

A STUDY OF ANALOGY IN 3,7,7-TRIMETHYLCYCLOHEPTATRIENE  
REACTIONS BY ELECTRON IMPACT, THERMAL AND PHOTOCHEMICAL MEANS

by

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## TABLE OF CONTENT

INTRODUCTION.....	1
REVIEW OF LITERATURE.....	2
Photochemical and Thermal Analogies to Mass Spectral Reactions....	2
Selective Rules for Thermal and Photochemical Reactions.....	6
Semiquantitative Theory for Reactions Induced by Electron Impact....	8
A New Test for Selection Rules Applied to Electron Impact Induced Reactions.....	12
3,7,7-Trimethylcycloheptatriene as a Further Test.....	13
Photolysis of 3,7,7-Trimethylcycloheptatriene.....	13
Pyrolysis of 3,7,7-Trimethylcycloheptatriene.....	16
Parameters in Qualitative Analogies.....	19
EXPERIMENTAL.....	21
Preparation of 3,7,7-Trimethylcycloheptatriene.....	21
Photolysis of 3,7,7-Trimethylcycloheptatriene.....	21
Pyrolysis of 3,7,7-Trimethylcycloheptatriene.....	21
Mass Spectral Measurements.....	22
RESULTS AND DISCUSSIONS.....	24
Mass Spectra.....	24
Clastrograms.....	33
Energetics.....	41
CONCLUSIONS.....	50
REFERENCES.....	55
ACKNOWLEDGMENT.....	57

## INTRODUCTION

There have been many studies on the analogy of organic reactions induced by electron impact in the mass spectrometer to those using heat or light as the source of energy. The thermal and photochemical reactions are readily studied because they can be observed and the products can be easily isolated and identified. This is not so with reactions in the mass spectrometer. The reaction time scale is so fast compared to the conventional experimental time scale and the ionic products formed with excess energy is in such small quantities that it is impossible under usual conditions to trap any of the products or intermediates for observation. The analysis of the reactions is based solely on the comparative interpretation of the mass spectra with those from other known reactions and on the energetics of the different fragments formed upon electron impact. It is, therefore, interesting to study analogous reactions by electron impact, thermal and photochemical means.

Statistical Theory<sup>1</sup> assumes that the molecular ion is initially equilibrated to an energized state before reactions take place in the mass spectrometer (eq. 1).



where M is the molecular ion

$M^*$  is the energized molecular ion

$M^+$  is the complex transition state of the reaction

The energized molecular ion can be one with a highly excited electronic and vibrational state or one which has undergone a radiationless decay to a hot ground state (vibrationally excited and electronically unexcited). The former type might correspond to a first excited state in photochemical reactions while the second type will correspond to a ground state thermal reaction.

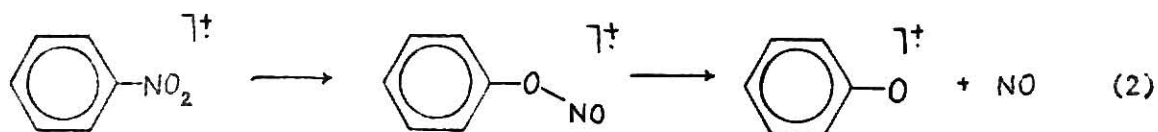
This research attempts to examine the direction of analogy (photochemical

or thermal) for the reactions of 3,7,7-trimethylcycloheptatriene under electron impact with Woodward-Hoffman products.

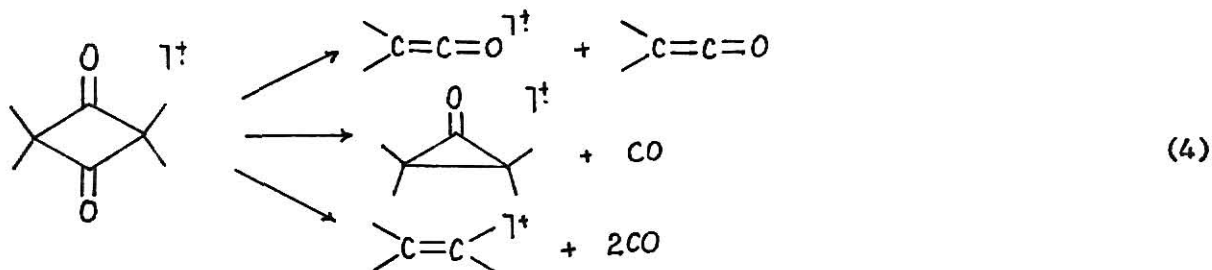
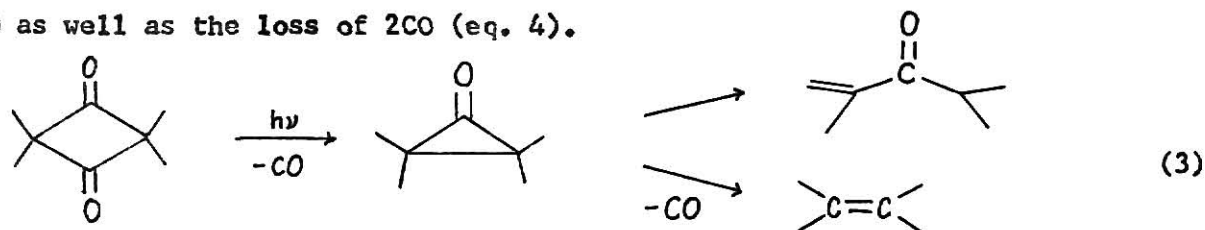
## REVIEW OF LITERATURE

### Photochemical or Thermal Analogies To Mass Spectral Reactions

Many different types of photochemical analogies to mass spectral reactions have been observed. Some of the more interesting studies includes the isomerization of the nitro group to the nitrite group. Beynon<sup>2</sup> et al. found that upon electron impact nitrobenzene loses NO from the molecular ion (eq. 2). This has been explained by the rearrangement of the nitro-group. A similar photochemical reaction was observed by Chapman et al.<sup>3</sup>

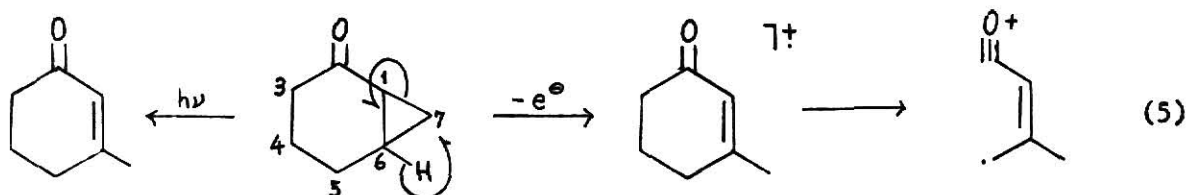


Dimethyl ketene dimer<sup>4</sup> losses CO under the influence of light to give cyclopropyl ketone. The cyclopropyl ketone has been observed to either rearrange to an allyl ketone or losses another CO to form 2,3-dimethyl-2-butene (eq.3). The mass spectrum of dimethyl ketene gives fragments for the loss of CO as well as the loss of 2CO (eq. 4).



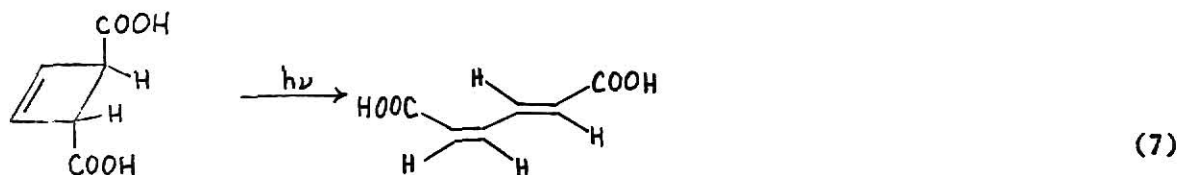
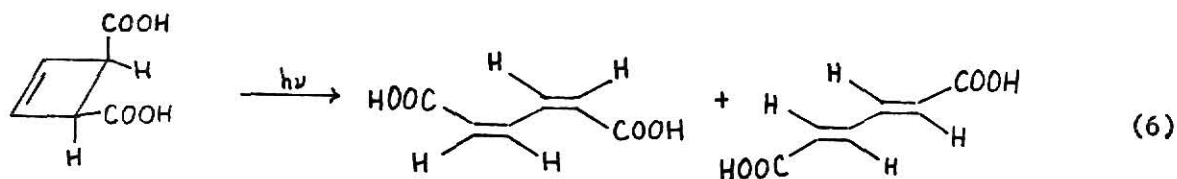


A more recent photochemical analogy has been observed for the bicyclo-[4.1.0]-heptane-2-one leads to 3-methyl-2-cyclohexenone via rearrangement. The mass spectrum of 3-methyl-2-cyclohexenone gives a major fragment at  $m/e=82$ ,

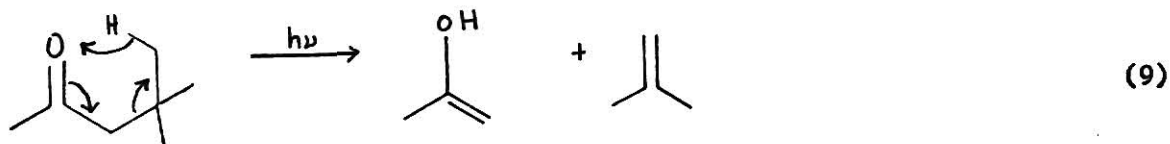
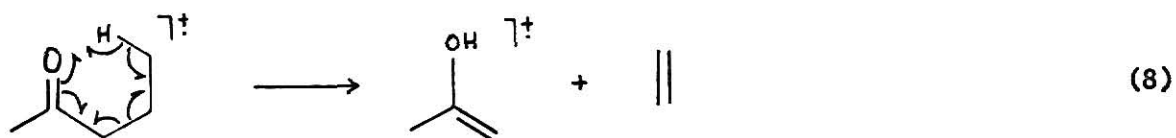


which is a retro Diels-Alder product. The fact that the bicyclo-[4.1.0]-heptane-2-ones under electron impact also give the same retro Diels-Alder fragment, except in the case when there is no 6-H available for transfer, indicates that a similar rearrangement must have taken place as well. It is also noted in this study that electron impact induced rearrangements with photochemical analogies will be prominent in the low-ev spectrum because it is a low-energy process.

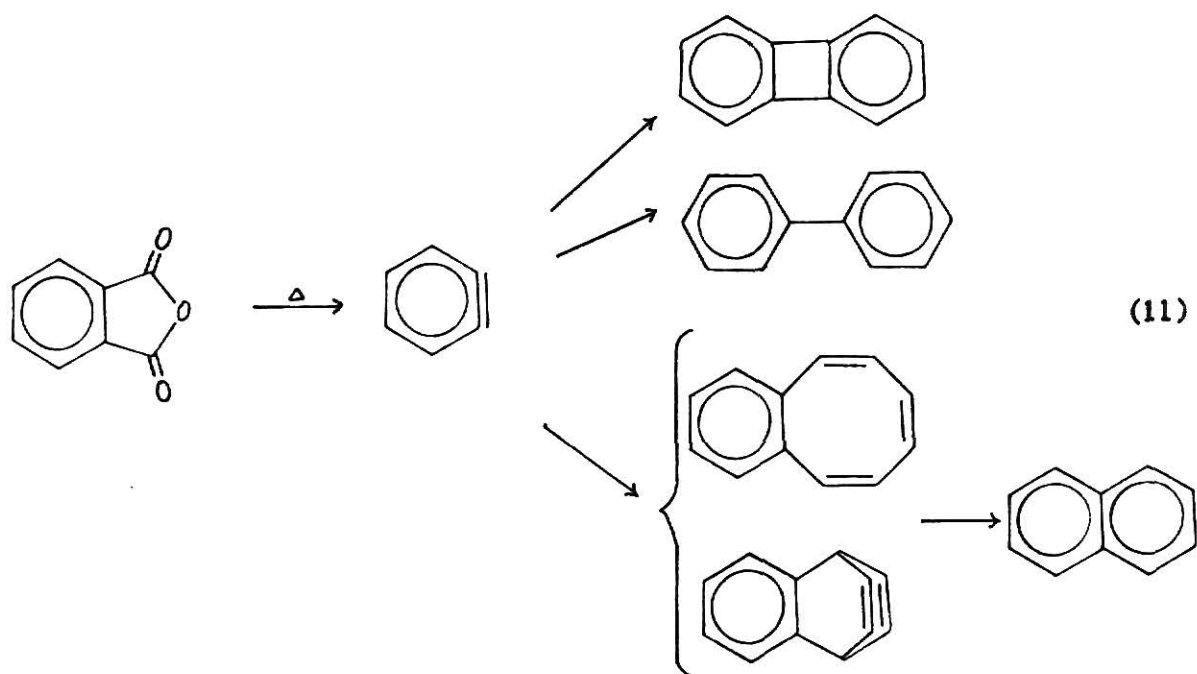
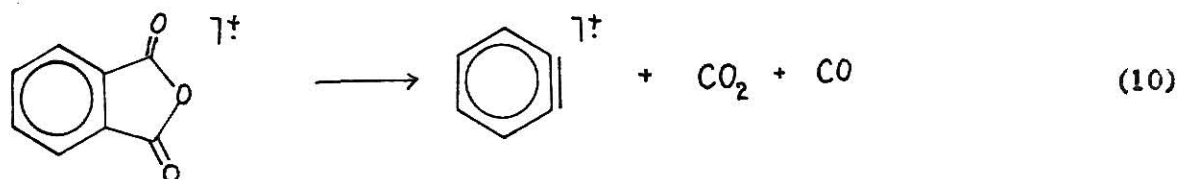
When the low-ev spectra of cis- and trans-3,4-cyclobutene-dicarboxylic acids and their muconic acid isomers were compared,<sup>6</sup> it was found that the isomers resulting from the photochemical rearrangement gave similar spectra. The cis-3,4-cyclobutene-dicarboxylic acid reaction induced by electron impact in the mass spectrometer is more like the cis, cis-muconic acid and the trans, trans-muconic acid, while the trans-3,4-cyclobutene-dicarboxylic acid resembles the trans, cis-muconic acid (eq. 6,7).



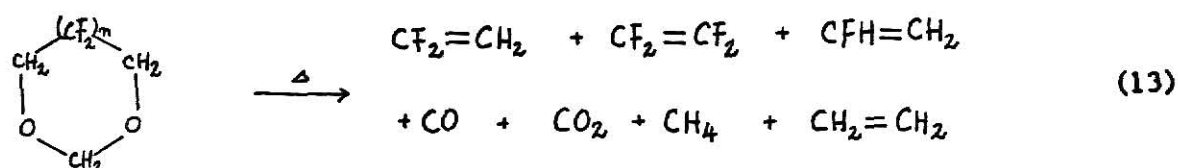
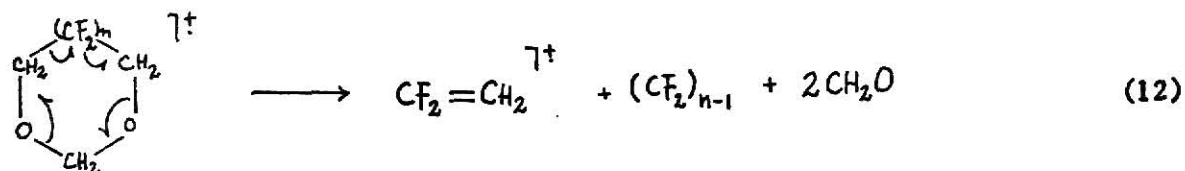
A very common rearrangement process found in aliphatic ketones is the McLafferty rearrangement<sup>7</sup> (eq. 8). Its photochemical analog, the Norrish Type II rearrangement<sup>8</sup> (eq. 9) is likewise a very common process.



Thermal analogy<sup>9</sup> has been found in the electron impact reaction of phthalic anhydride in the formation of an ion at  $m/e = 76$ , which is presumed to be similar in structure to benzyne (eq. 10, 11).

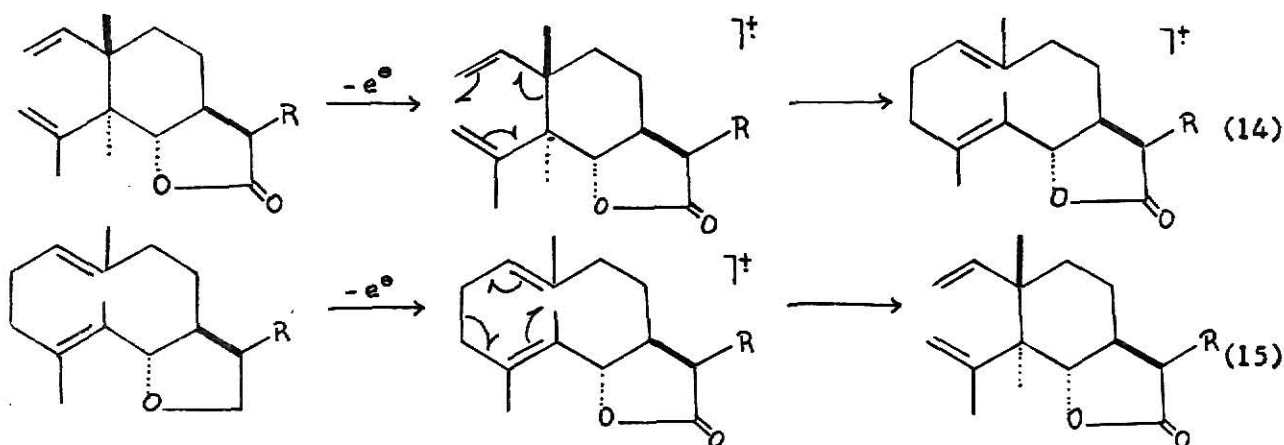


Cyclic fluoroethers have also been found to fragment by similar pathways upon electron impact or heating to give rise to difluoroethylene as one of the fragments<sup>10</sup>(eq. 12, 13).

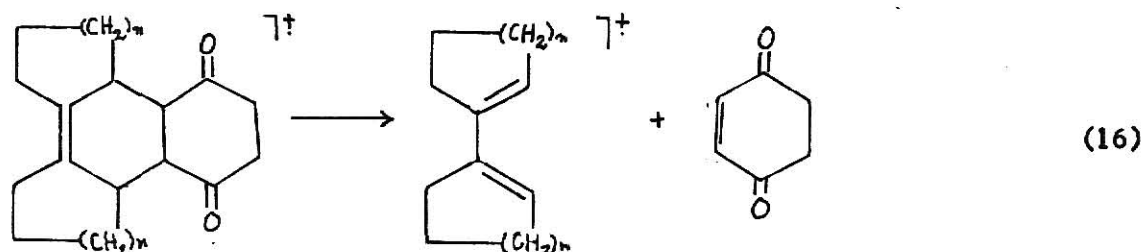


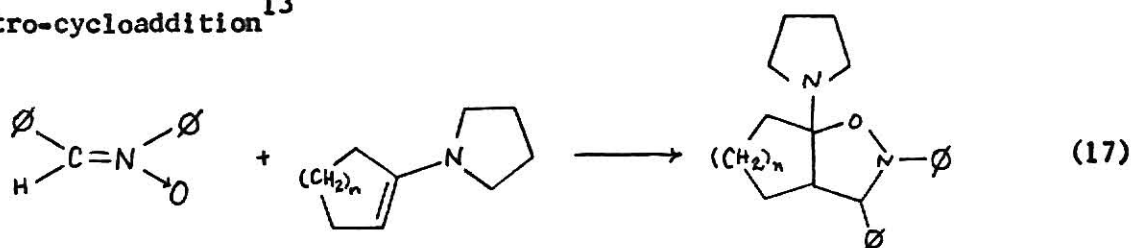
Some commonly observed reactions, such as the Cope rearrangement<sup>11</sup>(eq. 14,15), the retro Diels-Alder reaction<sup>12</sup>(eq. 16), and the retrocycloaddition reaction<sup>13</sup>(eq. 17), under thermal conditions are also found in the mass spectrometer.

#### Cope Rearrangement<sup>11</sup>



#### Retro Diels-Alder<sup>12</sup>

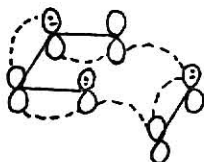


Retro-cycloaddition<sup>13</sup>

The mass spectrum of the product represented in eq. 17 is the same as that of the starting materials, indicating that rearrangement occurred prior to the ionization. It is possible that this particular reaction took place on the walls of the instrument, and is not a true mass spectral decomposition.

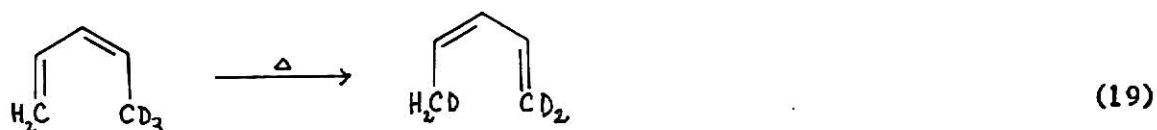
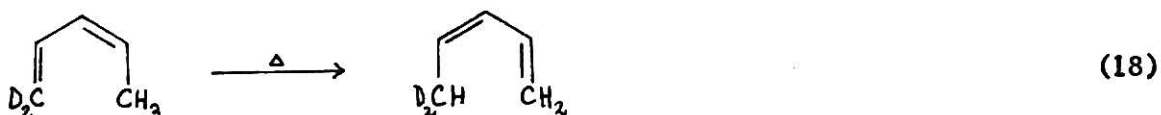
Selection Rules for Thermal and Photochemical Reactions

Woodward-Hoffman's selection rules<sup>14,15</sup> have been useful in explaining many thermal and photochemical reactions, especially those of pericyclic compounds. The concept of the selection rules to decide whether a compound will proceed to react photochemically or thermally is based on the conservation of orbital symmetry. The generalized rule states that all pericyclic transformations in the ground state are symmetry allowed when the total number of  $\pi$ -electrons  $(4q+2)s$  and  $(4r)a$  components is odd, where  $q$  and  $r$  are integers, and  $s$  and  $a$  represent suprafacial and antarafacial, respectively. In pericyclic reactions these components usually represent  $\sigma$  or  $\pi$  bonds taking part in the reaction, or just an unbonded orbital which is represented as  $\omega$ . Thus, for example, a Diels-Alder reaction can be represented as a ground state symmetry allowed, thermal process,  $[\omega 0s + \omega 2s + \omega 0a + \omega 2a + \omega 0s + \omega 2s]$ .



The type of reactions included under the heading of pericyclic reactions are cycloadditions, cycloreversions and sigmatropic reactions. An intra-

molecular cycloaddition or reversion in a concerted manner is also called electrocyclic reaction. The Diels-Alder reaction obviously belongs to the first two types while the migrations of a hydrogen or methyl, such as the Cope rearrangement<sup>16</sup> (eq. 18, 19), would belong to the third.

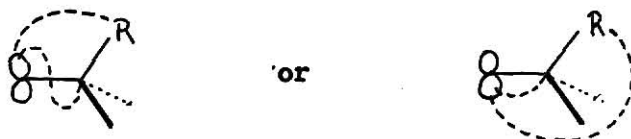


The large isotope effect observed for the above reaction<sup>16</sup> provides evidence of a symmetrical transition in a concerted manner.

The Woodward-Hoffmann rules can be easily applied to different types of electrocyclic systems involving carbonium ions, carbanions or radicals with either odd or even electrons present. The scope of the application should not give rise to complexity in the different systems. "It may be noted specially that electrocyclic transformations within odd electron systems should follow the same stereochemical course as the even electron systems containing one further electrons and that charged systems should behave in the same manner as neutral systems containing the same number of electrons."<sup>15</sup> Theoretically, Woodward-Hoffmann rules can be readily applied to mass spectral reactions, which involve odd electron species, by considering the neutral molecules before ionization.

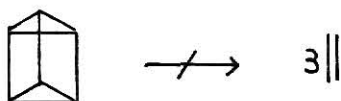
There seem to be no violations or exceptions to the Woodward-Hoffmann rules. However, there are cases when no product is observed although symmetry indicates that the reaction is allowed. This is not due to the failure of the selection rules, but rather due to one or both of the following factors:

1) The geometry of the compound may be such that the allowed transition cannot be physically realized. An example of this would be the 1,2-antarafacial shift with inversion at the migrating center. This reaction is symmetry allowed,  $[\omega 0s + \sigma 2s]$ , but physically impossible.



In the methyl migration of the trimethyl cycloheptatriene systems,<sup>26</sup> 1,3- and 1,5-methyl migrations are antarafacial and not observed because of the presence of the ring system.

2) The reacting components are directly joined by non-participating bonds forcing the antibonding orbitals to interact, thus forbidding the expected reaction to take place. An example of this would be the isomerization of prismane to three ethylenes,  $[\sigma 2s + \sigma 2a + \sigma 2a]$ .



Thus, in the prediction of the products using Woodward-Hoffmann rules for pericyclic reactions, precautions have to be taken to view each molecule individually in light of the principle of orbital symmetry conservation.

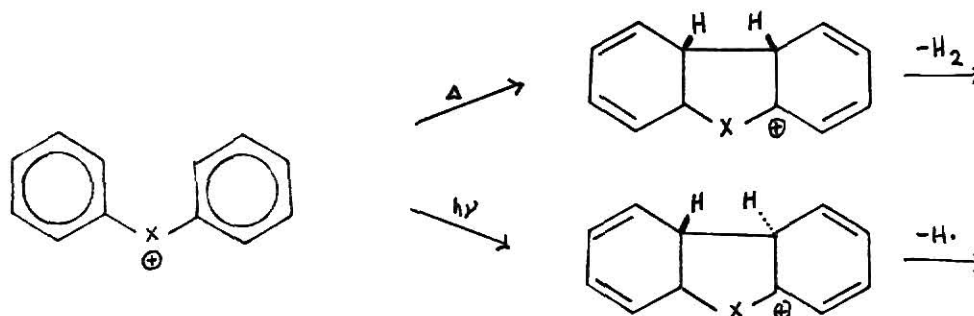
#### Semiquantitative Theory for Reactions Induced by Electron Impact

Up till now, there are no comparable selection rules for reactions induced by electron impact. The Woodward-Hoffmann rules are found to apply to some cases<sup>5,17,18</sup>, while in other cases they are not consistent.<sup>19</sup>

A limitation<sup>20</sup> for the development of a semiquantitative electronic theory for mass spectral fragmentation reactions is the difficulty in defining the reactive electronic states for ions that are produced by electron impact. The

Statistical Theory of the Quasi-Equilibrium Theory<sup>1</sup> of Mass Spectral Decomposition is sometimes used, but is considered impractical for large systems because it involves very complex calculations and assumes that the contributions to reactivity of the excited states all cancel. Another limitation is that the reactivity of molecular ions is not directly analogous to even-electron systems.

In the study of reactions given in the following equations, Johnstone<sup>12,18</sup>



suggested that the loss of H atom observed for the case where X is NH or CH=CH and the loss of  $H_2$  molecule when X is CH, corresponds to a rearrangement analogous to photochemical reactions. Fleming and Bishop<sup>19</sup> however disagreed and believed that it simply reflects a common mass spectral observation where radical cations tend to lose radicals, and even electron ions lose molecules.<sup>21</sup> They also suggested that the Woodward-Hoffmann rules for pericyclic reactions at the present state of knowledge are a poor probe into the energy levels of ion fragments in the mass spectrometer, and that the results just coincide with the theory fortuitously.

Other theories or methods need to be devised to give better correlation between the different systems in order to study their analogies.

#### Permutation Molecular Orbital Theory (PMO) and its Application

Dewar's PMO<sup>22</sup> treatment has been extended by Dougherty<sup>20</sup> to pericyclic reactions under electron impact and photolytic and thermolytic conditions. This application of the theory has found consistency in several reactions<sup>23</sup> ---

the hexahelicene rearrangement, and the retro Diels-Alder and McLafferty rearrangements.

PMO theory qualitatively not only describes the reaction coordinates, but it also provides a reasonable account of the energy separation between the first-excited states of a large number of conjugated systems. As it makes no allowance for electron correlation, the triplet states will be overestimated. However, with regard to electrocyclic reactions, it was concluded that the thermal electrocyclic reactions take place preferentially via aromatic transition states and that the photochemical electrocyclic reactions of closed shell molecules should tend to take place via excited forms of antiaromatic transition states.

Since the PMO theory deals with the energetics of the excited transition states relative to the ground states in the reaction, the analogies between reactions induced by electron impact, thermal or photochemical means will be more meaningful.

In the mass spectrometer at 50 to 70ev, fragmentation reactions can be classified into three categories:<sup>20</sup>

I. Reactions occurring from the low lying doublet or singlet states that give rise to significant metastable peaks and decomposition reactions of even electron ions that were initially formed in low lying singlet states belong to Class I.

II. Reactions with excited electronic states (including states with electrons in the antibonding orbitals), most decomposition of doubly-ionized molecules and reactions of molecules and reactions of molecule ions for which metastables cannot be detected belong to Class II.

III. Reactions for which reactive electronic states are indeterminant belong to Class III. This also includes many of the reactions of even electron frag-



ment ions or molecular ions for which only very low intensity metastables can be detected.

PMO theory extended to determine the energetics of the reactions of radical ions involves only the determination of the aromaticity of the systems that are isoelectronic with the transition states of the reaction. (Aromaticity is defined as the  $\pi$ -bond energy of a cyclic conjugated system being higher than that of an open chain conjugated analog). As a consequence of the type of calculation, it can be seen that electrocyclic reactions that belong to Class I, even electron systems, should follow the pattern established for neutral analogs.

Mass spectral Class I reactions are directly analogous to thermal processes. The thermal reactions should have a higher selectivity than the electron impact induced reactions since the former, being even electron systems, have greater aromaticity in the transition state.

Mass spectral Class II reactions correlate with photochemical processes in which the transition states are preferably antiaromatic. Class I compounds would also correlate with photochemical processes involving a  $n \rightarrow \pi^*$  transition and proceed via 5-orbital, 5-electron states.

Bishop and Fleming<sup>19</sup> essentially agree with Dougherty's conclusion that only those ions in the electronic ground state will be sufficiently long lived to give rise to metastable peaks upon fragmentation.

Before applying the PMO approach to analogies between electron impact induced reactions and thermal or photochemical reactions, two factors must be considered.

1) Highly selective thermal and photochemical processes will very often not have analogs in mass spectrometry and many high energy processes in the mass spectrometer will have no analog in the thermal and photochemical reactions because the internal excitation energy for ions that give rise to Class I

reaction will generally be larger than excitation energies in thermal and photochemical experiments.

2) It is always possible that a given class I reaction in the mass spectrometer occurs from a rearranged molecule ion that is not accessible at moderately high thermal or photochemical energies.

#### A New Test for Selection Rules Applied to Electron Impact Induced Reaction

It is noted that as the electron beam energy is lowered the extent of rearrangement often increases<sup>24</sup> and that the electron impact induced rearrangements which are analogous to photochemical transformations are relatively low energy processes and will remain prominent at low ionizing voltages.<sup>5</sup>

This is found to be the case in the study of trans- and cis-cyclobutene-dicarboxylic acids.<sup>6</sup> The low ev fragmentation mass spectra are relatively simple and are thought to be useful as a test for the selection rules for electrocyclic reactions induced by electron impact. It has been found that this case, the observation is consistent with the Woodward-Hoffmann rules for photochemical reaction.

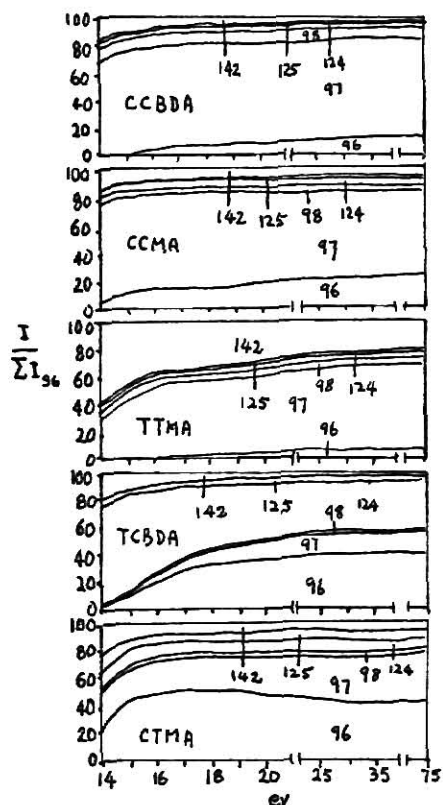
Cis- and trans-3,4-cyclobutene-dicarboxylic acids (CCBDA and TCBDA), cis-, cis-, cis,trans-, and trans,trans-muconic acids (CCMA, CTMA and TTMA) are related to each other in their thermal and photochemical reactions and conform to the selection rules of Woodward and Hoffmann.<sup>14,15</sup> An additive clastrogram<sup>25</sup> for the individual compounds was constructed from the intensities of the major ions formed in the mass spectrometer at the various electron voltages. By comparing the clastrograms (Fig. 1) of the different compounds, it was noted that CCBDA, CCMA and TTMA are similar while CTMA and TCBDA resembles one another. Further analogy was established from the observation that the mass spectrally similar compounds produce same metastable peaks for the same transitions. The Woodward-Hoffmann rules establish that, the similar compounds are related to

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each other by disrotatory process through an excited state. It seems, then, that ionization by electron impact for this system is similar to photochemical behavior, in other words, a photochemical analogy is derived.

Fig. 1. Clastrograms of cis-3,4-cyclobutene-dicarboxylic acid, cis, cis-muconic acid, trans, trans-muconic acid, trans-3,4-cyclobutene-dicarboxylic acid and cis,trans-muconic acid.

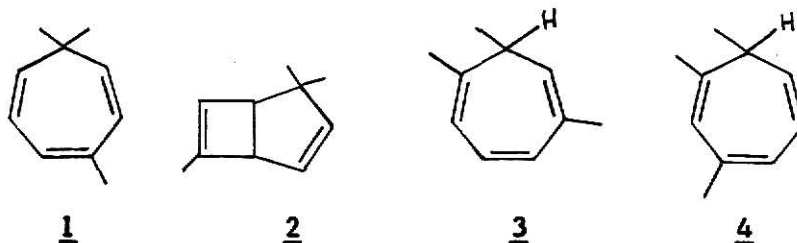


### 3,7,7-Trimethylcycloheptatriene System as a Further Test

3,7,7-Trimethylcycloheptatriene (3,7,7-TMCHT) has been well studied both thermally and photochemically and is a good system for further test of the selection rules in mass spectrometric reactions. The object of the investigation would be to observe from low ev spectra whether fragmentation patterns and clastrograms of the parent compound will be similar to those of the photo or thermal isomers, in an attempt to establish some photochemical or thermal analogy. Would it follow from the cyclobutene experimnt that a  $4n$  electron system will have a photochemical analogy, while a  $4n+2$  electron system will have a thermal analogy? Will it be independent of the selection rules? The results should give some insight to the application of the selection rules for electron impact induced reactions in the mass spectrometer.

### Photolysis of the 3,7,7-Trimethylcycloheptatriene<sup>26</sup>

On irradiation of the triene (1) in benzene solution, the compound isomerizes to three major products, 2,6,6-trimethylbicyclo- [3.2.0]-hepta-1,4-diene (2), 1,5,7-trimethylcycloheptatriene (3) and 1,3,7-trimethylcycloheptatriene (4).



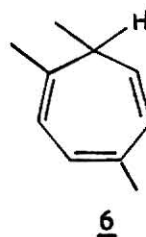
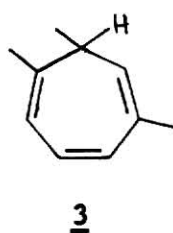
The last two products (3 and 4) isomerizes from highly selective 1,7-sigmatropic shift of the methyl and hydrogen. The bicyclic compound arises from a selective electrocyclic reaction. It has also been found that 4 was an equilibrium product from further irradiation of 3.

The electrocyclization observed for 1 is highly specific. Only one of the two possible valence tautomers, 2 and 5, is produced, although the Woodward-

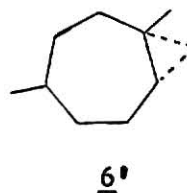
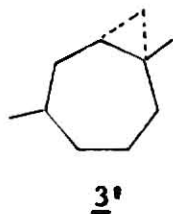


Hoffmann rules for electrocyclic reactions allow either compound to be formed through a disrotatory cyclization process. Similar conclusions may be drawn from molecular orbital calculation --- free valence indices and  $\pi$ -bond orders --- fail to explain the selectivity. Yet no trace of 5 was observed. The only explanation for the observation is that 5 is unstable relative to 2, because of the eclipsing of the methyl group on the unsaturated carbon in 2.

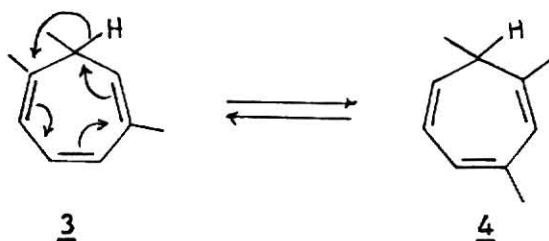
The selective formation of other tautomers can be more easily explained. Of the possible 1,7-methyl shifts to give 1,5,7-TMCHT (3) and 1,4,7-TMCHT (6), only compound 3 is detected among the photo-chemical products.



Symmetry considerations allow a 1,3- and 1,5- antarafacial sigmatropic methyl shifts in the cycloheptatriene systems, but because of the ring system it is impossible to migrate antarafacially. The choice between 3 and 6 was easily seen from the HMO calculation of the transition states, where the methyl substituent favors 3' (the transition state for 1,7-sigmatropic shift) by supplying electrons to the ring carbon by inductive and hyperconjugative interaction mechanisms.

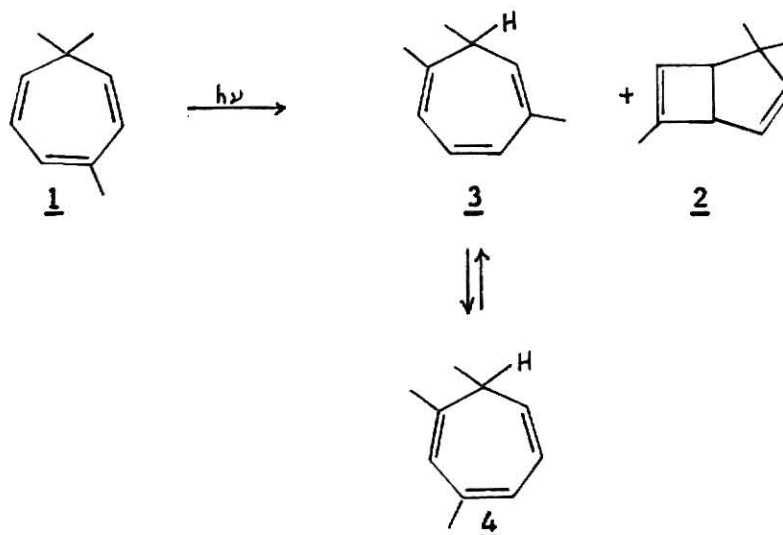


Similar considerations of the charge density and symmetry arguments indicate that compound 3 upon further irradiation should transform selectively to compound 4 and vice-versa via a hydrogen migration. This is indeed what has been observed (eq. 20).



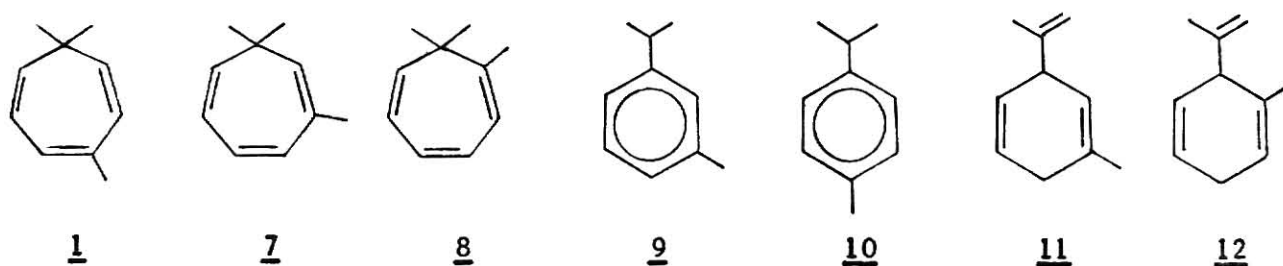
In summary, the photoreaction of 3,7,7-TMCHT can be represented by scheme 1.

Scheme 1



### Pyrolysis of 3,7,7-trimethylcycloheptatriene<sup>27,28</sup>

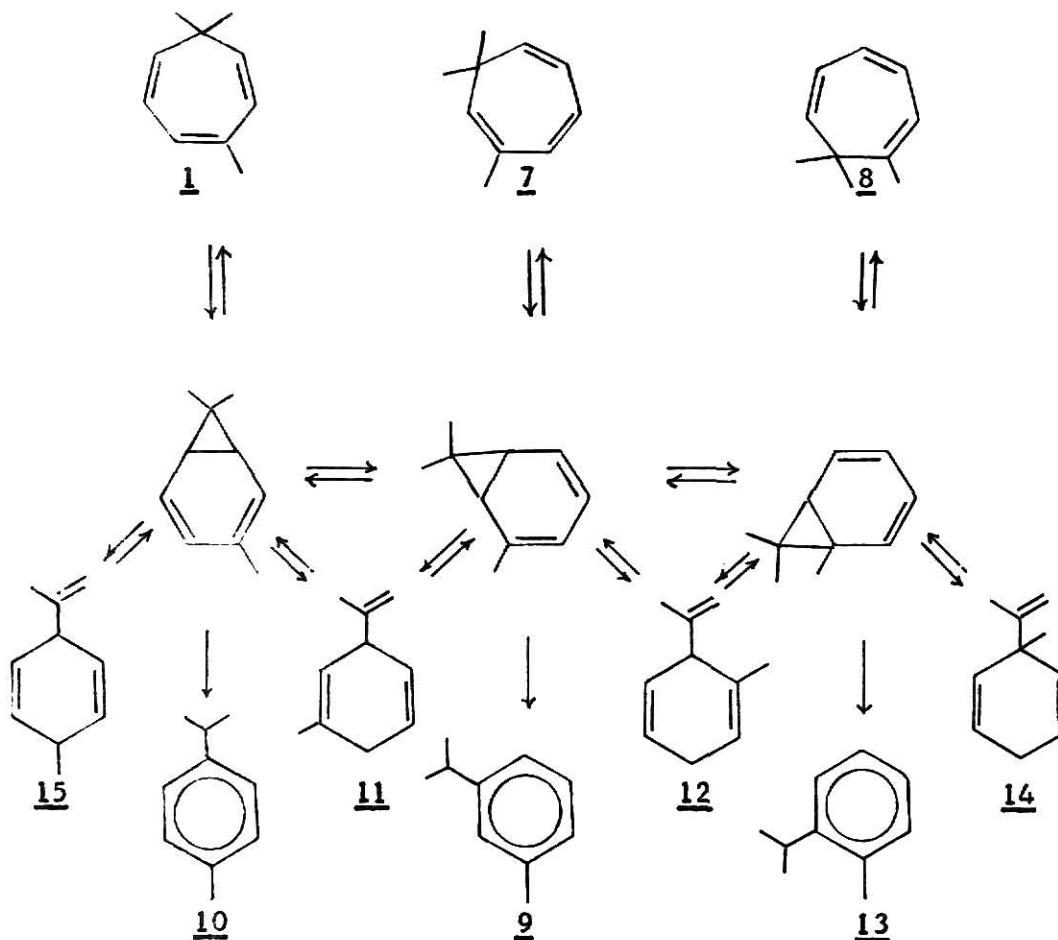
Pyrolysis of 3,7,7-TMCHT in the gas phase at 300° C produced a variety of products; 3,7,7-TMCHT (1), 2,7,7-TMCHT (7), 1,7,7-TMCHT (8), m-cymene (9), p-cymene (10), 3-isopropenyl-1-methylcyclohexa-1,4-diene (11) and 6-isopropenyl-1-methylcyclohexa-1,4-diene (12).



The pyrolytic reaction was postulated to take place via cycloheptatriene-norcaradiene interconversions. A rough estimation of  $11 \pm 4$  Kcal/mole (about 0.5 ev) of activation energy for this conversion has been calculated.<sup>29</sup> (An activation energy of  $14.6 \pm 0.4$  Kcal/mole has been estimated from the N.M.R. Study of the interconversion of 7,7-dicyano-2,5-bis-(difluoromethyl)-norcaradiene and 7,7-dicyano-2,5-bis-(difluoromethyl)-cycloheptatriene.)<sup>30</sup> It is

expected that the intermediate involved in the thermal reaction should have a norcaradiene like structure. Scheme 2 is the postulated mechanism.

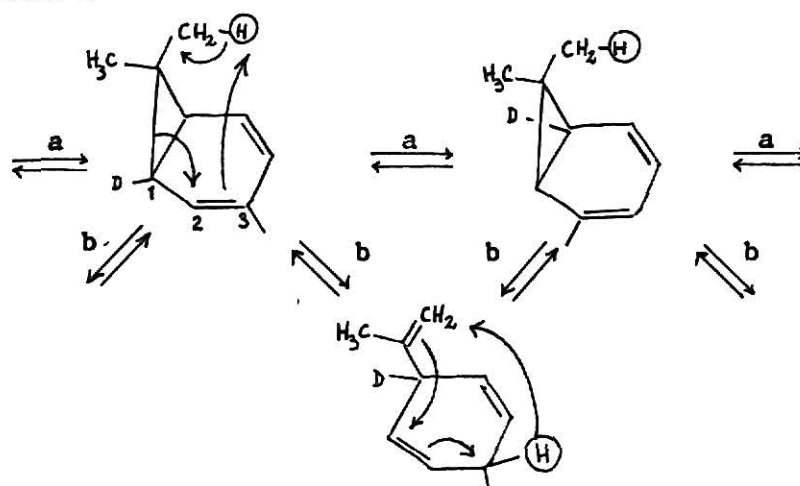
Scheme 2



The interconversion of the norcaradienes might be via the isopropenylcyclohexadienes, 11 and 12, which would involve hydride shifts due to the proximity of the methylhydrogens and 3-carbons. An alternate mechanism is an all carbon or direct transformation process. The two mechanisms can be best illustrated from the reaction schemes (scheme 3) of dideuterated cycloheptatriene-norcaradiene and related molecules. Path a is the direct transformation, while path b involves the hydride shifts. The distinction between the two processes is too fine and there is no concrete experimental results that distinguish as between them. However, in methyl substituted 7,7-dicyano-norcaradiene



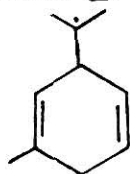
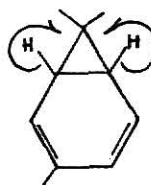
Scheme 3



31  
dienes, it has been found that an all carbon rearrangement is the mechanism for the interconversion of the isomeric norcaradienes.

The mechanism involved in the pyrolysis has two important features. First, the nonaromatizing rearrangements are reversible and second, rearrangements do not involve intermolecular hydrogen transfers. These features are supported by experimental results.

It has been noted from the deuterium labelling experiments that hydride shifts involved in these conversions are completely stereospecific since all labels are retained in their original positions on the carbon. It is not clear as to whether the shifts are due to diradical intermediates, A, or direct concerted reactions, B. Both mechanisms are allowed.

AB

According to Scheme 2, three additional products, 13, 14 and 15, are also available from the pyrolysis. They were not collected as major products, but they might be present as traces of uncharacterized compounds.

Though other mechanisms have also been suggested and are conceptionally possible, they are not consistent with labelling results that had been observed.

### Parameters in Qualitative Analogy

In order to develop a qualitative analogy between electron impact induced reactions and thermal or photochemical reaction systems, at least five parameters must be considered.<sup>32</sup>

1) Topography of the respective reaction surfaces. This is the most important factor. Only the electronic states of the ground state and first excited state of the molecule and molecular ions have to be considered since other surfaces have little effect on the reaction. Actually, mass spectral reactions are generally less selective than thermal or photochemical reactions. But the atomic coordinate space of the potential wells for reactions of the different systems are coincidentally such that their differences in the ground states and excited states correspond to one another.

2) Energy available to the reaction systems. The energy distribution only slightly affects the competition between different reaction pathways in the reactions induced by electron impact, thermal or photochemical means. The activation energy is by far more important. Accessibility to different pathways can be estimated from the appearance potentials. When low ev fragments are absent at the high ev spectrum, no analogy is obvious.<sup>23</sup>

3) Driving force for the reaction. In the thermal reactions an increase in the entropy and decrease in electronic energy is the driving force. In photochemical reactions, the relaxation of excitation energy is similar. The driving force for the ground state and excited mass spectrometric reactions is essentially the same as for neutral analogs.

4) Relative time scale. The time scale is important since mass spectrometric reactions are generally fast. However, as long as photochemical and thermal reactions give primary products which do not react subsequently, or multistep reactions are not being mistaken for primary products, the comparison should be

valid.

5) Medium effect. Any medium effect should be eliminated. Fortunately, the medium effect for radical processes are much smaller than for ionic reactions in condensed phase.

In addition to the above parameters, there are other factors<sup>32,33</sup> to be aware of in studies of this nature. Only primary photoproducts can be anticipated by studying mass spectral reactivity. Pyrolysis experiments should be conducted in such a way that primary products are preserved to the fullest possible extent. In the analysis of the mass spectrum, only major singly charged ions should be considered. Ions making up the top 80% of the total ionization would likely consist of all major pathways. Mass spectral fragmentations and fragments should be interpreted by use of models from conventional thermal and photochemistry. Low energy mass spectral reactions which do not show intense metastable ions are probably reactions from excited states with photochemical analogy. But if the activation energy is larger than 2-3 ev, the reaction can be considered equally well for ground state and excited state ions. Anticipated correspondence between mass spectral and thermal reactivity can be identified by the simple MO procedures.

## EXPERIMENTAL

Preparation of 3,7,7-Trimethylcycloheptatriene<sup>34</sup>

9 g of eucarvone (0.06 moles) in 20 ml of ether was added dropwise to an ethereal suspension of  $\text{LiAlH}_4$  (0.08 moles) and stirred for an additional 30 min.; 0.8 ml of  $\text{H}_2\text{O}$ , 0.8 ml of 15% KOH and 2.4 ml of  $\text{H}_2\text{O}$  were added in the order stated. After filtration, and evaporation of the ether, about 7.5 ml of eucarvol was obtained. After a drop of  $\text{H}_2\text{SO}_4$  was added to the eucarvol, it was distilled under reduced pressure of 20 mm in an oil bath of  $120^\circ\text{C}$ . Redistillation yielded about 1.8 g of the desired compound.

Photolysis of 3,7,7-Trimethylcycloheptatriene<sup>26</sup>

A solution of 0.6 g of 3,7,7-TMCHT in 25 ml of benzene was irradiated in pyrex soft glass tubes with a 450w Hanovia lamp for two 15 min. periods. The irradiation was interrupted to follow the reaction by means of gas chromatography, g.c. A glass beaded Vigreux column was used to fractionally distill the benzene over a range of temperature  $36.5^\circ\text{C}$  to  $37.5^\circ\text{C}$  at aspirator pressure and in an oil bath. The solvent was discarded and the residue was analyzed and isolated by g.c. using two columns.

Column A is a 6-foot column of 20% SE30 on 60-80 mesh Chromosorb P at  $115^\circ\text{C}$ . 2,6,6-Trimethylbicyclo-[3.2.0]-hepta-1,4-diene (2), the starting material, 3,7,7-TMCHT (1), and a mixture of 1,5,7-TMCHT and 1,3,6-TMCHT (3 and 4) were collected in the order of increasing retention time.<sup>26</sup>

Column B is a 6-foot column of NMPN on 80-100 mesh Chromosorb P at  $89^\circ\text{C}$ . 1,5,7-TMCHT (3) and 1,3,7-TMCHT (4) were separated in order of increasing retention time.

Pyrolysis of 3,7,7-Trimethylcycloheptatriene<sup>27</sup>

The pyrolysis reaction was carried out in a sealed Pyrex tube of about

150 ml capacity. The tube was washed with distilled water, conc.  $\text{NH}_4\text{OH}$  and rinsed thoroughly with distilled water again and then dried. After placing 0.75 g of 3,7,7-TMCHT (1) into the reaction vessel, it was attached to a vacuum manifold, cooled in liquid nitrogen, and evacuated to about  $4 \times 10^{-5}$  mm. After several freeze-thaw cycles, the tube was sealed and placed in an oven at  $300^\circ\text{C}$ , taking care that the tube did not touch the sides of the oven. After an hour the tube was removed from the oven. The narrow end was placed in liquid nitrogen and a heat gun used to drive off any material from the walls. Analysis and isolation of the contents was again carried out with the g.c. on the two following columns:

Column A is an 8-foot column of 30% UCON-HB200 on 80-100 mesh chromosorb P and used at  $138^\circ\text{C}$ . Five fractions, a mixture, 3-isopropenyl-1-methylcyclohexa-1,4-diene (11), m-cymene (9), p-cymene (10) and 1,7,7-TMCHT (8) were collected in order of retention time, (increasing).

Column B is a 15-foot column of 20% TCEP on 80-100 mesh chromosorb P and used at  $125^\circ\text{C}$ . The mixture from the above was separated into three fractions, 6-isopropenyl-1-methylcyclohexa-1,4-diene (12), 2,7,7-TMCHT (7) and the starting material 3,7,7-TMCHT (1) in order of increasing retention time.<sup>27</sup>

The Aerograph Gas Chromatograph, Manual Temperature Programmer, model A-90-P3 was used. All fractions was collected with a helium flow rate of 60 ml/min. The fractions were identified from the retention time of authentic samples whenever available.

#### Mass Spectrometric Measurements

All mass spectral measurements were taken from the AEI-MS9 double focusing mass spectrometer. The source and the system temperature were kept as low as possible to avoid any complications due to thermal reactions that might arise. Thus the source temperature was approximately  $120^\circ\text{C}$ , while the sample inlet

system temperature was approximately 75°C. The heated inlet system was used to maintain stabilized pressure conditions in the source while obtaining data.

The pressure in the source was less than  $1.5 \times 10^{-6}$  torr. Ionization and appearance potential measurements of the different major ions were calculated by the semi-log method<sup>35</sup> using naphthalene (IP = 8.12ev)<sup>25</sup> and chlorobenzene (IP = 9.07ev)<sup>25</sup> as standards.

Mass spectra of all the samples were taken at 50ev, 30ev and every electron volt down from 20ev to 12ev. The intensities of the major fragments were normalized and an additive clastrogram<sup>25</sup> was plotted to show the fraction of the ion current carried by the major ions at each voltage studied. This is done by plotting the intensities of each ion as a band above the band for the ions of lower m/e. The band width is proportional to the observed ion current produced by that particular ion.

## RESULTS AND DISCUSSIONS

Mass Spectra

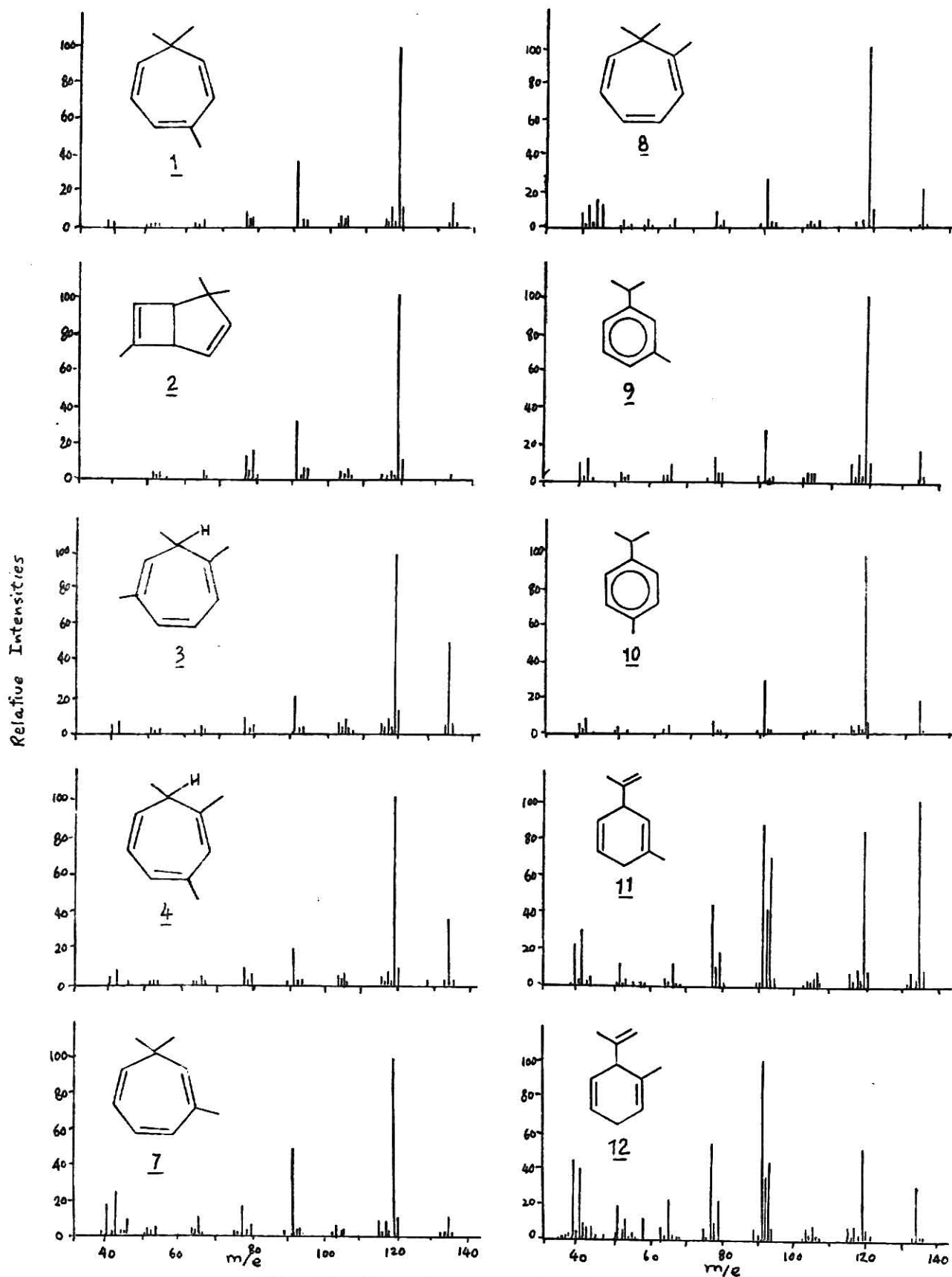
The 50ev and the 20ev mass spectra of 3,7,7-trimethylcycloheptatriene (1) and its photo and thermal isomers are given in Fig. 2 and 3 respectively. The relative intensities of the mass spectra are also tabulated in Tables 1 and 2.

It can be seen that all the trimethylcycloheptatrienes (TMCHTS), m- and p-cymenes (1,3,4,7-10) have similar mass spectra at 50ev. All show a base peak at  $m/e=119$  corresponding to the loss of 15 mass unit, (presumably a methyl group) from the molecular ion,  $m/e=134$ . The molecular ion and  $m/e=91$  are the next two most intense peaks in the TMCHT. There are small differences in the relative intensities of the major peaks among the different compounds.

At 20ev, all of the compounds still had  $m/e=119$  as the base peak, and in general,  $m/e=134$  increased in intensity while  $m/e=91$  decreased. The molecule ion of 1,5,7-TMCHT (3) and 1,3,7-TMCHT (4) are somewhat more intense than the molecular ions of the other compounds in this group, at high ev.

2,6,6-Trimethylbicyclo-[3.2.0]-hepta-1,4-diene (2), at 50ev shows the same base peak as that of the TMCHT's  $m/e=119$ , but the next most abundant peak is at  $m/e=91$  (26%) while the molecular ion is very weak (3.6%). This suggests the ease with which the molecular ion loses the 15 mass unit. At 20ev,  $m/e=119$  still predominates in the spectrum,  $m/e=91$  (10%) decreased in intensity and  $m/e=134$  remains very weak (4%).

The compounds 3-Isopropenyl-1-methylcyclohexa-1,4-diene (11) and 6-isopropenyl-1-methylcyclohexa-1,4-diene (12) show distinct differences from the spectra of the above mentioned isomers. But the spectra of the two compounds, contrary to what one would expect, also differ from one another. The 6-isopropenyl-1-methylcyclohexa-1,4-diene (12) has  $m/e=91$  as the base peak at





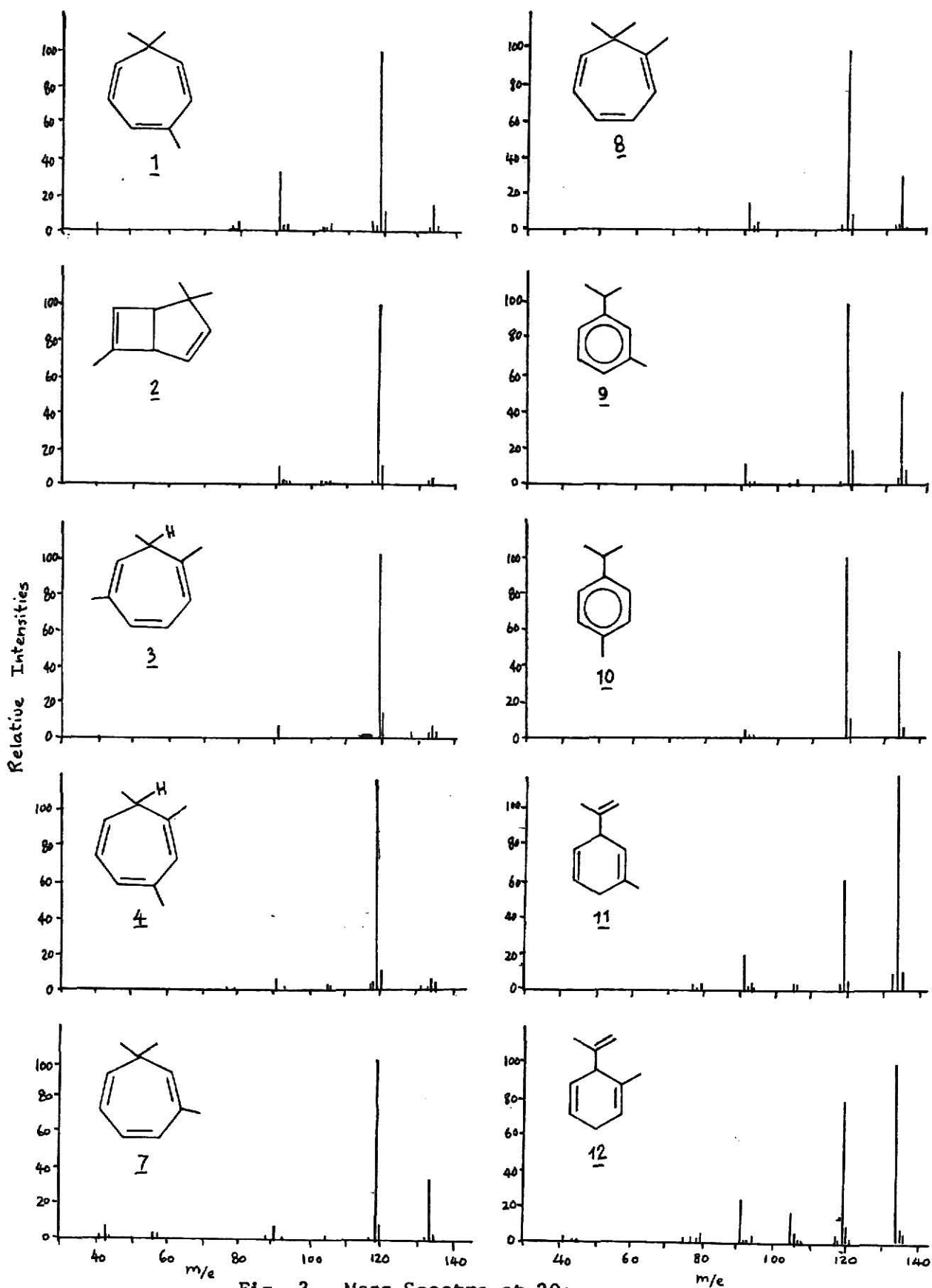


Fig. 3 - Mass Spectra at 20ev

Table 1

## Relative Intensities at 50ev

compounds	m/e	R.I.	m/e	R.I.	m/e	R.I
3,7,7-trimethyl- cycloheptatriene (1)	38	7.2	40	4.5	50	3.6
	51	1.4	52	2.0	62	2.2
	64	6.5	77	10.2	78	4.5
	79	5.6	89	1.6	91	42.0
	92	5.8	93	4.5	102	1.3
	103	6.8	104	4.6	105	6.8
	115	6.3	116	1.4	117	10.0
	118	1.6	119	100.0	120	10.5
	133	1.0	134	12.5	135	1.2
2,6,6-trimethylbicyclo- [3.2.0]-1,4-heptadiene (2)	50	1.4	51	5.2	52	2.3
	53	4.1	55	1.1	63	2.2
	65	5.0	66	1.0	77	2.2
	78	4.4	79	16.5	80	1.2
	91	26.0	92	3.6	93	5.6
	94	5.0	103	4.0	104	3.3
	106	1.0	115	3.3	116	1.0
	117	5.0	118	1.2	119	100.0
	120	10.8	133	1.7	134	3.6
1,5,7-trimethyl- cycloheptatriene (3)	40	5.2	42	7.2	51	2.8
	52	1.3	53	2.6	57.5	1.0
	58.5	1.0	63	1.7	65	5.0
	65.5	3.7	66	2.0	66.5	1.5
	77	9.2	78	2.8	79	4.6
	91	21.2	92	2.1	93	3.2
	103	4.5	104	3.1	105	8.3
	106	2.1	115	5.5	116	1.5
	117	9.3	118	2.2	119	100.0
	120	14.0	133	4.7	134	51.5
	135	5.5				
1,3,7-trimethyl- cycloheptatriene (4)	40	6.7	42	8.7	43	3.8
	51	3.3	52	1.3	53	2.7
	57	1.0	62	1.4	63	1.4
	65	5.4	66	1.7	77	9.1
	78	2.4	79	4.6	89	1.0
	91	23.0	92	1.8	93	2.2
	103	4.9	104	3.1	105	7.7
	106	1.8	115	4.6	116	1.2
	117	8.0	119	100.0	120	10.1
	128	1.6	133	3.2	134	36.0
	135	3.7				

Table 1 (continued)

2,7,7-trimethyl- cycloheptatriene (7)	40	8.1	41	1.1	42	12.3
	43	1.0	45	10.8	50	4.0
	51	4.0	52	1.5	53	2.5
	57.5	1.0	58	5.5	58.5	1.0
	59	1.4	63	1.7	65	5.5
	77	10.0	78	3.0	79	5.6
	89	1.4	91	27.0	92	4.5
	93	3.5	102	1.0	103	4.2
	104	3.0	105	4.2	115	4.0
	116	1.0	117	5.6	118	1.0
	119	100.0	120	10.5	133	22.2
	134	2.5				
1,7,7-trimethyl- cycloheptatriene (8)	39	1.0	40	19.5	41	3.1
	42	25.0	43	1.6	44	1.6
	50	2.1	51	5.0	52	3.8
	53	6.2	63	5.0	64	12.6
	66	1.5	75	1.0	76	1.0
	77	18.0	78	6.8	79	9.2
	89	3.0	91	52.0	92	7.5
	93	5.0	102	2.5	103	8.0
	104	5.0	105	5.5	115	8.5
	116	2.2	117	11.0	118	2.2
	119	100.0	120	11.0	132	2.3
	134	13.0	135	1.0		
m-cymene (9)	40	7.5	41	1.0	42	8.1
	44	1.5	50	1.0	51	4.0
	52	1.5	53	2.0	63	2.7
	65	6.6	77	8.0	78	3.0
	91	30.0	92	2.5	102	1.3
	103	2.8	104	2.5	105	3.3
	115	5.3	116	1.6	117	6.6
	119	100.0	120	6.2	134	19.5
	135	1.4				
p-cymene (10)	40	10.9	41	1.2	42	12.5
	44	1.0	50	1.4	51	5.4
	52	2.0	53	3.0	55	1.6
	63	4.0	64	1.1	65	10.1
	75	1.0	77	12.0	78	4.2
	79	4.0	89	3.0	91	28.5
	92	3.7	93	3.7	102	1.9
	103	5.8	104	4.2	105	5.1
	115	8.7	116	2.4	117	11.0
	118	3.0	119	100.0	120	10.0
	134	17.0	135	2.0		

Table 1 (continued)

3-isopropenyl-1-methyl-  
cyclohexa-1,4-diene (11)

39	1.3	40	25.0	41	33.5
42	1.5	43	6.5	50	2.1
51	11.1	52	4.1	53	6.5
55	2.9	57.5	1.2	58	3.6
64	4.0	65	2.1	66	15.5
67	2.1	68	1.1	77	45.8
78	11.0	79	19.0	80	2.2
89	2.7	90	1.0	91	91.5
92	45.0	93	73.0	94	6.3
102	1.3	103	5.4	104	3.4
105	5.5	106	9.0	107	1.7
115	8.0	118	2.4	119	88.0
120	9.0	131	1.8	132	9.3
133	5.6	134	100.0	135	10.7

6-isopropenyl-1-methyl-  
cyclohexa-1,4-diene (12)

36	1.0	37	3.0	38	4.8
39	48.0	40	8.2	41	42.0
42	11.7	43	10.6	44	9.8
45	3.0	47	1.6	50	4.3
52	20.2	52	8.2	53	13.6
54	1.3	55	5.0	56	1.0
58	14.0	62	1.5	63	8.5
65	24.5	66	3.8	67	2.6
68	1.8	75	6.9	77	54.0
78	17.2	79	22.0	80	3.0
89	4.8	90	2.0	91	100.0
92	40.0	93	48.0	94	6.0
102	1.6	103	7.0	104	3.3
105	2.0	106	8.0	107	3.0
108	1.0	115	7.2	116	1.8
117	8.0	119	56.0	120	6.4
121	3.3	132	1.1	133	1.5
134	30.0	135	3.2	136	1.3

Table 2

## Relative Intensities at 20ev

compounds	m/e	R.I.	m/e	R.I.	m/e	R.I.
3,7,7-trimethyl- cycloheptatriene ( <u>1</u> )	40	6.9	77	2.5	78	1.0
	79	6.5	91	32.6	92	3.7
	93	3.9	103	2.4	104	1.9
	105	4.4	114	1.0	117	5.5
	118	1.0	119	100.0	120	11.0
	133	1.1	134	15.6	135	1.5
2,6,6-trimethylbicyclo- [3.2.0]-1,4-hepta- diene ( <u>2</u> )	77	1.2	78	1.0	78	7.2
	91	10.0	92	2.0	93	2.6
	94	3.9	103	1.3	104	1.2
	105	2.5	106	1.0	117	1.8
	119	100.0	120	10.1	133	1.6
	134	4.0				
1,5,7-trimethyl- cycloheptatriene ( <u>3</u> )	77	1.0	79	1.3	91	6.3
	93	1.0	105	3.6	106	1.7
	117	2.0	118	1.0	119	100.0
	120	11.5	133	3.3	134	60.0
	135	5.7				
1,3,7-trimethyl- cycloheptatriene ( <u>4</u> )	7	1.0	87	1.2	89	1.0
	91	6.0	93	1.0	117	3.0
	119	100.0	120	14.0	128	3.0
	133	2.0	134	6.4		
2,7,7-trimethyl- cycloheptatriene ( <u>7</u> )	42	2.7	44	7.0	45	2.5
	57	5.3	79	1.9	91	8.3
	92	1.0	93	1.3	105	1.7
	117	1.0	119	100.0	120	11.1
	133	1.0	134	34.0	135	4.0
1,7,7-trimethyl- cycloheptatriene ( <u>8</u> )	77	2.5	91	16.5	92	3.1
	93	1.8	104	1.0	106	2.0
	117	4.1	119	100.0	120	10.0
	132	4.5	133	1.0	134	26.0
	135	2.7				

Table 2 (continued)

m-cymene ( <u>9</u> )	91	13.0	92	3.0	93	3.0
	103	1.0	105	2.5	117	3.6
	118	1.2	119	100.0	120	20.0
	133	1.2	134	50.0	135	10.2
p-cymene ( <u>10</u> )	91	4.7	92	1.0	93	1.0
	117	1.6	119	100.0	120	9.8
	134	48.0	135	5.0		
3-isopropenyl-1-methylcyclohexa-1,4-diene ( <u>11</u> )	42	5.0	45	2.2	58	2.0
	77	2.6	78	1.0	79	4.6
	91	21.0	92	2.9	93	34.5
	94	2.4	105	4.0	106	6.6
	118	3.2	119	62.5	120	6.2
	132	9.2	133	3.8	134	100.0
	135	10.2				
6-isopropenyl-1-methylcyclohexa-1,4-diene ( <u>12</u> )	42	4.2	44	3.2	45	2.1
	55	1.0	58	1.6	75	5.0
	77	4.3	78	1.8	79	5.5
	80	1.5	91	26.0	92	3.4
	93	3.8	94	4.8	105	18.0
	106	7.8	107	3.1	108	1.1
	117	2.7	119	80.0	120	8.9
	121	3.8	132	1.8	133	2.6
	134	100.0	135	11.2	136	4.3

50ev, with  $m/e=119$  (56%) and  $m/e=134$  (30%) as the next two intense peaks. At 20ev, the abundances of the peaks are reversed, such that  $m/e=134$  becomes the base peak followed by  $m/e=119$  (80%) and  $m/e=91$  (26%). This suggests a change in the dominating reaction pathway going from 50ev to 20ev. Perhaps the mechanism at 20ev is the same as that observed for 3-isopropenyl-1-methylcyclohexa-1,4-diene (11) at 50ev. At 50ev, compound 11 has a mass spectrum showing the same order of ion intensities for the major fragments observed as for compound 12, i.e.,  $m/e=134$  (100%),  $m/e=119$  (88%) and then  $m/e=91$  (91.5%). However, at 20ev, the  $m/e=119$  becomes more important.

All of the isomeric compounds studied show distinct metastables for the following transitions:

134 $\longrightarrow$ 119	$m^* = 105.7$
119 $\longrightarrow$ 91	$m^* = 69.58$
119 $\longrightarrow$ 117	$m^* = 114.87$

The intensity of  $m/e=117$  is very low compared to the major ions and therefore was not studied.

The major ions in all the spectra ( $m/e=134$ , 119, and 91) are present at 50ev as well as 20ev. These ions carry more than 80% of the total ion current at both high and low electron energies, and include all of the major reaction pathways for the molecules being studied.

From the mass spectra, (Fig. 1 and 2) it can be seen that 1,7,7-TMCHT (1) does not resemble all of its photoisomers nor all of its thermal isomers at 50 or 20ev. Spectra of 3- and 6-isopropenyl-1-methylcyclohexa-1,4-diene (11 and 12), which are thermal isomers, are very different from the spectrum of the starting material. The compounds, 1,5,7-TMCHT (3) and 1,3,7-TMCHT (4) have a more intense molecular ion than  $m/e=91$  which is reversed for the 3,7,7-TMCHT (1). The remaining isomers from thermal rearrangements have spectra that look more or

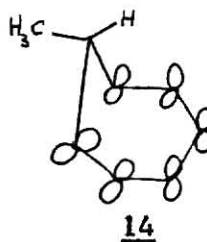
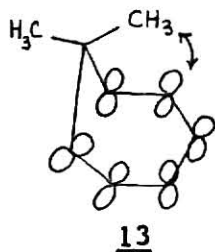
less similar to the parent compound.

The fact that all these compounds (1-4, 7-12) have the same major fragment ions ( $m/e=134$ ,  $m/e=119$  and  $m/e=91$ ) and the same metastable ions, suggests that they undergo the same fragment loss. It would be difficult to say, however, whether at 50ev or 20ev, these compounds share a common energy manifold and/or structural intermediate to give rise to the same fragmentation. If the small differences in the intensities of the spectra of the cycloheptatrienes are considered to be significant, then, it is unlikely that any of the compounds fragment via one common intermediate.

### Clastrograms

The additive clastrograms of the 3,7,7-TMCHT (1) and its isomers (2-4, 7-12) are given in Fig. 4. The normalized relative intensities are tabulated in Table 3.

The clastrogram of 3,7,7-TMCHT (1) over the entire energy range does not show resemblance to any of its isomers. However, below 20ev, the clastrogram of the starting material looks more like that of 2,7,7-TMCHT (7) and 1,7,7-TMCHT (8). The clastrograms of compounds 7 and 8 are almost identical and so are that of 1,5,7-TMCHT (3) and 1,3,7-TMCHT (4). In fact, clastrograms of all TMCHTs look similar, differing only in the amount of ion current carried by the  $m/e=119$  ion. This could be explained by the sterically unfavorable structure of the 7,7-dimethyl system compared to the 7-methyl system.



The stereochemistry of 7,7-dimethyl-TMCHT (13) is such that one of the 7-methyl groups is situated above the 7-orbitals of the double bonds. Whereas



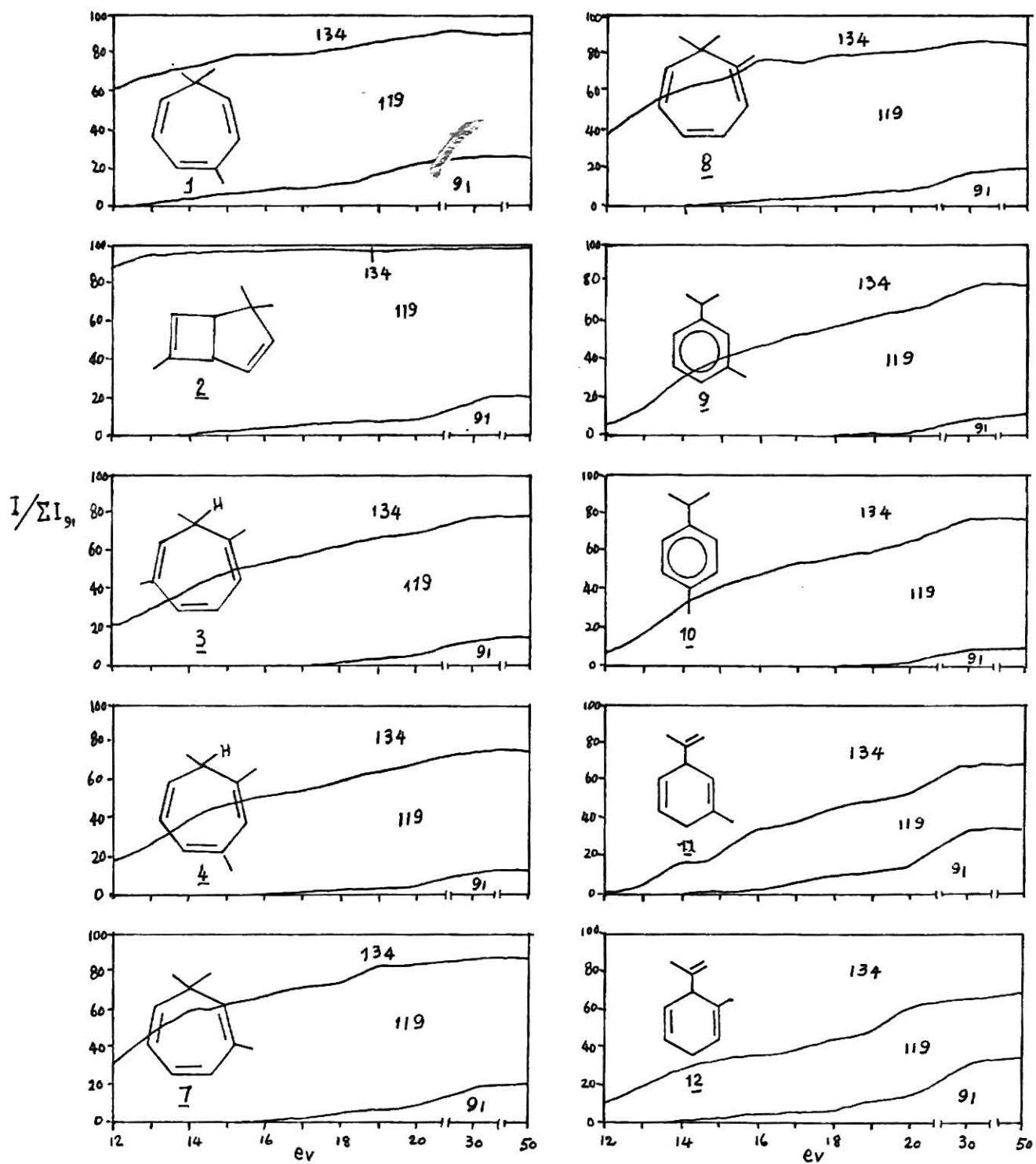


Fig. 4 Clastrograms

Table 3

NORMALIZED RELATIVE INTENSITIES

## 3,7,7-trimethylcycloheptatriene (1)

m/e	ev=	50	30	20	19	18	17	16	15	14	13	12
134		9.68	10.88	10.53	13.93	19.80	20.42	20.01	22.49	28.04	32.28	39.52
119		64.52	63.04	67.48	69.64	68.07	71.23	71.84	68.40	66.14	59.88	50.51
91		25.81	27.55	22.00	16.43	11.95	11.50	8.76	5.68	3.56	1.59	0.60

## 2,6,6-trimethylbicyclo-[3.2.0]-1,4-heptadiene (2)

m/e	ev=	50	30	20	19	18	17	16	15	14	13	12
134		2.80	3.05	3.26	3.28	3.35	3.75	3.62	4.58	5.87	6.98	12.28
119		75.53	78.31	88.18	88.97	90.50	91.49	92.94	93.46	93.19	93.02	87.72
91		21.68	18.64	8.55	7.74	6.15	4.76	3.44	1.96	0.94	0.00	0.00

## 1,5,7-trimethylcycloheptatriene (3)

m/e	ev=	50	30	20	19	18	17	16	15	14	13	12
134		24.84	26.45	32.62	36.47	40.62	46.10	48.99	53.48	60.98	74.07	83.83
119		62.11	62.97	63.94	60.79	57.21	52.69	50.51	46.52	39.02	25.93	16.18
91		13.04	10.58	3.45	2.74	2.17	1.20	0.51	0.00	0.00	0.00	0.00

## 1,3,7-trimethylcycloheptatriene (4)

m/e	ev=	50	30	20	19	18	17	16	15	14	13	12
134		21.67	24.10	32.32	36.19	37.93	43.50	47.12	52.08	60.17	71.94	81.97
119		62.03	63.25	63.78	60.31	60.20	55.07	52.36	47.92	39.83	28.06	18.03
91		16.25	12.65	4.28	3.50	1.87	1.43	0.52	0.00	0.00	0.00	0.00

Table 3 (continued)

2,7,7-trimethylcycloheptatriene (7)

m/e	ev=	50	30	20	19	18	17	16	15	14	13	12
134		15.53	15.82	23.52	25.17	27.93	28.76	33.44	37.27	41.86	52.91	68.67
119		62.11	64.56	67.20	67.11	66.49	67.34	64.31	62.11	58.14	47.09	31.33
91		22.36	18.98	9.27	7.72	5.98	3.47	2.25	0.62	0.00	0.00	0.00

1,7,7-trimethylcycloheptatriene (8)

m/e	ev=	50	30	20	19	18	17	16	15	14	13	12
134		14.74	18.09	21.26	23.45	27.39	30.83	35.30	38.00	47.37	55.56	74.07
119		64.10	65.79	64.43	68.97	68.00	67.02	63.05	61.27	52.63	44.44	25.93
91		21.15	16.12	7.86	7.59	5.81	2.14	1.64	0.74	0.00	0.00	0.00

m-cymene (9)

m/e	ev=	50	30	20	19	18	17	16	15	14	13	12
134		20.67	21.05	35.67	37.74	41.93	46.28	52.91	59.52	69.44	85.47	95.79
119		66.67	70.18	61.50	60.39	56.66	53.19	47.09	40.48	30.56	14.53	4.42
91		12.67	8.77	2.82	1.87	1.18	0.53	0.00	0.00	0.00	0.00	0.00

p-cymene (10)

m/e	ev=	50	30	20	19	18	17	16	15	14	13	12
134		20.67	21.05	35.67	37.74	41.93	46.28	52.91	59.52	69.44	85.47	95.79
119		66.67	70.18	61.50	60.39	56.66	53.19	47.09	40.48	30.56	14.53	4.21
91		12.67	8.77	2.83	1.87	1.18	0.53	0.00	0.00	0.00	0.00	0.00

Table 3 (continued)

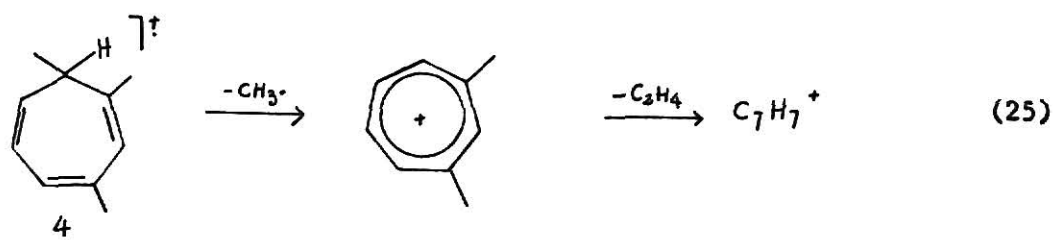
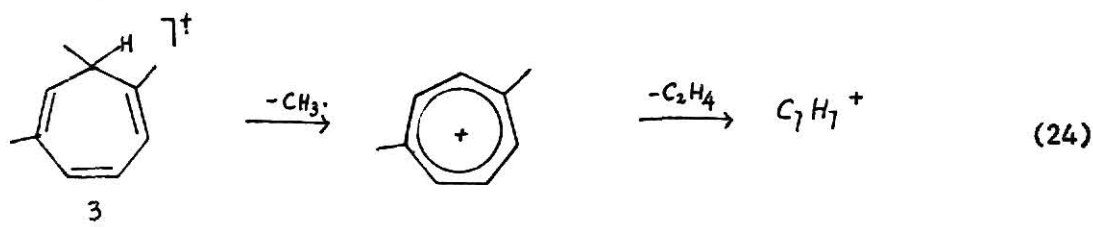
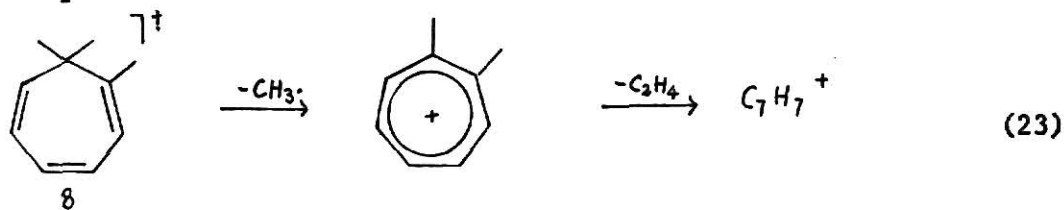
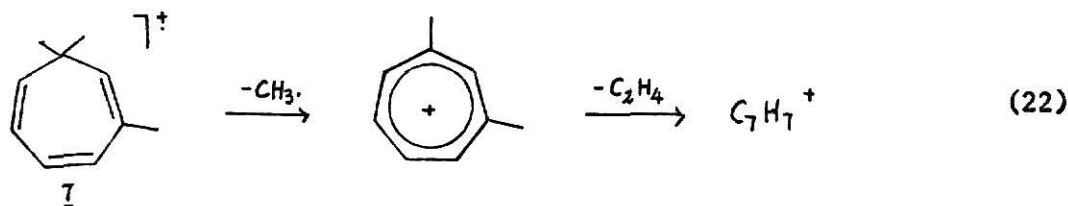
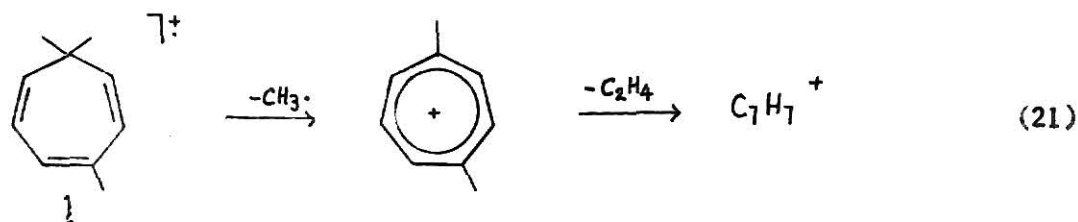
**3-isopropenyl-1-methylcyclohexa-1,4-diene (11)**

m/e	ev-	50	30	20	19	18	17	16	15	14	13	12
134		30.70	33.22	47.85	50.50	53.76	58.55	65.93	80.39	84.67	96.99	99.11
119		31.84	33.56	35.89	35.86	34.41	33.96	31.64	17.68	14.31	2.04	0.89
91		37.45	33.22	16.27	13.64	11.83	7.49	2.44	1.93	1.02	0.97	0.00

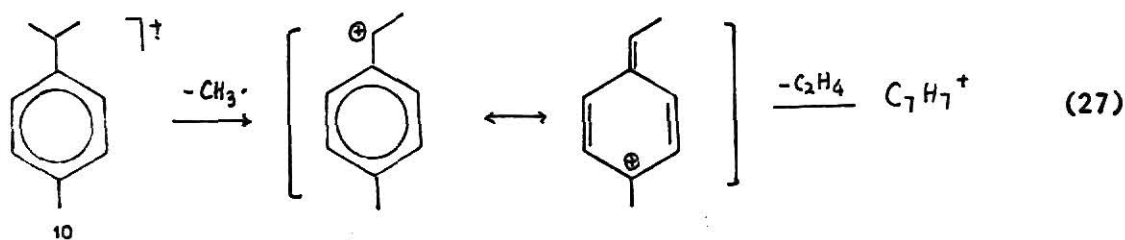
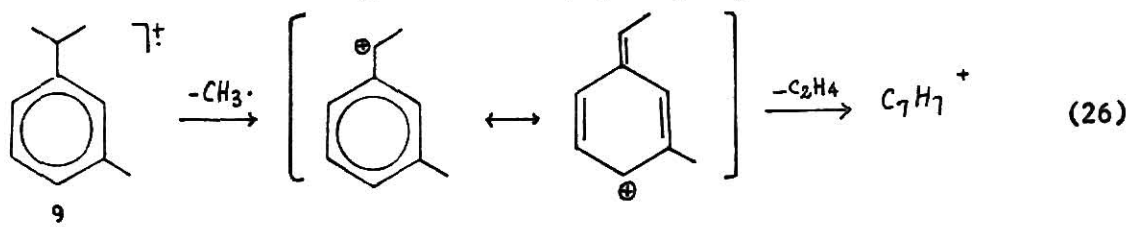
**6-isopropeneyl-1-methylcyclohexa-1,4-diene (12)**

m/e	ev-	50	30	20	19	18	17	16	15	14	13	12
134		32.04	35.71	48.00	51.07	56.72	60.94	64.30	66.40	72.31	80.00	88.50
119		32.75	33.93	36.97	36.26	35.73	32.91	32.96	30.54	26.97	20.00	11.50
91		35.21	30.36	15.03	12.67	7.54	6.15	4.37	3.05	0.85	0.00	0.00

in the 7-methyl-TMCHT (14), the preferred structure is one in which the H atom is on the same side as the  $\pi$ -orbitals. There would be smaller steric repulsion between a H atom and the  $\pi$ -orbitals than between a methyl group and the  $\pi$ -orbitals. Similar reasoning can be applied to 1,7,7-TMCHT (1) and 1,3,7-TMCHT (4) and 1,5,7-TMCHT (3). The 7,7-disubstituted TMCHT lose a 7-methyl more readily to form a stable tropylium ion (eq. 21, 22, 23, 24, and 25) and will carry more ion current than for the TMCHTs with just one methyl substituted at the 7 position. It should also be noted, however, that loss of H from the molecular ion of the 1,3,7- and 1,5,7-TMCHT's is not a very important pathway.

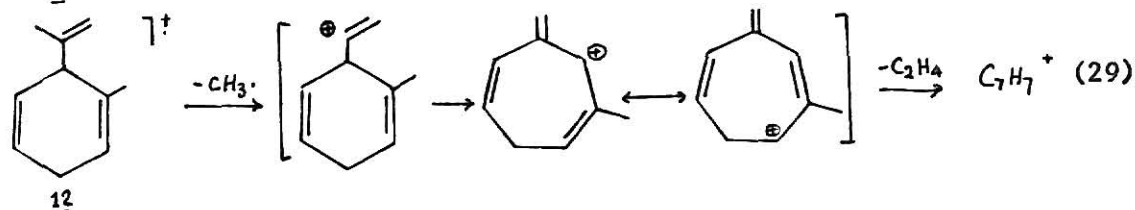
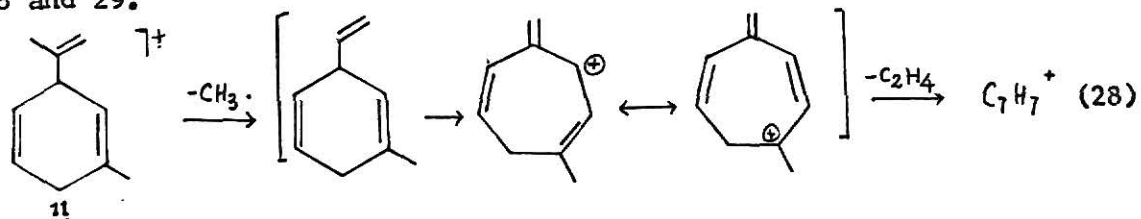


Clastrograms of *m*-cymene (9) and *p*-cymene (10) are similar to each other as expected and also have some similarity with the TMCHTs. The ion current carried by their molecular ion is more than that of the TMCHTs, and could be rationalized from the following mechanism (eq. 26, 27).



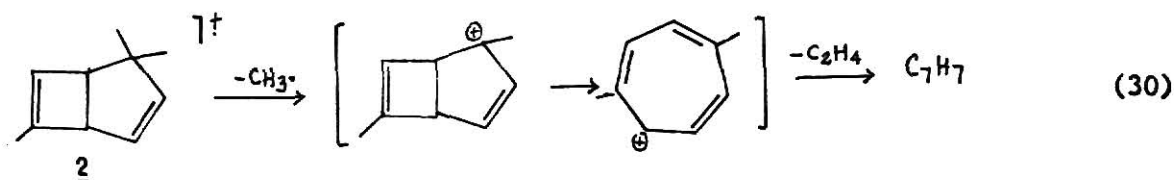
The loss of a methyl group from the cymenes reduces the resonance stabilization of the phenyl ring and is an unfavorable process. Therefore the more stable molecular ion would be expected to carry more ion current than in the TMCHTs where aromaticity is increased by the loss of a methyl group (eq. 21-25).

The 3-isopropenyl-1-methylcyclohexa-1,4-diene (11) and 6-isopropenyl-1-methylcyclohexa-1,4-diene (12) have clastrograms similar to each other, but different from the other isomers, as was also observed to be the case in their mass spectra. The ion currents carried by the molecular ion,  $m/e=134$ , for these two compounds are about 50% of the total ion current and more than observed in any of the other isomers. A postulated mechanism for 11 and 12 is illustrated in eq. 28 and 29.



Rearrangement provides a conjugated structure for the  $m/e=119$  ion, which is more stable than the vinyl carbonium ion structure which is formed if rearrangement had not occurred.

2,6,6-Trimethylbicyclo- [3.2.0]-hepta-1,4-diene (2) has a clastrogram that is distinctly different from all the other isomers. The ion current carried by  $m/e=119$  dominates the entire energy range. The molecular ion carries only about 4-5% of the total ion current. A rationale for this particular observation might be the ease with which the molecular ion loses the methyl and rearranges to a tropylium ion (eq. 30).



The bicyclic compound is postulated to aromatize to the substituted tropylium ion with the loss of methyl. Substituted bicyclo- [3.2.0]-heptanes have been found to rearrange to TMCHTs.<sup>36</sup> The bicyclic molecule is a strained system and is highly susceptible to rearrangement and fragmentation, particularly when the rearranged structure is resonance stabilized. Therefore, the molecular ion,  $m/e=134$ , of 2,6,6-trimethylbicyclo- [3.2.0]-hepta-1,4-diene (2) will carry very little current since most of the ion will decompose to form the more stable  $m/e=119$  ion.

The observation from the 50ev mass spectrum of 2,6,6-trimethylbicyclo- [3.2.0]-methylhepta-1,4-diene (2) that the relative intensity of the  $m/e=119$  (100%) and  $m/e=91$  (26%) is quite similar to that of 3,7,7-TMCHT (1) ( $m/e=119$  (100%) and  $m/e=91$  (23%)), can be explained from the fragmentation mechanism postulated above. Both compounds have a 1,4-dimethyltropylium ion as a possible structure for  $m/e=119$ ev.

The clastrograms of the different compounds show some similarities among

the TMCHTs (1, 3, 4, 7, 8) and cymenes (9, 10), while that of 3- and 6-isopropenyl-1-methylcyclohexa-1,4-dienes (11, 12) show little resemblance to them. The 2,6,6-trimethylbicyclo-[3.2.0]-hepta-1,4-diene has a clastrogram that is significantly different from all other isomers.

## ENERGETICS

### Appearance potentials, ionization potentials and activation energies

The ionization potential is the minimum energy necessary to ionize a neutral molecule by losing an electron to form a molecular ion in about  $10^{-6}$  sec. Appearance potential usually applies to the energy necessary for the formation of daughter ion from the molecule in about  $10^{-6}$  sec. Because of this kinetic effect, known as the kinetic shift, ions formed at the "threshold" have small amount of excess energy. An activation energy is the minimum energy required to activate the molecular ion so that it can undergo reaction and proceed to the product. The relationship between the appearance potentials (AP), ionization potentials (IP) and activation energies are given in the thermal energy relationship diagram of a unimolecular ion decomposition in the mass spectrometer<sup>37</sup> below (Fig. 5).

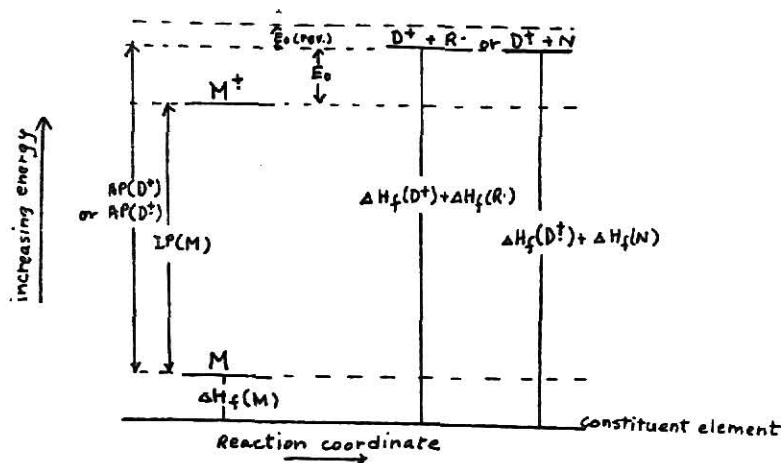


Fig. 5. Thermochemical energy relationships for unimolecular ion decompositions in the mass spectrometer.



It can be seen that the AP and IP values are related to the heat of formation of the respective species involved. The activation energy is also calculated from the difference between the AP and IP of the ions in the reaction (eq. 31, 32, 33, and 34).

$$IP (M) = \Delta H_f (N) - \Delta H_f (M) + E' \quad (31)$$

$$AP (D^+) = \Delta H_f (D^+) + \Delta H_f (N) - \Delta H_f (M) + E' \quad (32)$$

$$\text{or } AP (D^+) = \Delta H_f (D^+) + \Delta H_f (R') - \Delta H_f (M) + E' \quad (33)$$

$$E_o (D^+) = AP (D^+) - IP (M^+) + E' \quad (34)$$

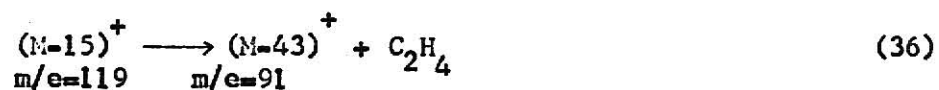
where  $\Delta H_f$  = heat of formation

$E'$  = excess energy

$E_o$  = activation energy

The activation energy might be higher than the calculated value. This excess energy can be seen in the reverse reaction. For cleavage reactions there is no activation for the reverse reaction. For skeletal rearrangement leading to more stable species, there will be some activation energy for the back reaction,<sup>38</sup> i.e., the measured activation energy will include some excess energy.

The appearance potentials and the ionization potentials of the major ions are tabulated in Table 4. The values are reproducible within  $\pm 0.05\text{ev}$ . The activation energies for the reactions (eq. 35, 36) are calculated from the average APs of  $m/e=119$  and  $m/e=91$  and the IP of  $m/e=134$ . They are given in Table 5.



The compounds *m*-cymene (9) and *p*-cymene (10) have IP measurements within  $\pm 0.1\text{ev}$  of each other. The first fragmentation of both compounds is a loss of 15 mass unit which is most likely the loss of methyl group from the isopropyl

Table 4

## Ionization and Appearance Potentials

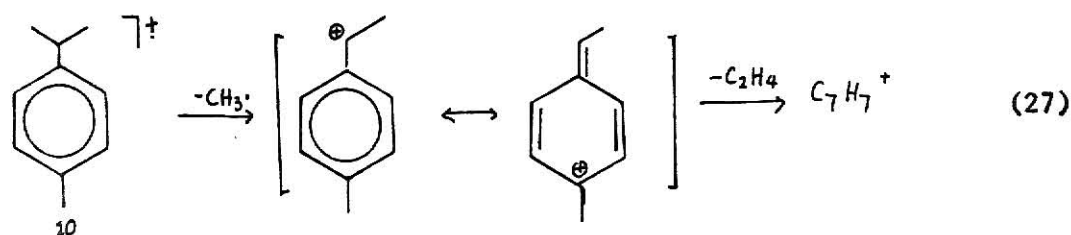
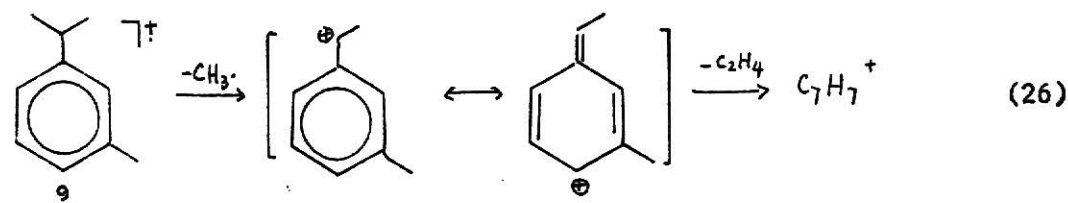
compounds	m/e=134	m/e=119	m/e=91
3,7,7-trimethyl- cycloheptatriene ( <u>1</u> )	6.58 $\pm$ .014ev	9.02 $\pm$ .021ev	11.99 $\pm$ .021ev
2,6,6-trimethylbicyclo- 3.2.0 -hepta-1,4- diene ( <u>2</u> )	7.76 $\pm$ .013ev	8.57 $\pm$ .006ev	11.44 $\pm$ .014ev
1,5,7-trimethyl- cycloheptatriene ( <u>3</u> )	6.35 $\pm$ .017ev	9.38 $\pm$ .038ev	11.80 $\pm$ .020ev
1,3,7-trimethyl- cycloheptatriene ( <u>4</u> )	7.41 $\pm$ .025ev	9.33 $\pm$ .010ev	12.65 $\pm$ .006ev
2,7,7-trimethyl- cycloheptatriene ( <u>7</u> )	7.45 $\pm$ .044ev	9.68 $\pm$ .013ev	12.91 $\pm$ .010ev
1,7,7-trimethyl- cycloheptatriene ( <u>8</u> )	7.34 $\pm$ .016ev	8.93 $\pm$ .021ev	12.12 $\pm$ .000ev
m-cymene ( <u>9</u> )	7.92 $\pm$ .013ev	10.40 $\pm$ .021ev	13.18 $\pm$ .014ev
p-cymene ( <u>10</u> )	7.99 $\pm$ .006ev	10.29 $\pm$ .035ev	13.37 $\pm$ .024ev
3-isopropenyl-1- methylcyclohexa- 1,4-diene ( <u>11</u> )	7.94 $\pm$ .022ev	9.05 $\pm$ .010ev	11.02 $\pm$ .040ev
6-isopropenyl-1- methylcyclohexa- 1,4-diene ( <u>12</u> )	7.75 $\pm$ .041ev	8.72 $\pm$ .021ev	11.20 $\pm$ .012ev

Table 5

## Activation Energies

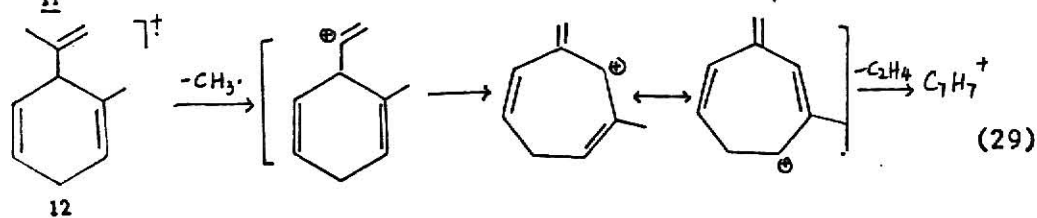
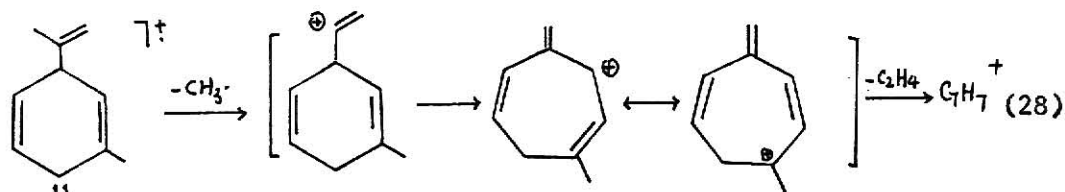
compound	m/e=134	m/e=119	m/e=119	m/e=91
3,7,7-trimethyl- cycloheptatriene (1)		2.44ev		2.97ev
2,6,6-trimethylbicyclo- 3.2.0 -hepta-1,4-diene (2)		0.18ev		2.87ev
1,5,7-trimethyl- cycloheptatriene (3)		3.03ev		2.42ev
1,3,7-trimethyl- cycloheptatriene (4)		2.92ev		3.32ev
2,7,7-trimethyl- cycloheptatriene		2.23ev		3.23ev
1,7,7-trimethyl- cycloheptatriene (8)		1.59ev		3.19ev
m-cymene (9)		2.48ev		2.78ev
p-cymene (10)		2.30ev		3.08ev
3-isopropenyl-1-methyl- cyclohexa-1,4-diene (11)		1.13ev		1.97ev
6-isopropenyl-1-methyl- cyclohexa-1,4-diene (12)		0.97ev		2.48ev

substituent. The activation energies for the loss of the methyl from both compounds are almost the same (2.48ev and 2.30ev), therefore the position of the methyl substituent on the phenyl ring has little or no effect on this reaction. Once the methyl radical is lost from the isopropyl group, however, we can see (eq. 26, 27) that the  $m/e=119$  ion formed from the *p*-cymene (10) is



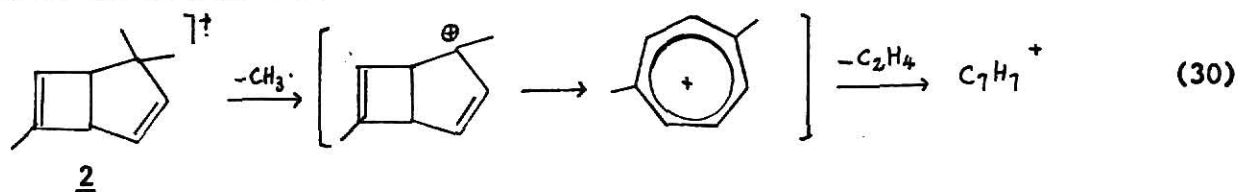
slightly more stable than that of the *m*-cymene. This is because a more stable tertiary carbonium ion is present as a resonance structure and could explain why the activation energy for the subsequent fragmentation is higher for the *p*-cymene (10).

The compounds, 3-isopropenyl-1-methylcyclohexa-1,4-diene and 6-isopropenyl-1-methylcyclohexa-1,4-diene (11 and 12) have a 0.14ev difference between their IP measurements. The fragmentation is most likely a loss of methyl from the isopropenyl substituent concomitant with or followed by rearrangement to form a more stable conjugated structure (eq. 28, 29).



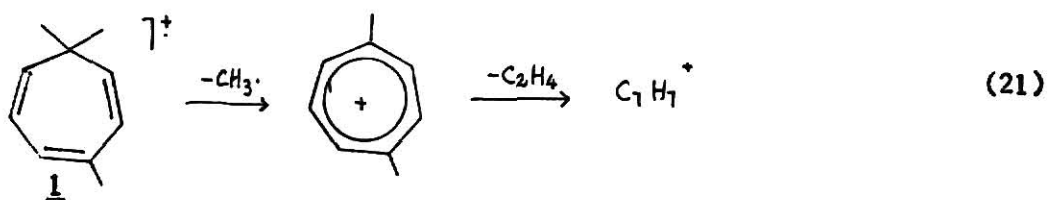
The activation energies for the initial loss of methyl are similar (0.97ev and 1.13ev) suggesting that the methyl substituent on the cyclic structure is not an important influence on the reaction.

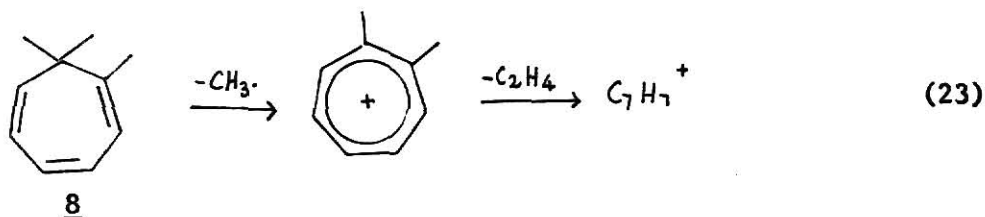
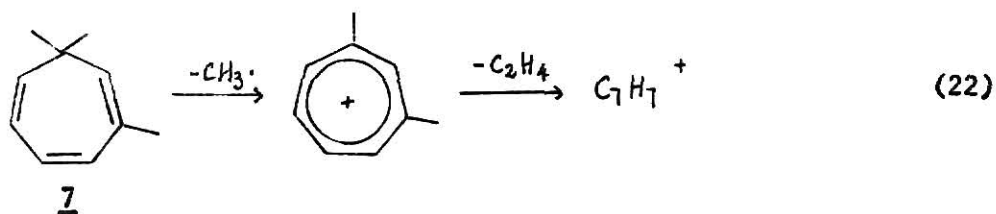
The IP (7.76ev) and AP ( $m/e=119$ , 8.57ev;  $m/e=91$ , 11.44ev) of 2,6,6-trimethylbicyclo-[3.2.0]-hepta-1,4-diene (2) are closer to that of isopropenyl-1-methylcyclohexa-1,4-dienes (11, 12) than to that of other compounds being studied, but this does not necessarily mean that they have rearranged to a common intermediate within the molecular ion. In fact, the more logical mechanism is rearrangement to the cycloheptatriene structure concomitant with loss of the 6-methyl group (eq. 30).



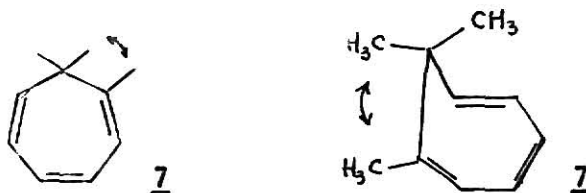
The TMCHTs that showed similarities among each other in the previous comparisons do not show the same similarities in their energetics for the reactions under study. The differences between them can be explained by looking into the activation energies and fragmentation patterns.

The activation energies for the loss of methyl from the 1,7,7-TMCHT (8), 2,7,7-TMCHT (7) and 3,7,7-TMCHT (1) are 1.59ev, 2.23ev and 2.44ev respectively. The methyl loss, earlier presumed to be the 7-methyl, produces a substituted tropylium ion  $m/e=119$ , which appears to be more easily formed when the three methyl groups are closer together (eq. 21, 22, 23).



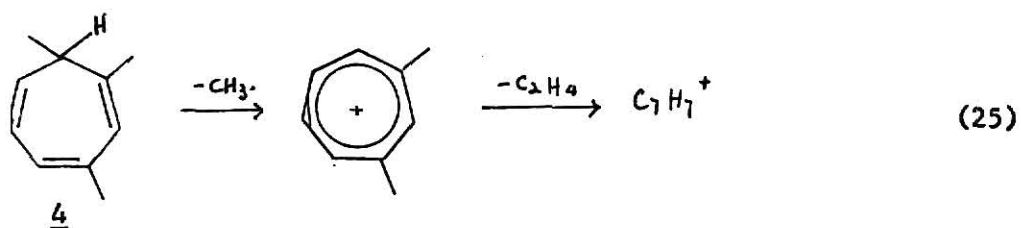
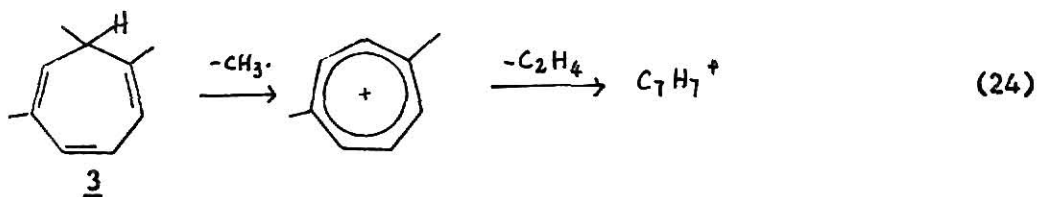


Steric interaction between the 7-methyls and 1-methyl in the 1,7,7-TMCHT (8) could explain the lower activation energy (1.59ev vs. 2.23ev, 2.44ev) for the initial loss of methyl from this compound, than for 2,7,7-TMCHT (7) or 3,7,7-TMCHT (1).



The 2- and 3-methyl groups on the TMCHT ring for compounds 7 and 1 are further away from the 7-methyls. A lower activation energy for the decomposition of 3,7-dimethyltropylium ion than for the 1,7- and 2,7-dimethyltropylium ion (2.97ev vs. 3.23 and 3.19ev) is also observed.

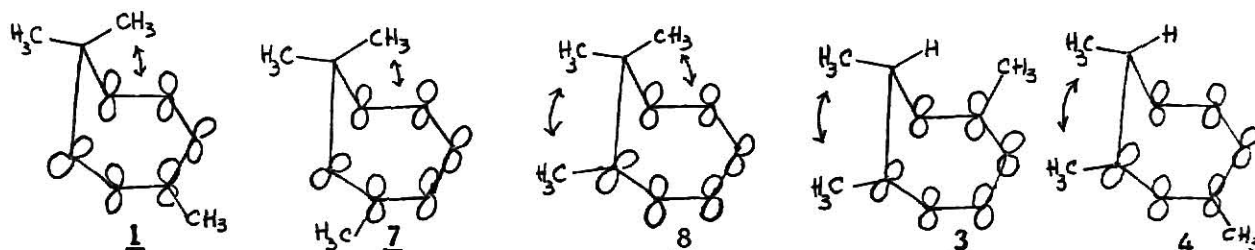
Finally, the activation energies for 1,3,7-TMCHT (4) and 1,5,7-TMCHT (3) ( $m/e=134 \rightarrow m/e=119$ , 2.92ev and 2.42 ev,  $m/e=119 \rightarrow m/e=91$ , 3.03ev and 3.32ev) follow the same trend as for the other TMCHTs (eq. 24, 25).



Loss of a hydrogen from these compounds does not seem to be important. The  $[M-H]^+$  ion intensities for the 1,5,7-TMCHT (3) and 1,3,7-TMCHT (4) are only 4.7% and 2% respectively at 50ev. This is explained by the fact that the loss of a more stable methyl radical is preferred over the loss of a hydrogen atom.

1,5,7-TMCHT (3) and 1,3,7-TMCHT (4) are more stable compared with 3,7,7-TMCHT (1), 2,7,7-TMCHT (7) and 1,7,7-TMCHT (8) where a methyl must be situated unfavorably above the  $\pi$ -orbitals. This does not show up in the IP values, but it does show up in the activation energy. The activation energies for the 7,7-disubstituted TMCHTs would be expected to be and are lower for the loss of methyl in this system.

A methyl group substituted on the 7-position of cycloheptatriene will be expected to have a configuration in which the methyl group is away from the  $\pi$ -orbitals to reduce steric repulsion between the methyl and the  $\pi$ -orbitals. By doing so, however, it cannot avoid any interaction with the substituent on carbon 1. Compound 1,7,7-TMCHT (8) has methyls in which one has to be situated above the  $\pi$ -orbitals of the triene and the other is close to the 1-methyl group. The 3,7,7-TMCHT (1) and 2,7,7-TMCHT (7) are expected to have the methyl- $\pi$ -orbital interaction, while the 1,3,7-TMCHT (4) and 1,5,7-TMCHT (3) would have the methyl-methyl interaction if they are to avoid a interaction with  $\pi$ -orbitals.

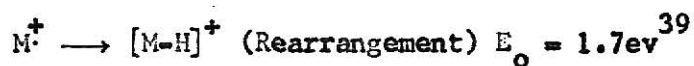


It is also seen that 6-isopropenyl-1-methylcyclohexa-1,4-diene (12) and 3-isopropenyl-1-methylcyclohexa-1,4-diene (11) and 2,6,6-trimethylbicyclo-[3.2.0]-hepta-1,4-diene (2) which are postulated to rearrange in their initial loss of methyl, ( $m/e=134 \rightarrow m/e=119$ ), have the lower activation energies for

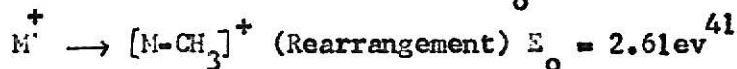
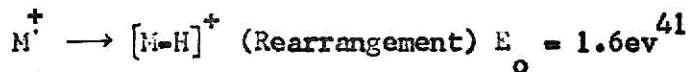
this transition than the other compounds under study. It is likely that rearrangements occur concomitantly with the loss of methyl radical in all three compounds. This observation would be consistent with the idea that rearrangement reactions have the lower activation energies than cleavage.

Probably all losses of methyl in this series of compounds with an activation energy of less than 3ev involve rearrangement. Data from other known rearrangement reactions observed in the mass spectrometer indicate that the activation energy for rearrangement is about 2-3ev.

#### Toluene



#### 7-Methyl-cycloheptatriene



#### Cycloheptatriene





## CONCLUSIONS

The similarities in the mass spectra of isomers illustrate one of the drawbacks of mass spectrometry as a tool for structural analysis as compared to nuclear magnetic resonance or infrared spectroscopy. Unless the isomers have definite structural differences, such as the isopropenyl-1-methylcyclohexa-1,4-dienes and the TMCHTs, it is difficult to distinguish between isomers simply from their mass spectra alone.

Comparison of the different isomers by logical fragmentation considerations and energetics of the different transitions in the mass spectrometer serves as a better method for the analysis of the different compounds when simple mass spectra cannot.

Clastrograms and energetics of the various compounds studied provide similar conclusions, but the former cannot offer as much explanation in detail of the reaction as the latter. On the other hand, the clastrograms have the advantage over mass spectra at particular  $ev$  in that it gives, at a glance, the amount of ion current the major fragment ions carry over a range of ionizing energies.

If the Woodward-Hoffmann rules are applicable to the 3,7,7-TMCHT (1), we would expect it to react in either one of the two ways. It can react via an electronically excited state and show photochemical analogy or via a vibrationally excited electronic ground state and show thermal analogy.

The photochemical rearrangement (as shown in Scheme 1 on p.16) to the isomers 2 to 4, apparently does not go through any intermediate. However, 1,3,7-TMCHT (4) is not a primary product from the starting material but an equilibrium product from further irradiation of 1,5,7-TMCHT (3). Upon equilibration, it would be impossible to distinguish between the 1,5,7-TMCHT (3) from the starting material or from 1,3,7-TMCHT (4). This might explain the differences

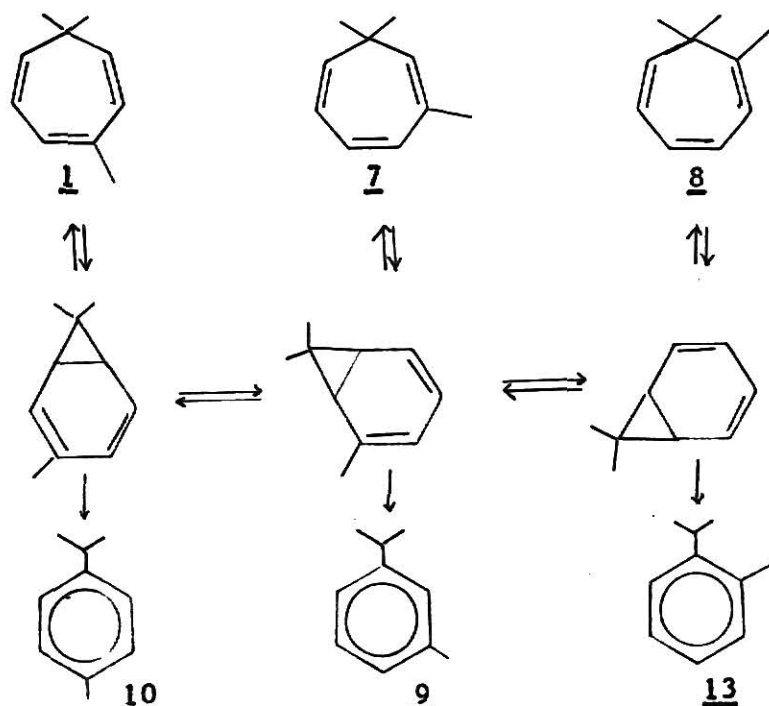
observed among these compounds. It is a little more difficult to explain why 2,6,6-trimethylbicyclo- 3.2.0 -cyclohepta-1,4-diene (2), which is a primary photochemical product, should be so different from the starting material upon electron impact, unless the mass spectral decomposition reactions for the two systems have different energy manifolds. It has already been pointed out that these two isomers, 1 and 2, could share the same structure for their  $m/e=119$  daughter ion after a (?) losing methyl group. But this is not a rearrangement prior to fragmentation, which is where the interest lies in this study. Therefore, we can conclude that the mass spectra, clastrogram and energetics of 3,7,7-TMCHT indicate that equilibration does not occur through an electronically excited state upon electron impact and that the decomposition cannot be said to be a "photochemical" analogy.

Thermally, the 3,7,7-TMCHT (1) is postulated to rearrange to all isomeric products via a norcaradiene intermediate (Scheme 2 on p. 17). It is possible that the life time of the norcaradiene 'intermediate' is long compared to that of the mass spectral time scale so that all isomeric products are considered as subsequent reaction products instead of primary products. The observed spectral similarities with the 1,7,7-, and 2,7,7-TMCHTs and m-, p-cymenes would be accounted for by the fact that these compounds are only one step away from the starting material or that after rearrangement consistent with the low activation energy of the subsequent processes the norcaradienes formed are slightly different in their structure. 3-isopropenyl-1-methylcyclohexa-1,4-diene (11) and 6-isopropenyl-1-methylcyclohexa-1,4-diene (12) show marked differences from all the other isomers, suggesting that unlike the thermal reaction, these compounds are not formed from the norcaradienes under electron impact. Thus, the discrepancies as to whether norcaradiene equilibrate via a direct all carbon transition or a hydride shift through a isopropenyl-1-methylcyclohexa-1,4-diene

structure is eliminated in the mass spectral reactions. The rearrangement of the TMCHTs via a norcaradiene equilibration by an all carbon direct process is estimated<sup>42</sup> to decrease the activation energies for the rearrangement by  $11 \pm 4$  Kcal/mol<sup>29</sup> over the postulated thermal process (Scheme 2) if hydride shift is the equilibration mechanism in that case.

There does not seem to be a definite analogy between the mass spectra, clastrograms and energetics of the thermal isomers of 3,7,7-TMCHT either, although there appears, in several cases, to be some equilibration of structure. A possible scheme in the mass spectrum can be represented by Scheme 4.

Scheme 4



Other reasons for the differences observed for the compounds studied could be the selectivity of mass spectral reactions and the kinetic factor. The Mass spectral reactions may be more selective than the thermal reactions. This appears to be the case for 3,7,7-TMCHT (**1**). Thermolysis yields at least seven products including the starting material, while photolysis is complicated by a subsequent equilibrium reaction. Unimolecular ionic reactions in the mass

spectrometer have a finite and short ( $10^{-6}$  sec.) life time before collection and analysis, and complete equilibration among so many varied and complex structures may not occur.

The kinetic factor might be more important than what has been suggested. The kinetics of non-equilibrium gas phase unimolecular reactions is best seen from the Quasi-Equilibrium Theory (Q.E.T.).<sup>1</sup> The rates of the reactions are represented in a simplified form by eq. 35.

$$k = \nu \left[ \frac{E - E_0}{E} \right]^{n-1} \quad (35)$$

where  $k$  = rate of reaction

$\nu$  = frequency factor

$E$  = total internal energy

$E_0$  = activation energy

$n$  = no. of effective oscillators in the ion

At high energy, it was postulated that the frequency factor is more important than the activation energy in determining the rate of the reactions; at low energy, the reverse is true.<sup>37</sup> The frequency factor is based on very complex manipulation of the vibrations of the molecular ion and complex transition state and therefore is dependent on the molecular structures. The activation energy is based on the relative stability of the reacting species and is therefore dependent on the type of reaction. Rearrangement reaction with lower activation energy is expected to dominate at low internal energy. Nevertheless, these two factors go hand in hand in kinetic considerations.

Summarizing from the above one can conclude the following:

1. No definite photochemical analogy is apparent.
2. There appears to be some thermal analogy. Evidence for similar energy manifolds among 3,7,7-, 2,7,7-, 1,7,7-TMCHTs, m- and p-cymenes (1, 7, 8, 9 and 10)

is observed, but the equilibration to a common energy manifold is incomplete because of kinetic factors.

## REFERENCES

1. H.M. Rosenstock, M.B. Wallenstein, A.C. Warhftig and E. Eyring, *Proc. Nat. Acad. Sci., U.S.*, 38, 667 (1952).
2. J.H. Beynon, R.A. Saunders and A.E. Williams, *Ind. Chim. Belge*, 29, 3111 (1964).
3. O.L. Chapman, P.G. Cleveland and E.D. Hoganson, *Chem. Comm.*, 101 (1966).
4. N.J. Turro, D.C. Neckers, P.A. Leermakers, D. Seldner and P. D'Angelo, *J. Am. Chem. Soc.*, 87, 4097 (1965).
5. C. Fenselau, G.W. Shaffer and W.G. Dauben, *Org. Mass Spec.*, 3, 1 (1970).
6. M.K. Hoffman, M. Bursey and R.E.K. Winters, *J. Am. Chem. Soc.*, 92, 727 (1970).
7. H. Budzikiewicz, C. Fenselau and C. Djarassi, *Tetrahedron*, 22, 1391 (1966).
8. R.G. Norrish and M.E.S. Appleyard, *J. Chem. Soc.*, 8741 (1934).
9. E.K. Fields and S. Meyerson, *Chem. Comm.*, 474 (1965).
10. J.L. Cotter, *Org. Mass Spec.*, 6, 345 (1972).
11. C.J. Tikan, J.E. McClosky and C.M. Banks, *Org. Mass Spec.*, 5, 751 (1971).
12. J. Deutsch and A. Mandelbaum, *Org. Mass Spec.*, 5, 53 (1971).
13. Y. Takenchi, Y. Nomura and F. Furusaki, *J. Org. Chem.*, 37, 502 (1972).
14. R.B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Verlag Chemie GmbH, Academic Press Inc., 1970.
15. R.B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, 87, 395 (1965).
16. W.R. Roth and J. Konig, *Liebigs Ann. Chem.*, 699, 24 (1966).
17. R.A.W. Johnstone and S.D. Ward, *J. Chem. Soc. (C)*, 234 (1968).
18. R.A.W. Johnstone and S.D. Ward, *J. Chem. Soc. (C)*, 1805 (1968).
19. M.J. Bishop and I. Fleming, *J. Chem. Soc. (C)*, 1714 (1969).
20. R.C. Dougherty, *J. Am. Chem. Soc.*, 90, 5780 (1968).
21. F.W. McLafferty, "Interpretation of Mass Spectra", Benjamin, New York, 1966.
22. M.J.S. Dewar, *Tetrahedron, Supp.*, 8, 75 (1967).

23. R.C. Dougherty, J. Am. Chem. Soc., 90, 5788 (1968).
24. R.G. Cooks and D.H. Williams, Chem. Comm., 663 (1968); A.N.H. Yeo, R.G. Cooks and D.H. Williams, *ibid.*, 1269; F.W. McLafferty and R.B. Fairweather, J. Am. Chem. Soc., 90, 5915 (1968); W. Carpenter, A.M. Duffield and C. Djarassi, *ibid.*, 160.
25. R. Kiser, "Introduction to Mass Spectrometry and Its Applications", Prentice-Hall, Inc., Englewood Cliffs, N.J., 1965.
26. L.B. Jones and V. Jones, J. Am. Chem. Soc., 89, 1880 (1967).
27. J.A. Berson and M.R. Willcott III, J. Am. Chem. Soc., 87, 2751 (1965).
28. J.A. Berson and M.R. Willcott III, J. Am. Chem. Soc., 88, 2494 (1966).
29. M.R. Willcott III, Ph.D. Dissertation, Yale University, 1963.
30. H.J. Reich, E. Ciganek and J.D. Roberts, J. Am. Chem. Soc., 92, 5166 (1970).
31. J.A. Berson, M.R. Willcott III, P.W. Grubb and R.A. Clark, J. Am. Chem. Soc., 89, 4076 (1967).
32. R.C. Dougherty, J. Am. Chem. Soc., 93, 7187 (1971).
33. S. Meyerson and E.K. Fields, Acc. of Chem. Res., 2, 273 (1969).
34. E.J. Corey, H.J. Burke and W.A. Remers, J. Am. Chem. Soc., 78, 180 (1956).
35. F.P. Lossing, A.W. Tickner and W.A. Bryce, J. Chem. Phys., 19, 1254 (1951).
36. H.L. Dryden Jr., J. Am. Chem. Soc., 76, 2841 (1954).
37. F.W. McLafferty, T. Wachs, C. Lifshitz, G. Innota and P. Irving, J. Am. Chem. Soc., 92, 6867 (1970).
38. R.G. Cooks, Org. Mass Spec., 2, 481 (1967).
39. S. Meyerson, P.N. Rylander, J. Chem. Phys., 27, 901 (1957).
40. J.R. Majer, and C.R. Patrick, Trans. Faraday Soc., 58, 17 (1962).
41. F. Meyer, P. Haynes, S. McLean and A.G. Harrison, Can. J. Chem., 43, 211 (1965).
42. J.A. Berson, Acc. of Chem. Res., 1, 152 (1968).

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A STUDY OF ANALOGY IN 3,7,7-TRIMETHYLCYCLOHEPTATRIENE  
REACTIONS BY ELECTRON IMPACT, THERMAL AND PHOTOCHEMICAL MEANS

by

MARGARET SHUK-YEE CHAN

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## ABSTRACT

3,7,7-Trimethylcycloheptatriene (1) was studied in an attempt to establish a photochemical or thermal analogy for the electron impact induced reaction of this compound. Pyrolysis of 3,7,7-Trimethylcycloheptatriene (1) gives seven major products including the starting material. They are 3,7,7-Trimethylcycloheptatriene (1), 2,7,7-Trimethylcycloheptatriene (7), 1,7,7-Trimethylcycloheptatriene (8), m-cymene (9), p-cymene (10), 3-Isopropenyl-1-methylcyclohexa-1,4-diene (11), and 6-Isopropenyl-1-methylcyclohexa-1,4-diene (12). Photolysis of the same compound (1) gives only three other isomers: 2,6,6-Trimethylbicyclo-[3.2.0]-hepta-1,4-diene (2), 1,3,7-Trimethylcycloheptatriene (4) and 1,5,7-Trimethylcycloheptatriene (3).

The mass spectra of all the isomeric compounds were taken at high and low ev. The major peaks on the mass spectra for all the compounds are the molecular ion,  $m/e=134$ , and fragment ions  $m/e=119$ ,  $m/e=91$ . These ions comprise more than 80% of the total ion intensities at all voltages. The ion currents for each of the major ions for these series of compounds over an energy range of 20ev to 12ev, were plotted in individual clastrograms and compared. The ionization potential of  $m/e=134$  and the appearance potentials of  $m/e=119$  and  $m/e=91$  for the various compounds were also determined for comparison.

Results indicated that there are no absolute similarities among the isomers. A photochemical analogy does not seem to exist for the electron impact induced reaction of 3,7,7-Trimethylcycloheptatriene (1). The possibility of a thermal analogy, however, cannot be ruled out. Dissimilarities are explained in terms of secondary reaction products, selectivity of mass spectral reactions and a kinetic effect.