somewhat higher temperatures. Probe temperature was determined with a methanol sample by utilizing the temperature dependance of the hydroxyl and methyl proton chemical shifts. Regarding kinetic runs the temperature variability, according to specifications was  $\pm 2^{\circ}$ , but in reality was found to be somewhat less reliable in that a constant temperature was occasionally maintained for extended periods but sometimes a drift of  $3-4^{\circ}$ was noted. Thus the temperature was determined prior to and immediately after each kinetic run. Nevertheless only an average temperature is known as a temperature gradient of several degrees exists between the top and bottom of the sample.

More refined work involving greater resolution and decoupling was performed on a Varian model HA-100 also equipped with a variable temperature probe.

#### P) Mass Spectroscopy

All but one spectrum were obtained from a Perkin-Elmer Hitachi RMU-6A mass spectrometer. For the precise mass determination of 1,3,5-trimethylbicyclo [3.1.0] hex-3-en-2-one a Consolidated Electrodynamics Corporation model 21-110 high reolution, double focusing mass spectrometer was employed.

Interpretation of the latter spectrum was performed with the aid of the HIREZ program<sup>94</sup> modified at M<sup>C</sup>Master University by R.K. Shepard, L. Baczynskyj, and T.I. Martin.

## Q) Infrared Spectrometry (ir)

All infared spectra were obtained from a Perkin-Elmer model 337 grating infrared spectrophotometer using cells of  $\sim 5$  mm path length. Carbon tetrachloride was used as solvent to prepare the approximately 10% solutions.

## R) Ultraviolet Spectrometry (uv)

Low temperature uv spectra were obtained from a Cary model 14 recording spectrophotometer using 1 cm quartz cells. To reach low temperatures ( $\sim -75^{\circ}$ ) a special quartz dewar was employed. This dewar had 4 flat quartz windows to pass the analysing beam and a circular opening at the top in which a cork stopper, bearing a nitrogen lead and gas exit, was secured. A variable voltage heater in a large dewar boiled off liquid nitrogen which was conducted to the cell-bearing dewar. A thermocouple served to monitor temperature.

Solutions were prepared by crudely weighing or estimating an appropriate amount of the compound in the cell which was then cooled in a dry ice-methanol bath  $(-78^{\circ})$ . FSO<sub>3</sub>H (or FSO<sub>3</sub>H/SbF<sub>5</sub>) previously cooled to this temperature was then added and stirred with a cold glass rod. A cork platform with a wire suspension served both to lower the chilled cell into the cold dewar and maintain the cell in a suitable position during analysis.

S) Irradiation of Cations---Light Sources and Systems

All irradiations were carried out in clear, thin-walled nmr tubes which cut off light with  $\lambda < 255$  nm. Light sources used for various experiments follow:

(A) Phillips SP-500 high pressure Hg light source

(B) Bausch and Lomb HP-100 low pressure Hg lamp

(C) Toshiba 125 watt low pressure Hg light source

(D) Bausch and Lomb SP-200 high pressure lamp
 (D) was used in conjunction with a Bausch and Lomb monochromator
 (grating 2700 grooves/mm). Figure 26 depicts the SP-500 lamp
 and accompanying light shield as well as the light collimating
 and sample cooling systems.

Light from lamps A,B and D was focused on the sample by means of a cylindrical quartz lens of 5.08 cm focal length. For B a collimator lens of 2.54 cm focal length was employed while a highly polished aluminum tube and a glass tube with an aluminum foil coating were used for A and D respectively. An aluminum foil shroud surrounded both lamp C and sample during irradiation.

Filters (5 cm x 5 cm) were employed with lamps A and B. For A these were placed in an aluminum water-cooled filter box equipped with quartz windows (figure 26). A pyrex sleeve when placed around lamp C served as a crude filter.

T) Sample Cooling System

A quartz dewar (see figure 26) was inserted in a 2-holed rubber stopper which fitted snugly in the mouth of a 2 gallon dewar. A thermistor was suspended in the gas stream several centimeters below the bottom of the sample tube. This resistance was balanced against a variable resistor which



# Key to Figure 27

A	Phillips SP-500 high pressure mercury light source
B	Polished aluminum collimator
С	Quartz windows
D	Cylindrical lens
E	Quartz dewar
F	Cover plates to contain stray light
G	Water cooled filter box
H	Water cooling
I	Transformer
J	Temperature regulator (see text for brief description)
K	Two gallon dewar
L	Shutter (copper)
M	Thin-walled nmr tube containing sample
N	Cork insulation

in turn was connected to 250 watt heater immersed in the liquid nitrogen of the 2 gallon dewer. Imbalance of the two resistances, caused by an increase in the thermistor temperature, initiated a heater current which boiled off liquid nitrogen to cool the thermistor (and indirectly the sample) until the resistance balance was re-established. Thus temperatures in the range  $-120^{\circ}$  to  $-40^{\circ}$  were attained. However, irradiation of the sample increased its temperature by as much as  $50^{\circ}$ with lamps A and C so that temperature settings had to be correspondingly lowered.

To keep the surface of the quartz dewar clear of condensed water vapour a stream of compressed air was played over its surface.

Sources of Commercial Chemicals

Chemical	<u>Source</u> *
1,3,5-trimethylbenzene (mesitylene)	D
1,2,4,5-tetramethylbenzene (durene)	D
pentamethylbenzene	D
1,2,3,5-tetramethylbenzene (isodurene)	с
1,2,3,4-tetramethylbenzene (prehnitene)	A
1-amino-2,4,6-trimethylbenzene (mesidine)	в
2,3-dimethylphenol	A
2,4- "	в
2,5- "	A
2,6- "	E
3,4- "	F
3 <b>5 –</b> "	E
2,3,5-trimethylphenol	A
2,3,6- "	В
2,4,5- "	A
2,4,6- "	В
3,4,5- "	A
2,3,5,6-tetramethylphenol	B
potassium fluorosulphonate	С
sulphuric acid-d <sub>2</sub> (99 Atom% D)	G
diethylene glycol	I
phosphorous oxychloride	J
N,N-dimethyl formamide	I

continued on next page

# <u>Chemical</u> carbon tetrachloride carbon disulphide diethyl ether

- \* A -- Baker
  - B --- Aldrich

C --- Pfaltz and Bauer

- D -- Eastman Kodak
- E -- British Drug Houses
- F --- Matheson, Coleman and Bell
- G -- Merck Sharp and Dohme
- H --- Mallinckrodt
- I -- Eastman Chemical
- J -- Fisher Scientific
- L -- Allied Chemical

Source \*

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