

PHOTOCHEMISTRY OF LEWIS ACID COMPLEXES OF EUCARVONE

by

HOR YEE-CHEE, B.A.

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HOR YEE-CHEE

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AUTHOR: Hor Yee-Chee, B.A. (Agnes Scott College, Decatur, Georgia, U.S.A.)

SUPERVISOR: Dr. R.F. Childs

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SCOPE AND CONTENTS:

This thesis describes several attempts to determine the multiplicity of the excited states involved in the photoisomerization of 2,6,6-trimethylcyclohepta-2,4-dienone, eucarvone. Attempts were made to quench any triplet state involved in the photorearrangement of protonated eucarvone (1H). However, in view of the low triplet energy of 1H, it was not possible by this method to prove or rule out any involvement of a triplet excited state.

A further method used was to try and incorporate a heavy atom into eucarvone and so promote intersystem crossing. To this end the preparation, thermal stability and photochemistry of the boron trihalide complexes of eucarvone, 1-BX₃ (X = F, Cl and Br) have been studied. Eucarvone reacts with various Lewis acids to generate σ -complexes in which the Lewis acid is bonded to the carbonyl oxygen. The zwitterions have been characterized using pmr, ¹³C nmr and UV spectroscopy. These zwitterions exhibit temperature

dependent pmr and ^{13}C nmr spectra. This can best be explained in terms of a non-planar seven-membered ring and the interconversions of two conformations.

An investigation of the photoisomerizations of 1-BX₃ has shown that a new photoproduct, 2-methyl-6-isopropylphenol, was obtained after quenching the solutions of the complexes. The photoisomerizations of protonated eucarvone and the BF_3 and BCl_3 complexes of eucarvone are similar at least in as much as the same types of products are formed. The photoisomerization of the BBr_3 complex of eucarvone is more complicated in view of the extreme photolability of one of the photoproducts, namely the complex of 3,7,7-trimethylbicyclo[4.1.0]hept-2-en-4-one. The photochemical and thermal stability of the other photoproducts of 1-BX₃ were examined.

A mechanism has been suggested to account for the formation of photoproducts of 1-BX₃.

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I wish to thank Mr. Brian Sayer for running the Bruker WH90 MHz pmr spectra and 22.63 MHz ^{13}C nmr spectra. I would also like to thank Mr. Ian Thompson for running the 100 MHz pmr spectra and Mr. Claus Schonfeld for technical assistance.

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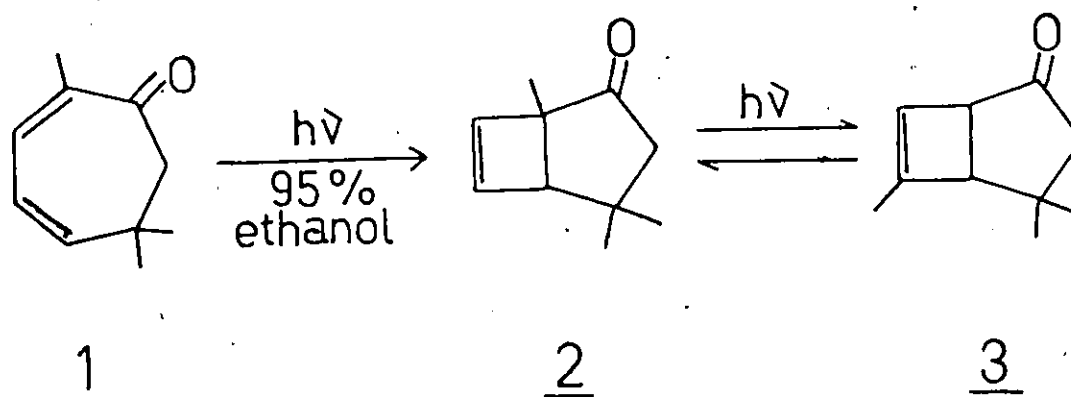
Glpc retention times of the photoproducts (after
quenching) of 1H and 1-BX₃ relative to 1.

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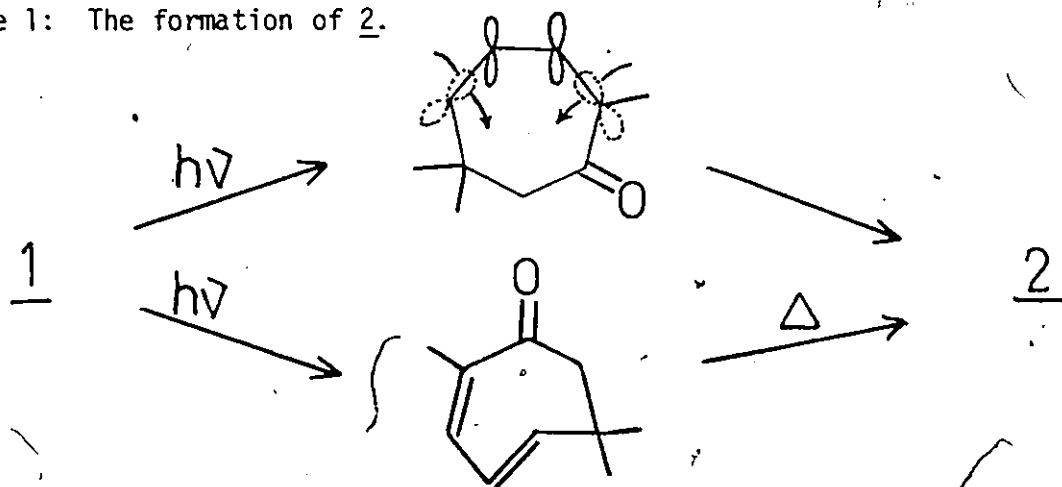
The extreme propensity of eucarvone, 1, to undergo light-induced transformations was noted in the literature as early as 1960. Büchi and Burgess, who investigated the photolysis of 1 in 95% ethanol, reported that two isomeric ketones, 2 and 3, were formed on irradiation⁶. The former was shown to originate from the irradiation of 1, while the latter derived from further reaction of 2. The two isomers could be equilibrated photochemically in n-hexane, containing some triethylamine, to a mixture of



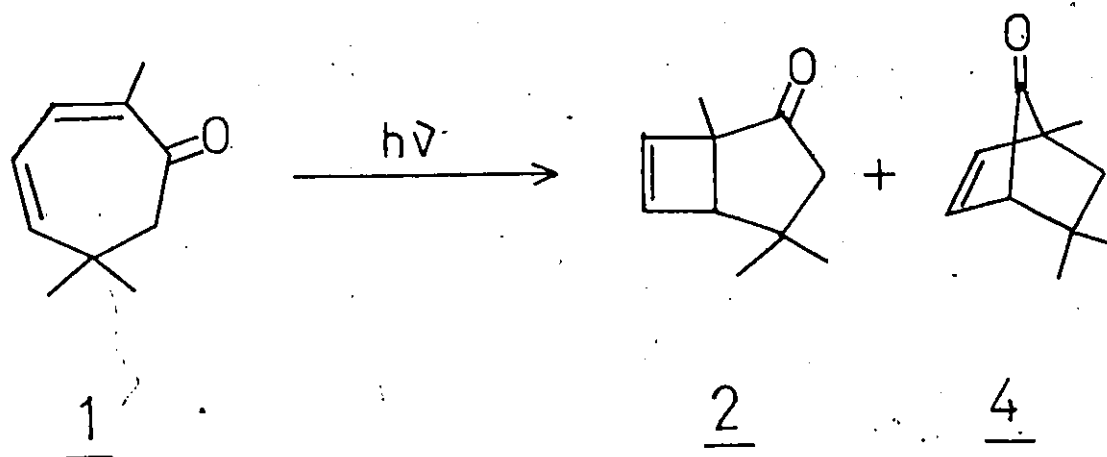
four parts of 2 and one part of 3. This photoisomerization (2 \rightarrow 3) was the first reported example of a photolytic 1,3-acyl migration in a β,γ -unsaturated ketone. In refluxing benzene containing a small amount of *p*-toluenesulfonic acid, 2 rearranged thermally to 3. It was claimed that this acid-catalyzed reaction provided evidence for a cis ring juncture in 2.

Quantitative studies reported by Schuster on the conversion of 1 to 2 indicated that this is a rather inefficient process in benzene solution ($\phi = 0.0025$). Moreover, Schuster found that the efficiency of the photoisomerization of 1 was increased with solvent polarity⁷. Quenching and sensitization studies suggested that 2 was formed from both a singlet state (60%) and a triplet state (40%) of 1, the energy of the latter state being 61 ± 1 kcal/mole. The formation of 2 from 1 can be thought of as involving a symmetry allowed closure which would be predicted to occur photochemically in a disrotatory fashion⁸. However, recent results of Hart⁹ would suggest that the formation of 2 could involve a photo *cis*/*trans* isomerization of eucarvone followed by a thermal cycloaddition.

Figure 1: The formation of 2.

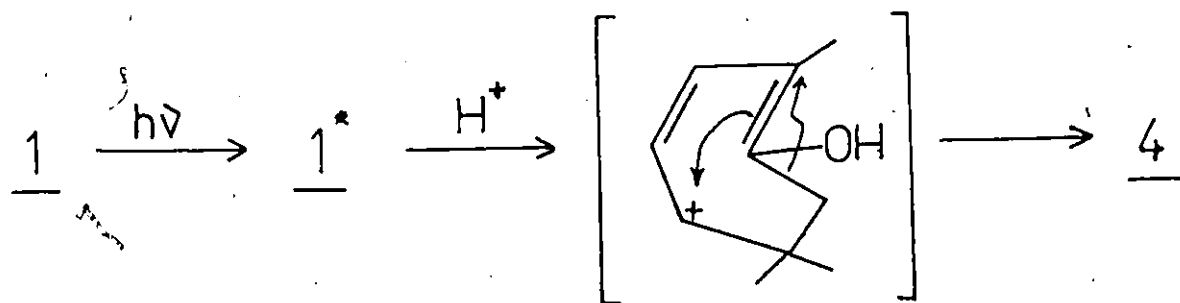


Subsequent to the work of Büchi and Burgess, Hurst and Whitham reported that another product was obtained on irradiation of 1 in 40% aqueous acetic acid with sunlight¹⁰. This new product was identified as 1,5,5-trimethyl-norborn-2-en-7-one, 4, and was formed in approximately

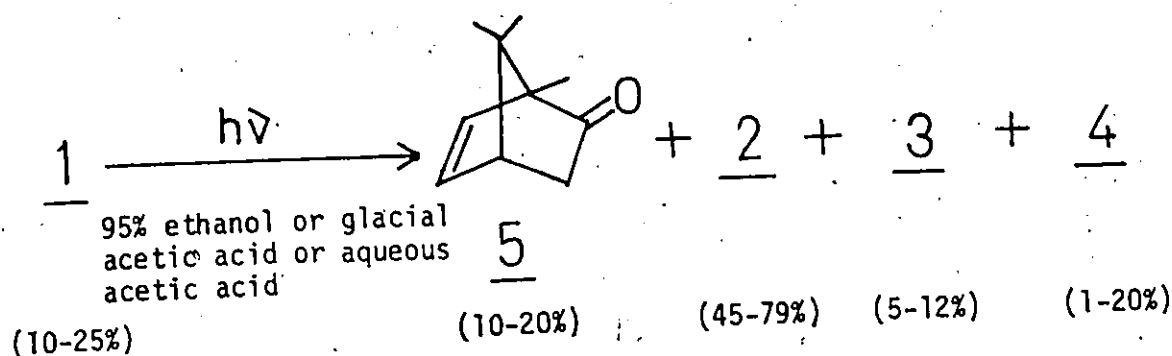


equal amounts with 2. The authors postulated that since 4 was only produced in acidic solvents, its formation might involve a protonated (π, π^*) excited state of 1.

Figure 2: The formation of 4 according to Hurst and Whitham.

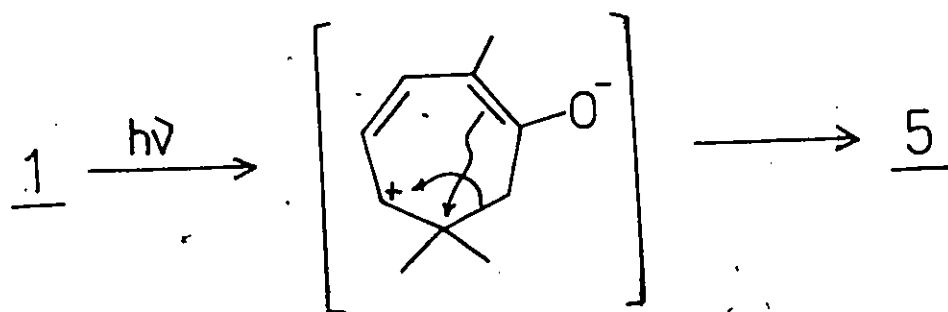


Studies by others demonstrated that the photochemistry of eucarvone was even more complex. Schuster reported that another photoproduct, identified as dehydrocamphor, 5, was formed in a variety of solvents. As shown below, the product distribution was observed to vary with the solvent¹¹.

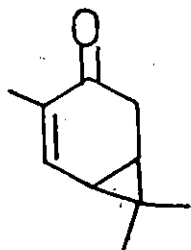


To account for the formation of these products, Schuster proposed that either an ionic intermediate was involved or several competing processes participated concurrently, the rates of which depended upon the nature of the solvent.

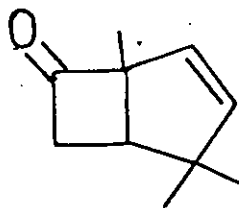
Figure 3: The formation of 5 as suggested by Schuster.



Several years later, Takino and Hart¹² found that the absorption maximum of 1 in the ultraviolet region was red-shifted from 303 nm in ethanol, to 310 nm in trifluoroethanol and to 318 nm when absorbed on silica-gel in cyclohexane. No appreciable change in intensity was detected as the solvent was changed. These workers reported that when solutions of 1 in a silica-gel cyclohexane slurry or in trifluoroethanol were photolyzed, a complex mixture of products resulted. In addition to the previously reported products, two new products were observed and identified as 6 and 7.



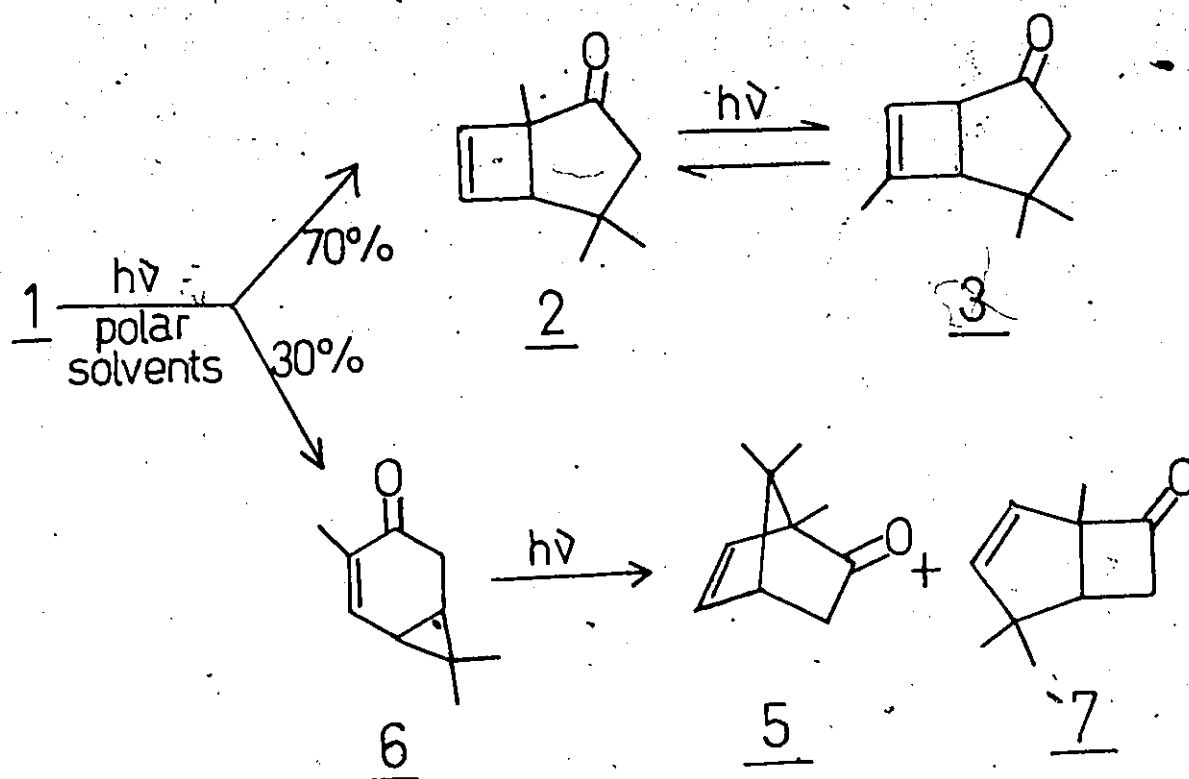
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The photoisomerization of 1 in silica-gel cyclohexane or trifluoroethanol was found to be more efficient than that in cyclohexane and moreover in the non-polar solvent, cyclohexane, only the isomerization of 1 to 2 was observed. In separate irradiations it was found that the new product 6 rearranged in silica-gel cyclohexane to give 5 and 7. The authors concluded that 1 isomerized in highly polar media via two routes that resulted in only 2 and 6 as primary products. The other products were considered to arise by further photoreactions of 2 and 6.

Figure 4: Photoisomerization of eucarvone in polar media.



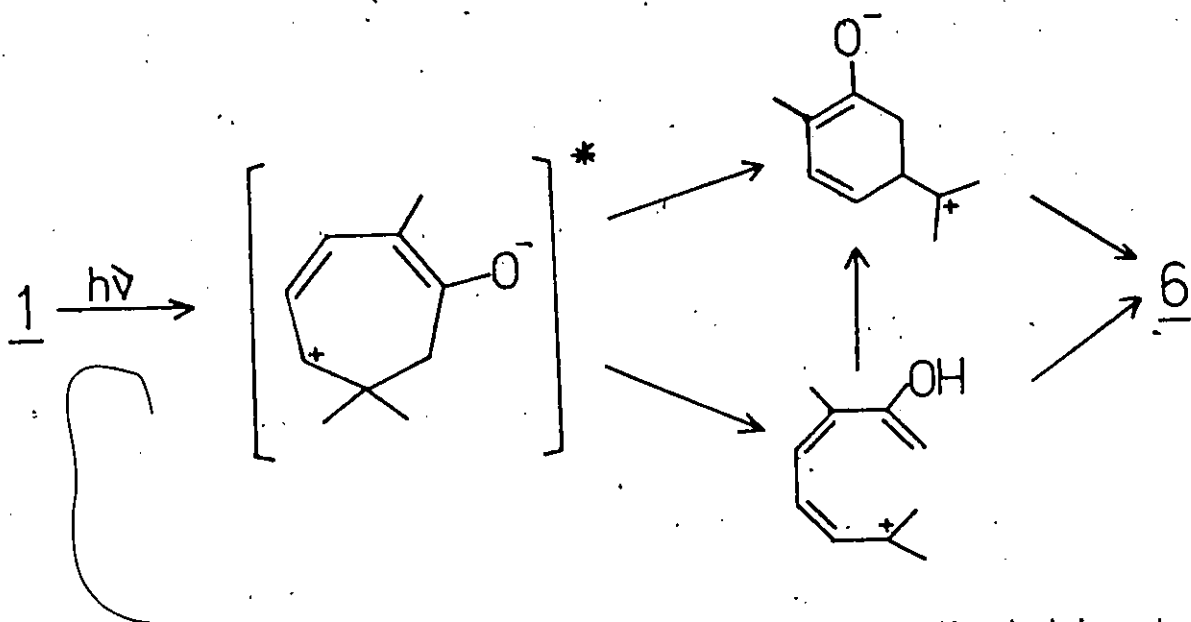
Several months later, Hart and Takino published a full paper in which they elaborated on their earlier results¹³. Since it was found that neither cyclohexa-1,3-diene nor piperylene could appreciably quench the formation of 2 and 6, it was suggested that the two products might come from the same excited singlet state of 1 or from two different states, close in energy.

Since 6 was not obtained in acidic solvents, it was further suggested that trifluoroethanol or silica-gel cyclohexane did not act as proton donors and that a protonated excited state of 1 was not involved in the formation of 2 and 6. Instead the authors postulated that these highly polar solvents might have changed the relative energies of the

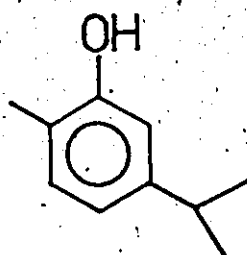
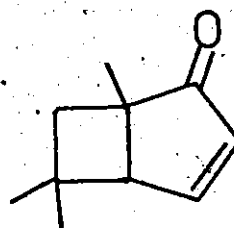
(n, π^*) and (π,π^*) excited states of eucarvone and that the products 2 and 6 might arise from different excited states.

The formation of 6 was suggested to occur via a stepwise process involving, probably, several ionic intermediates, Figure 5. A concerted $\sigma_{2a} + \pi_{2a}$ pathway was disfavoured on the basis that 6 was obtained in polar media.

Figure 5: Hart's and Takino's proposed mechanism for the formation of 6.



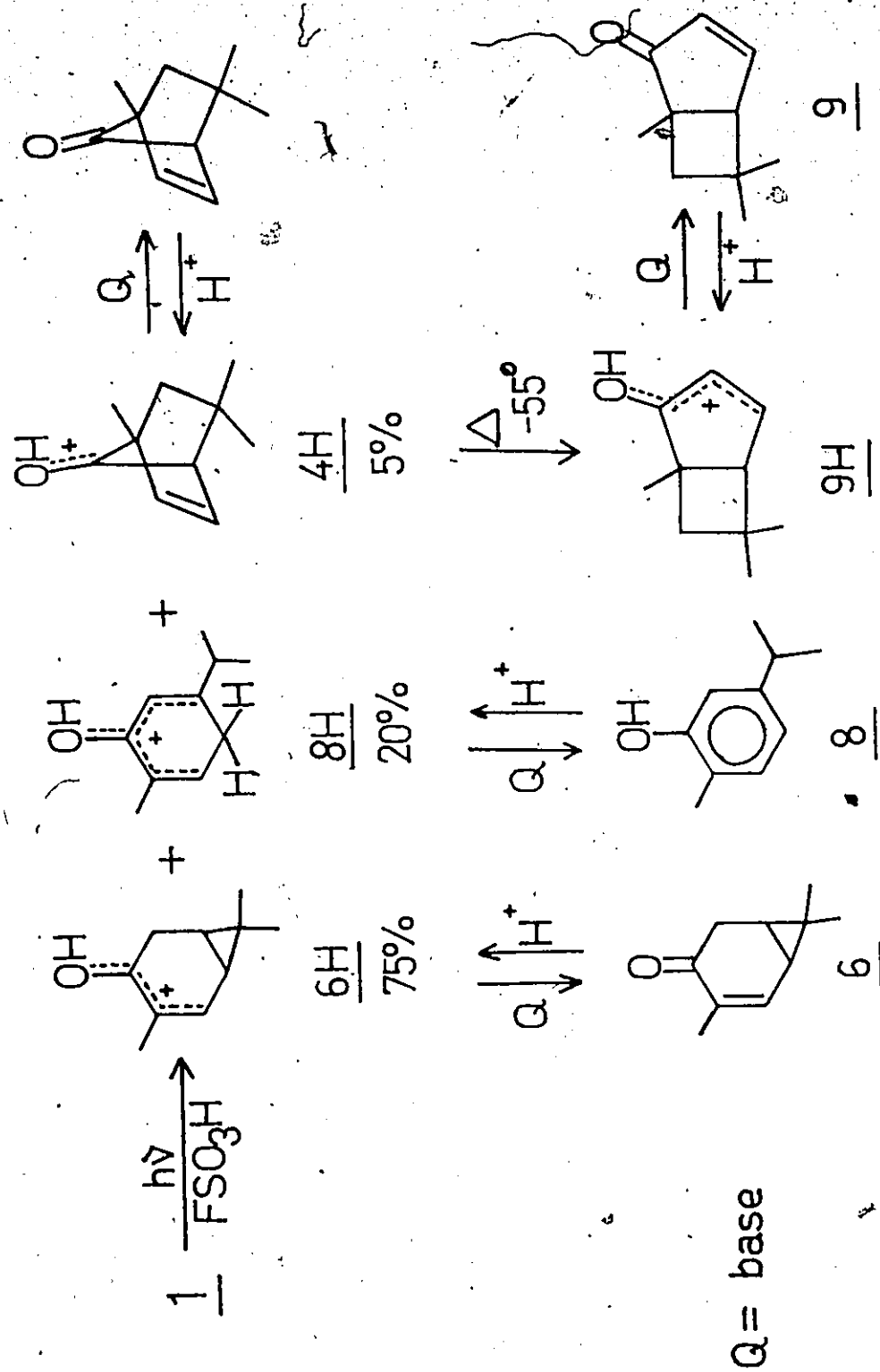
At the time of Hart and Takino's work, Childs and Hine had investigated the photochemistry of eucarvone in $\text{FSO}_3\text{H}^{14}$ and observed a parallel between the photoisomerization of the protonated and neutral dienone. The absorption maximum of 1 in the ultraviolet region was reported to have shifted bathochromically from 303 nm in methanol to 400 nm in 96% H_2SO_4 . Upon low temperature irradiation (-75° , $\lambda > 370$ nm), protonated 1 (1H) cleanly rearranged to give three products which, after quenching the acid solution, were identified as 6, 8 and 9. Separate experiments indicated

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that 9H was a thermal product of 4H in FSO_3H ($t_{1/2} \approx 10$ min at -55°) and that 4H and not 9H was the initial product, Figure 6. Although the major product 6H could be isomerized to 8H either thermally ($t_{1/2} = 16$ min at -15°) or photochemically in FSO_3H , it was found to be stable under the conditions of the photoisomerization of 1H. The protonated phenol 8H was then the only new photoproduct, probably derived from the same intermediate that also leads to 6H.¹⁴

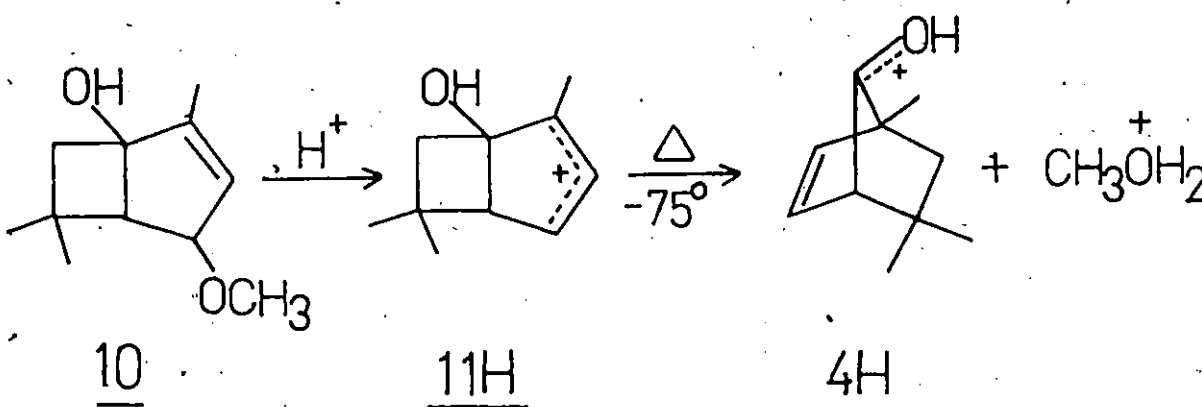
As the protonation of a carbonyl compound, such as an aldehyde or a ketone, is known to invert the relative energies of the n, π^* and π, π^* states¹⁵⁻¹⁷, it is expected that in FSO_3H all the products formed must derive from (π, π^*) state or states. Thus the absence of any products related to protonated 2 in the photoisomerization in FSO_3H , was suggestive that in more conventional media, 2 had its origin in a (n, π^*) state (or states). Conversely, products such as 6 most likely derived from a (π, π^*) state (or states).

Figure 6: Photoisomerization of Eucaryone in FSO_3H .



$Q = \text{base}$

In the investigation of the photochemical behaviour of eucarvone in buffered methanolic solutions of constant polarity but differing acidity, Childs and Hine observed a new photoproduct in addition to 2, 4 and 6.¹⁸ This new product which was identified as 10, gave 4H when dissolved in $\text{FSO}_3\text{H-SO}_2\text{ClF}$ at -75° .



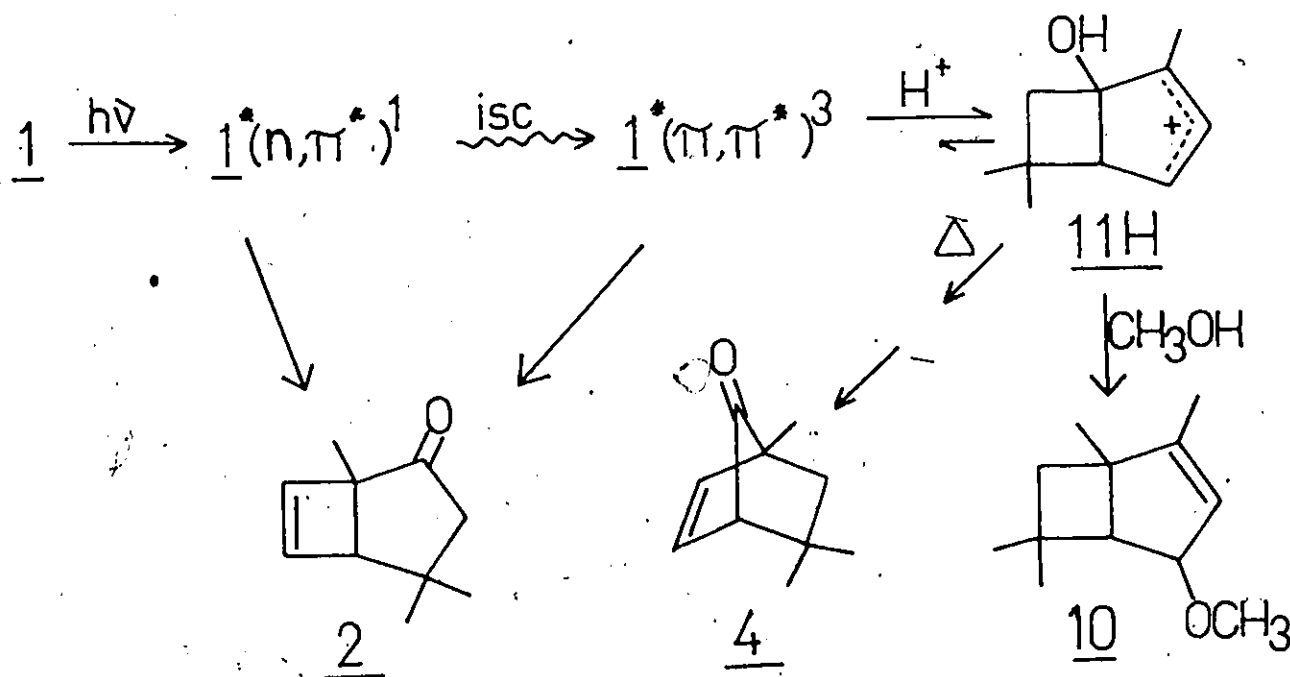
It was suggested that 10 was produced in the irradiation of 1 via a nucleophilic capture by methanol of an ionic intermediate, 11H, which could also lead to 4H. Since 4 and 10 were obtained in more acid solvents and exclusively at the expense of 2 (Table 1), the authors proposed that they arose from the same excited state as 2 and that they occurred in the protonation of the $(\pi, \pi^*)^3$ state of 1. In the absence of protonation, this triplet state led to 2. Schuster had suggested that the lowest triplet would have a (π, π^*) configuration on the basis of the absorption spectrum of 1.⁷ The overall mechanistic scheme proposed is shown in Figure 7.

Table 1: Product Distribution as a Function of Solvent Acidity.^a

pH	% Recovery	% Conversion	Product ratios %			
			<u>2</u>	<u>4</u>	<u>6</u>	<u>10</u>
6.16	98	9.5	73	nd ^b	27	nd ^b
3.34	98	8.5	70	≤0.5	29	≤0.5
1.62	100	8.5	53	2	27	18
0.70	97	8.5	43	4	28	23

a. Results taken from reference 18.

b. Non-detectable

Figure 7: Childs' and Hine's proposed relationship between the formation of 2, 4 and 10.

The results given in Table 1 show that protonation is essential for the formation of 4 and 10. Their formation can be considered to occur by a disrotatory motion resulting in bonding between C_1 and C_5 in a protonated

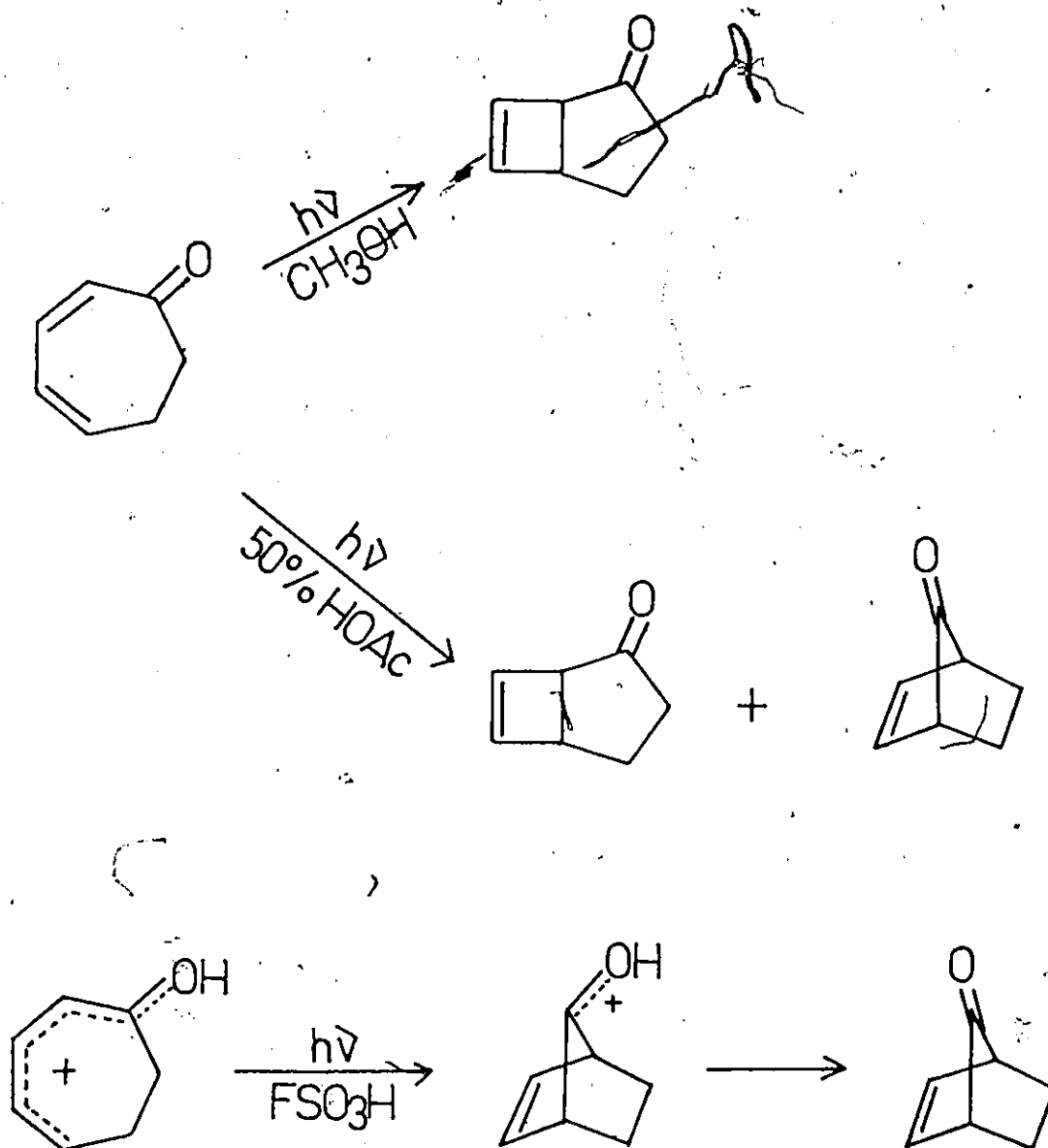
excited state of 1. This process was thought to be of higher energy than the alternate route, i.e. C₂-C₅ bonding to form 2, unless prior protonation of the excited state occurred.¹⁸

Other Related Systems

Several other dienones¹⁹ are known to undergo photoisomerization reactions and again a parallel seems to exist between the photoisomerization of the dienones and their protonated analogues.²⁰ As is shown in Figure 8, cycloheptadienone shows a similar type of photochemical behaviour to that of eucarvone.²¹

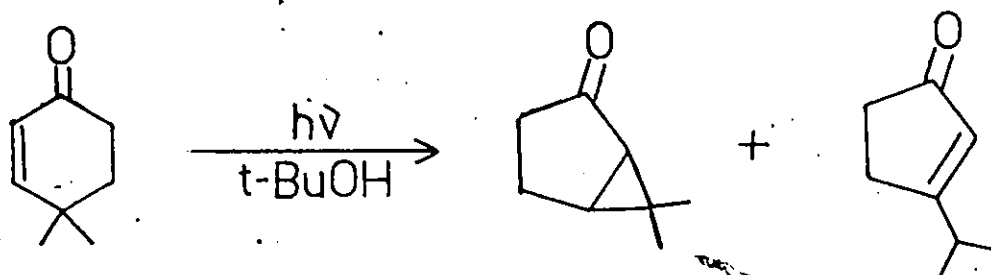
The aim of the work described in this thesis was to investigate the multiplicity of the excited states of eucarvone that give rise to the various products. In particular, it was intended to test the proposed scheme of Childs and Hine and to determine whether compound 4H originated from a triplet excited state of protonated eucarvone. The results of several approaches to this problem will be described in this thesis.

Figure 8: Photoisomerization of cyclohepta-2,4-dienone.



RESULTS AND DISCUSSION

One widely employed method of determining the spin multiplicity of the excited state responsible for a photochemical reaction is to examine the effect of quenchers on the reaction.^{22,23} For example, 4,4-dimethyl-2-cyclohexenone gives two primary products on irradiation. In the presence of a triplet quencher, di-*t*-butyl nitroxide, the yields of the two products were decreased as the concentration of the quencher was increased. A linear relationship was found between the amount of product formed and the concentration of the nitroxide.²⁴



Although quenching is a useful technique in regular media, it cannot be easily employed in a super acid system since the acid is usually capable of protonating any suitable quencher. Sulfur dioxide is a known triplet quencher²⁵ that can dissolve in FSO_3H without being protonated. The energy of the first triplet state of SO_2 is reported to be 73.5 kcal/mole,²⁶

which is higher than that estimated for the first triplet state of protonated eucarvone, 55 ± 1 kcal/mole.^{8a} Nevertheless, in view of the uncertainty in this estimate of the triplet energy of protonated eucarvone, the effect of the addition of SO_2 upon the photoisomerization was examined.

1(a) The Irradiation of Protonated Eucarvone

The addition of 1 to FSO_3H at -78° resulted in the formation of the cation 1H, the pmr spectrum of this deep yellow solution, Table 5, was identical to that previously reported.¹⁴

Solutions of 1H in FSO_3H , contained in clear-walled nmr tubes, were irradiated under the same conditions as reported by Childs and Hine (-75° with light of $\lambda > 370$ nm). Low temperature neutralization of the acid solution yielded 4, 6 and 8 as previously reported.¹⁴ However, the product ratio 1:7:2 respectively, which was completely reproducible, is different to that previously reported, 1:15:4 respectively. The reason for the dissimilarity in product distribution is not known.

(b) Attempted Quenching with SO_2

The irradiations of 1H in FSO_3H were repeated under identical conditions to those described above but with varying amounts of SO_2 added. The results of this study are given in Tables 2 and 3.

The results in Table 2 show that as far as can be detected, the addition of SO_2 to the FSO_3H solution of 1H does not alter the product distribution at all. The ratio of the three photoproducts does not change even when very large amounts of SO_2 were added to the acid. However, as

Table 2: Effect of SO_2 on the Photoproduct Distribution of Protonated Eucarvone in FSO_3H .

SO_2 Added	Relative % ^a		
	<u>6</u>	<u>8</u>	<u>4</u>
0	72	17	11
10	72	18	10
15	73	17	11
20	70	19	11
30	69	20	11

a. $\pm 2\%$

Table 3: Effect of SO_2 on the Relative Quantum Efficiency of Irradiation of Protonated Eucarvone in FSO_3H .

% SO_2 added	10%	20%	30%
% conversion ^a with SO_2 added	71	70	70
% conversion ^a without SO_2	40	46	44

a. % of 1 reacted.

is shown in Table 3, the relative quantum efficiency of the photoisomerization of 1H is altered as SO_2 is added. The relative quantum efficiencies were measured by placing identical nmr tubes containing the same amount of 1H dissolved in the same volume of either FSO_3H or $\text{FSO}_3\text{H}/\text{SO}_2$, in a light beam for identical length of times. Although some fluctuation in the output of the lamp could have been expected, the results obtained by this procedure could be reproduced to $\pm 2\%$ and consistently showed that the amount of 1H isomerized was increased as SO_2 was added to FSO_3H .

The lack of change in the ratio of the photoproducts and enhancement in the overall quantum efficiency of the photoisomerization of 1H, clearly shows that SO_2 is not quenching a triplet state of 1H that leads to a photoproduct. This does not, however, rule out the involvement of such a triplet state as if it were of lower energy than the triplet state of SO_2 , then no quenching could be expected. It is not certain at this stage why SO_2 alters the relative quantum efficiency of this photoisomerization. Under the condition of the experiment it would not be expected that SO_2 could be absorbing any of the incident light, since the first allowed absorption band of SO_2 is reported to lie between 2400 and 3200 Å.²⁷

An alternative technique that has been used to probe the multiplicity of excited state involved in a photochemical reaction is to examine the effect of the introduction of heavy atoms into the system. It has been established that heavy atoms can enhance the rate of intersystem crossing.^{28,29} For instance, the results in Table 4 show²⁸ that substitution of naphthalene by one iodine atom increases the ratio of the quantum yields for phosphorescence and fluorescence $(\phi_p/\phi_f)^0$ by a factor of nearly 10^4 . This is thought to result mainly from the increased probability of the occurrence of intersystem

crossing of the S_1 to T_1 state of naphthalene as iodine is introduced into the molecule.

Table 4: Effect of Halogen Substitution in Naphthalene on the Rates of Intersystem Crossing.^a

Compounds	ϕ_p/ϕ_f
Naphthalene	0.09
1-Fluoronaphthalene	-
1-Chloronaphthalene	5.2
1-Bromonaphthalene	164
1-Iodonaphthalene	>1000

a = Data are from reference 28.

ϕ_p, ϕ_f = quantum yield for phosphorescence and fluorescence, respectively.

Thus an alternative approach to the question of the excited states involved in the photoisomerization of protonated eucarvone would be to examine the effect of the introduction of a series of halogen atoms into the molecule. One possible way that this could be done is to use a series of Lewis acids, bearing different halogen atoms, to complex with the oxygen of 1. As the preparation of boron trihalide complexes of certain ketones³⁰⁻³³ has been described and these complexes appear to be well behaved, it was decided to investigate the preparation and photochemistry of boron trihalide complexes of eucarvone. Subsequent sections of this thesis deal with these studies.

2(i) Complexation of Eucarvone with Lewis Acids

Eucarvone, 1, was reacted with the boron trihalides, BX_3 ($X = F, Cl, \text{ and } Br$), by condensing the appropriate boron trihalide into a solution of 1 in $CDCl_3$ or CH_2Cl_2 at -78° . These reactions were carried out on a high vacuum line to ensure that water was kept out of the solutions. The spectroscopic properties of the resulting yellow solutions indicated that the various boron trihalides had, in each case, formed a complex with 1.

Dilute solutions of these complexes were stable at room temperature and could be quenched at 0° in a suspension of $NaHCO_3$ in ether, to quantitatively regenerate the original ketone. The complexes slowly decomposed on standing at room temperature for a few hours. This decomposition was somewhat more rapid when BBr_3 was used as the Lewis acid or when the concentration of the complexes was increased.

The pmr spectra of the solutions of 1 complexed with the various Lewis acids, were not found to change as more than an equimolar amount of the Lewis acid was added. This would indicate that only a 1:1 adduct between the Lewis acid and the ketone is formed. This 1:1 adduct formation is not unexpected in view of other reported studies of ketone: boron trihalide complexes.³⁴⁻³⁶

In all cases, the formation of a Lewis acid complex of 1 was shown by the downfield shift of the nmr signals of the complex as compared to those of the neutral ketone, Tables 5, 6 and 7. The pmr spectra of 1H and the three complexes, 1- BX_3 , are all very similar. This would clearly indicate that the Lewis acid has coordinated with the carbonyl oxygen and not to the diene moiety of 1.

Table 5: Pmr Spectra of Eucarvone, Protonated Eucarvone and Lewis Acid Complexes of Eucarvone.^a

Compound	Chemical Shifts (ppm)						Coupling Constants ^b (Hz)
	H ₃	H ₄	H ₅	H ₇	C ₂ methyl	C ₆ methyls	
<u>1</u> ^c	6.36	5.68	5.90	2.53	1.84	1.03	J _{3,4} = 8.0 J _{4,5} = 11.3
<u>1H</u> ^d	7.86	6.87	6.50	3.33	2.22	1.28	J _{3,4} = 8.2 J _{4,5} = 11.5
<u>1-BBr₃</u> ^e	7.62	6.68	6.34	3.72	2.14	1.27	J _{3,4} = 8.0 J _{4,5} = 11.5
<u>1-BCl₃</u> ^e	7.53	6.62	6.27	3.62	2.11	1.21	J _{3,4} = 8.0 J _{4,5} = 11.5
<u>1-BF₃</u> ^e	7.50	6.60	6.24	3.64	2.10	1.20	J _{3,4} = 8.0 J _{4,5} = 11.5

a/ HA-100 spectra using TMS (δ 0.00) for 1 and CH₂Cl₂ (δ 5.30) for 1H,
1-BBr₃, 1-BCl₃, and 1-BF₃, as internal standards.

b/ \pm 0.3 Hz.

c/ in CDCl₃ at room temperature.

d/ in FSO₃H at -50°.

e/ in CDCl₃ at -50°.

Table 6: Carbon-13 Nuclear Magnetic Resonance Spectra of Eucarvone and Lewis Acid Complexes of Eucarvone.^a

Carbon ^d	Chemical Shifts (ppm)			
	<u>1</u> ^b	<u>1-BF₃</u> ^c	<u>1-BCl₃</u> ^b	<u>1-BBr₃</u> ^c
1	200.1	210.6	210.9	209.8
2	138.5	138.0	138.3	138.2
3	133.8	157.5	156.8	159.9
4	122.2	124.7	124.7	125.3
5	148.8	159.7	159.6	161.0
6	33.1	33.4	33.5	33.3
7	54.1	47.2	47.6	47.1
C ₂ methyl	19.9	20.2	20.1	20.3
C ₆ methyls	26.9	24.5	24.8	24.3

a/ 22.63 MHz Spectra in CDCl₃ using TMS (0.00 ppm) for 1 and CDCl₃ (77.21 ppm) for the Lewis acid complexes of 1, as internal standards.

b/ at room temperature.

c/ at -40°.

d/ carbon resonances were assigned on the basis of gated decoupling and selective proton decoupling spectra.

Table 7: Change in ^{13}C Chemical Shifts on Protonation or Complexation of Eucarvone.^a

Carbon	Carbon Shifts (ppm)			
	^1H ^b	1-BF_3	1-BCl_3	1-BBr_3
1	7.1	10.5	10.8	9.7
2	- 4.2	- 0.5	- 0.2	- 0.3
3	32.6	23.7	23.0	26.1
4	3.9	2.5	2.5	3.1
5	19.5	10.9	10.8	12.2
6	1.5	0.3	0.4	0.2
7	- 4.6	- 6.9	- 6.5	- 7.0
C ₂ methyl	- 2.2	0.3	0.2	0.4
C ₆ methyl	- 3.3	- 2.4	- 2.1	- 2.6

a/ ± 0.1 ppm, negative sign indicates upfield shift.

b/ Results taken from reference 40.

The similarity of the structure of 1H and the three complexes is also shown by their comparable ultraviolet absorption spectra, Table 8. This provides further support for the zwitterionic nature of the complexes and the site of coordination. A shift of this magnitude, of what would appear to be a $\pi-\pi^*$ band, is consistent either with O-coordination³⁷ or protonation³⁸.

Table 8: U.V. Spectra of Eucarvone, Protonated Eucarvone and Lewis Acid - Complexes of Eucarvone.^a

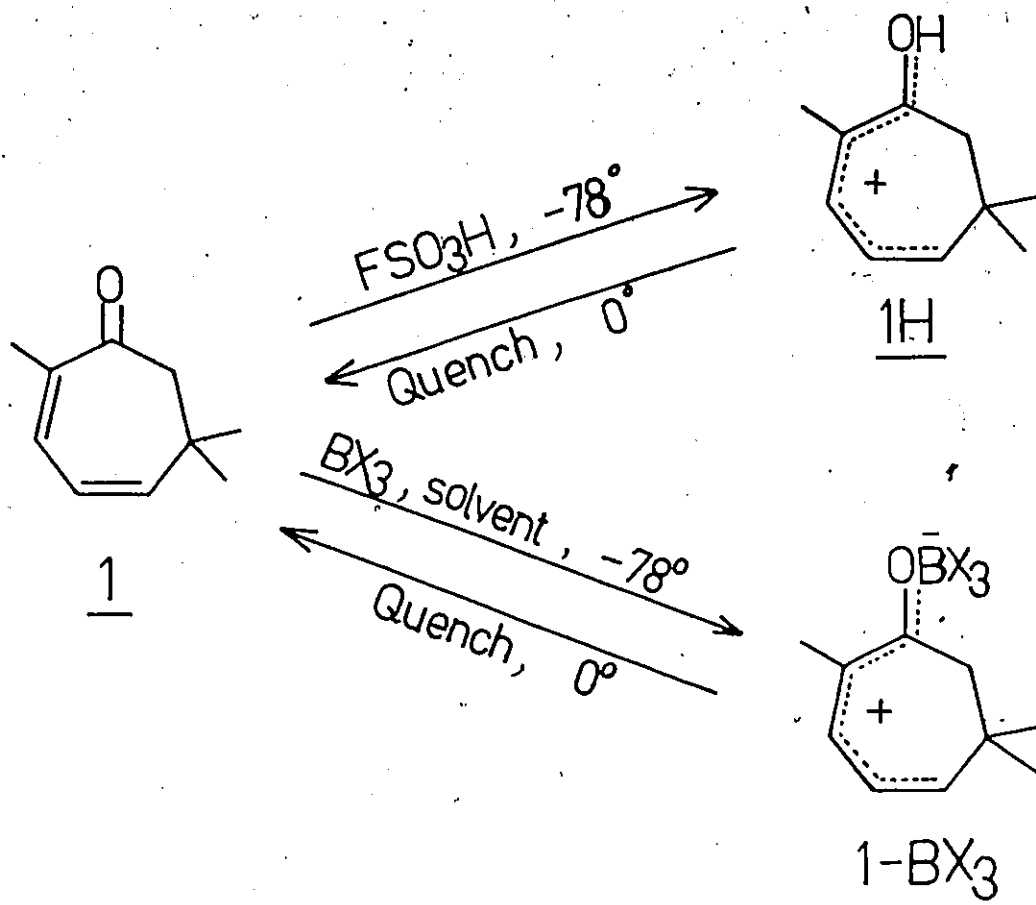
Compounds	Solvent	λ_{\max} (nm)	log ϵ
<u>1</u> ^b	CH ₃ OH	303	3.93
<u>1H</u> ^b	96% H ₂ SO ₄	400	3.63
<u>1-BF₃</u>	CH ₂ Cl ₂	389	3.85
<u>1-BCl₃</u>	CH ₂ Cl ₂	389	3.89
<u>1-BBr₃</u>	CH ₂ Cl ₂	400	3.93

a/ at 25°

b/ Results taken from reference 14.

Taken together, the evidence presented above clearly shows that the structure of the complexes formed on reaction of the various Lewis acids with 1, is 1-BX₃, as shown in Figure 9.

Figure 9: Complexation and Protonation of Eucarvone

(ii) Charge Distribution in 1-BX₃ Complexes

It has been suggested that the changes occurring in the positions of the ^{13}C chemical shifts on the protonation of an enone reflect the changes in charge distribution in the molecule³⁹. In Table 7, the changes in chemical shifts of the various carbon atoms of 1 are shown as the ketone is reacted with either a proton, BF_3 , BCl_3 or BBr_3 . The largest shifts were associated with the resonances of C_3 , C_5 and C_7 , which were all substantially deshielded on reaction. This would suggest that the bulk of the positive charge resides on these carbons and oxygen rather than on C_2 and C_4 . The

much larger deshielding observed for the resonance of C_3 than that of C_5 in 1H, has led Cornelis and Lazzalo⁴⁰ to suggest that a counter ion, FSO_3^- , is specifically associated with the central carbon of the pentadienyl unit, thus inducing more positive charge at this site. This specific solvation would seem to be unlikely in media such as FSO_3H , with its very high dielectric constant⁴¹, and is rendered untenable by the similar effect noted with the 1-BX₃ complexes, where the counterion is not free to associate at this position.

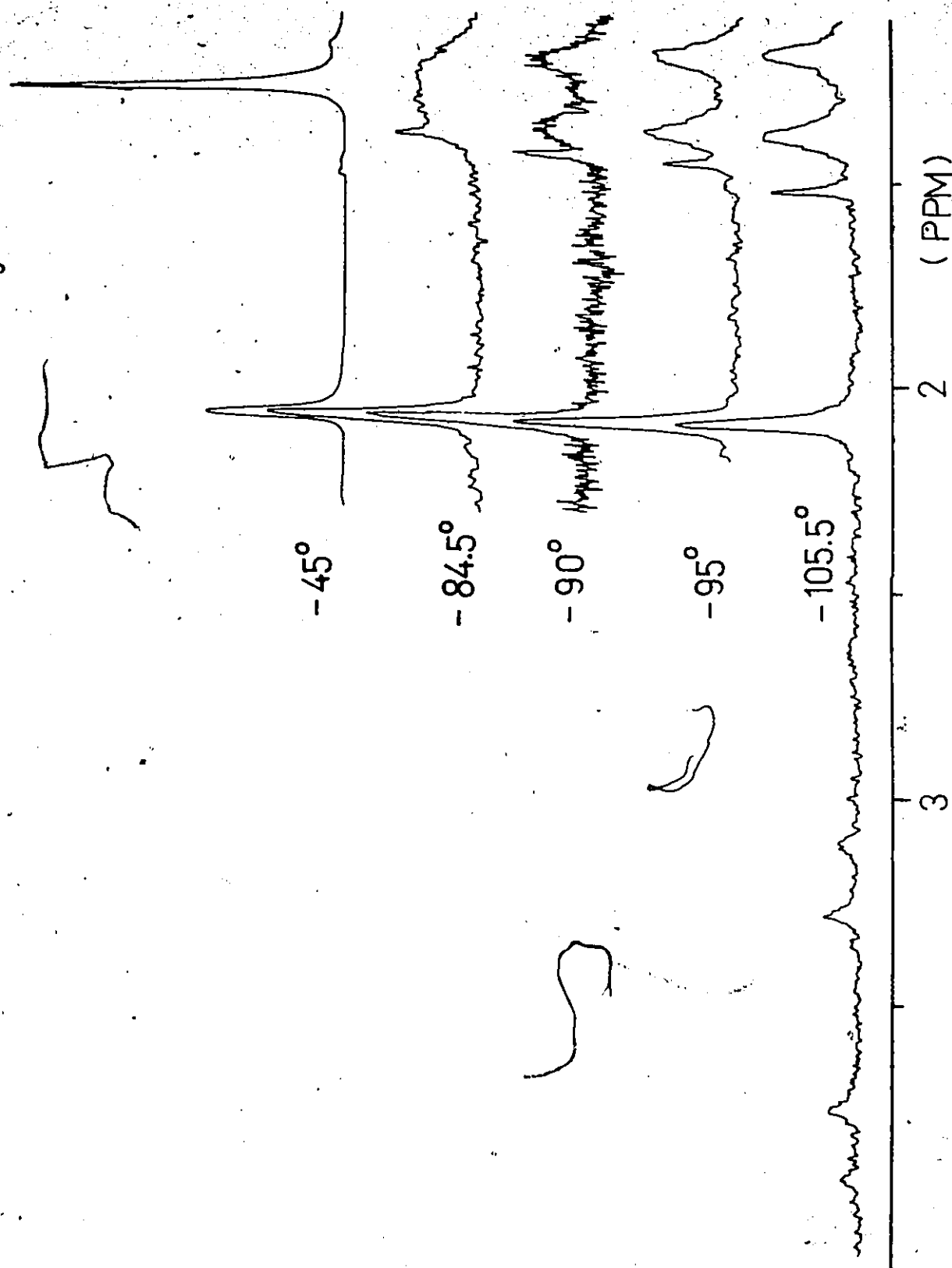
It will also be noticed on examination of the data given in Tables 5 and 7, that the downfield shifts experienced by the various resonances of protons and carbons of 1 on complexation are somewhat less than those observed on protonation. This would indicate that less charge is induced on the dienyl part of the molecule when Lewis acids rather than a proton are coordinated to the carbonyl oxygen.

(iii) Low Temperature Pmr and ¹³C nmr Studies of the Lewis Acid Complexes of 1

The nmr spectra of the boron trihalide complexes of 1 were found to exhibit a reversible temperature dependence. In particular, a broadening of the resonances attributed to the α -methylene protons and C_6 methyl protons was observed at very low temperatures. In order to obtain spectra of 1-BF₃ and 1-BCl₃ at lower temperatures than was possible in CH_2Cl_2 or $CDCl_3$, 1 was complexed with the Lewis acids using a 1:1 CD_2Cl_2 and $CHClF_2$ (Freon 22) mixture as the solvent.

As is shown in Figure 10, at -105.5° , the pmr spectra of the BF_3 complex of 1 showed two fairly broad resonances for the C_6 gem-dimethyl

Figure 10 Temperature Dependent Pmr Spectra of 1-BF₃



protons and an AB quartet attributable to the resonances of the α -methylene protons ($J = 16.75$ Hz). No broadening of the C_2 methyl proton resonance, other than that expected for a general viscosity effect, could be detected. As the sample was warmed up slowly, the resonances attributable to the C_6 methyl protons broadened, coalesced at -84.5° and became a single sharp line at higher temperatures. It was difficult to follow the changes occurring with the C_7 methylene proton resonances, however, at high temperatures only a single sharp signal was again observed for these two protons. The separation of the two methyl resonances at various temperatures was measured and the rate constants for exchange were calculated using the slow exchange approximation.⁴² The results so obtained are given in Table 9.

Table 9: Rate Constants for Interconversion of the Different Conformations of 1-BF₃.

Temperature $^\circ\text{C}$	Separation of C_6 methyl proton resonances (Hz) ^a	Rate Constant sec^{-1}
-105.5^b	19.0	-
- 95	18.0	11
- 90	16.0	23
- 84.5	Coalescence	42

a/ obtained using a Bruker WH90

b/ assumed to be limiting low temperature spectrum.

The free energy of activation, ΔF^\ddagger , associated with this interconversion at the coalescence temperature was calculated to be 9.4 kcal/mole.

The variable temperature ^{13}C nmr spectra of 1-BF_3 also exhibited a temperature dependence. Thus the resonance attributable to the C_6 methyl carbons was observed to broaden at low temperatures. Below -80° , two singlets at 33.1 ppm and 20.1 ppm were observed for these methyl carbon resonances whereas above -40° only a single averaged resonance was seen. No changes of the other carbon resonances were detected.

Similarly, the pmr spectrum of 1-BCl_3 was shown to exhibit directly comparable changes to those outlined above for 1-BF_3 . The rate constants for the interconversion in this complex were evaluated in the same way as those for 1-BF_3 and are shown in Table 10. In this case, the coalescence of the C_6 methyl proton resonances occurred at -89° and ΔF^\ddagger was calculated to be 9.2 kcal/mole.

Table 10: Rate Constants for Interconversion of the Different Conformations of 1-BCl_3 .

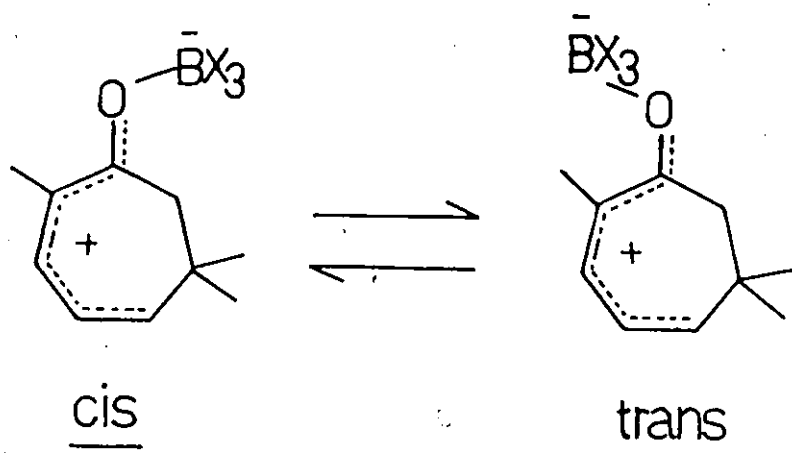
Temperature	Separation of C_6 methyl proton resonances (Hz) ^a	Rate Constant sec ⁻¹
-109.5^b	19.25	-
- 99.5	17.5	18
- 95.5	16.0	24
- 92.5	14.5	28
- 89.0	Coalescence	43

a/ using Bruker WH90.

b/ assumed to be limiting low temperature spectrum.

Similar temperature dependencies of the pmr spectra of the C_6 methyl proton resonances of $1-BBr_3$, $1H$ and even 1 itself have been observed, however, quantitative data has not yet been obtained.

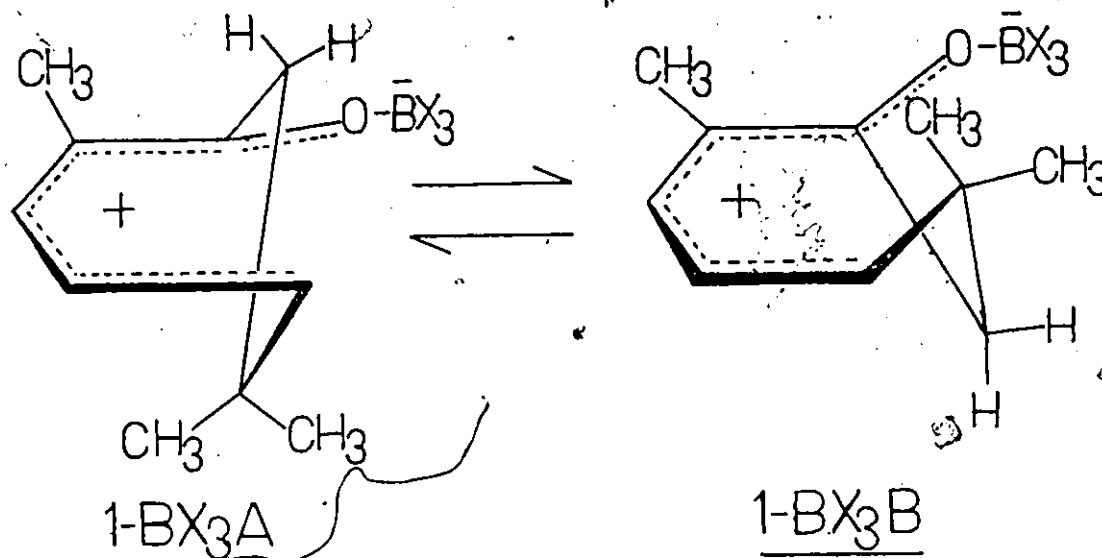
Two possible explanations have been considered in order to account for this temperature dependence; either it could be due to a cis-trans interconversion of the Lewis acids about the partial double bond of



the carbonyl group or to conformational inversion of a non planar seven-membered ring. The former explanation seems untenable since the C_2 methyl proton resonances do not change at all as the temperature is lowered nor do the ^{13}C resonances of C_2 , C_2 methyl, and C_7 carbons change at all as the signals due to the methyl carbons on C_6 broaden, and split into two separate signals at low temperature.

It would appear that the seven-membered ring of the $1-BX_3$ complexes is not completely flat. Models indicate that it most likely exists in a puckered shape with the five carbons of the pentadienyl unit tending to be somewhat flat and with C_7 and C_6 respectively above and below the plane of

the other ring carbons. As such the two methylene protons and two C_6 methyl



groups would be expected to be non-equivalent and at low temperature exhibit distinct pmr resonances. The magnitude of the coupling constant between the two methylene protons ($J = 16.75 \text{ Hz}$) is just that expected for the coupling between two non-equivalent methylene protons in such a system.⁴³

At higher temperatures, the ring can flip between 1-BX₃A and 1-BX₃B and in doing so will make the two methylene protons and two C_6 methyl protons equivalent on a time averaged basis. The changes in the ^{13}C spectra are also completely consistent with an interconversion between such conformations.

3. Irradiation of the Boron Trihalide-Eucarvone Complexes

(i) Product Identification

Solutions of 1-BX₃ were irradiated in clear-walled nmr tubes at temperatures below - 90° with light of $\lambda > 370$ nm. The reactions were monitored by pmr which showed that a mixture of products was being formed. The solution containing the photoproducts was carefully neutralized at - 90° to give, after work up, an oil, the glpc analysis of which suggested that five products were present. The distribution of these products varied with the Lewis acid employed and with the irradiation time. All the photoproducts were separated and collected by preparative glpc.

The first product, which was the major product obtained with the BF₃ and BCl₃ complexes of 1, was shown to be 6 by comparison of its pmr, Table 11, and ir* spectra with those reported by Hart¹² and Hine¹⁴. This product was identical in all respects to an authentic sample of 6 obtained by the procedure of Childs and Hine¹⁴.

The second major product, which was particularly dominant when BBr₃ was used as the Lewis acid, was shown to be 2-methyl-5-isopropyl phenol, 8, on the basis of its pmr, Table 11, and ir spectra, which resembled those of the authentic carvacrol in every respect.

*ir spectra of all photoproducts are given in experimental section.

Table 11: Pmr Spectra of the Products Resulting from Quenching Solutions of the Irradiated Eucaryone - Lewis Acid Complexes. ^a

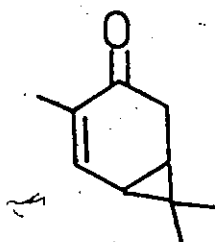
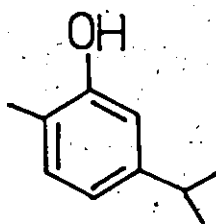
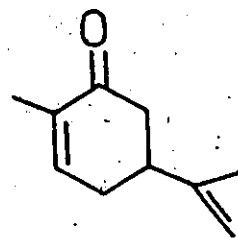
Compound	Chemical Shifts (ppm)						Coupling Constants ^b (Hz)
	H ₁	H ₂	H ₃	H ₄	H ₅	H ₆	
<u>6</u>	1.20	6.65	-	-	2.42	1.20	0.88, 1.18, 1.66
<u>8</u>	-	-	6.96	6.64	-	6.52	2.76 1.18 ^d , 2.18 J _{3,4} =7.5, J _{4,6} =1.9
<u>12</u>	-	-	6.50	2.05-2.74	-	2.05-2.74	4.65 ^c 1.66, 1.66
<u>13</u>	-	-	6.92	6.67	6.82	-	3.14 1.15 ^d , 2.20 J _{3,4} =7.74, J _{4,5} =7.54, J _{3,5} =1.66
<u>5</u>	-	5.47	6.27	2.53	1.84	-	0.81, 0.88, 0.97 J _{2,3} =6, J _{4,5} =3

a/ at 100 MHz in CCl₄ at +37° (TMS as internal reference)

b/ ± 0.3 Hz

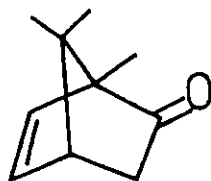
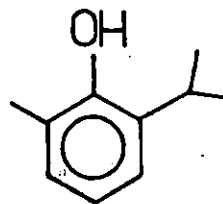
c/ vinyl proton

d/ doublet with J = 7 Hz.

6812

The third major product, whose ir spectrum (1670 and 1640 cm^{-1}) suggested that it was an α,β -unsaturated ketone, was shown to be carvone, 12. Comparison of its pmr, Table 11, and ir spectra to those of authentic carvone confirmed the assignment.

The fourth photoproduct, which was formed consistently in very small amounts, ca. 1% with all the Lewis acid complexes, was shown to be dehydrocamphor, 5, by comparison of its pmr, Table 11, and ir spectra with those reported by Schuster.¹¹ An authentic sample of 5, prepared by K.E. Hine using the procedure of Schuster, had identical properties to the material isolated from the photochemical reactions.

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A fifth product, which occurred to the extent of some 8-10% on the irradiation of all the Lewis acid complexes of 1, was demonstrated to be 2-methyl-6-isopropylphenol, 13, on the following evidence. It was shown to be isomeric with 1 by mass spectroscopy ($m/e = 150$) and it had a strong ir band at 2690 cm^{-1} but no carbonyl absorption. Its pmr spectrum, Table 11, which differed very little from that of 8 suggested it to be an isomer of 8. The high field region consisted of a singlet and a doublet, corresponding to three and six protons respectively. These were assigned to the C_2 methyl and the C_6 isopropyl methyls. The isopropyl methine proton resonance was observed at 4.24δ as a septet. The relatively broad peak near the vinyl region was assigned to the hydroxyl proton. The aromatic region consisted of resonances attributable to three protons which were extensively coupled. At 100 MHz, these protons appeared to be mutually coupled and gave the complex spectrum as shown in Figure 11.

A simulated pmr spectrum of the aromatic protons of 13 was generated with a Nicolet 1080 Mini-Computer, using the Nuclear Magnetic Resonance Spectrum Calculation Program (NMRCAL NIC-80/S-7117-D). The calculated spectrum was very similar to that observed for 13, Figure 11. The chemical shifts and coupling constants for the three protons were found to be $H_A = \delta 6.67$, $H_B = \delta 6.82$ and $H_C = \delta 6.92$, $J_{AB} = 7.54\text{ Hz}$, $J_{AC} = 7.74\text{ Hz}$ and $J_{BC} = 1.66\text{ Hz}$. These values are completely consistent with that expected for a 1, 2 and 3 substituted benzene.

The ^{13}C nmr spectrum of 13, Table 12, which was very similar to that of 2,6-dimethylphenol, was quite consistent with the formulation of the structure of the product as 13.

Figure 11: Pmr Spectrum of the Aromatic Protons of 2-methyl-6-isopropyl-phenol.

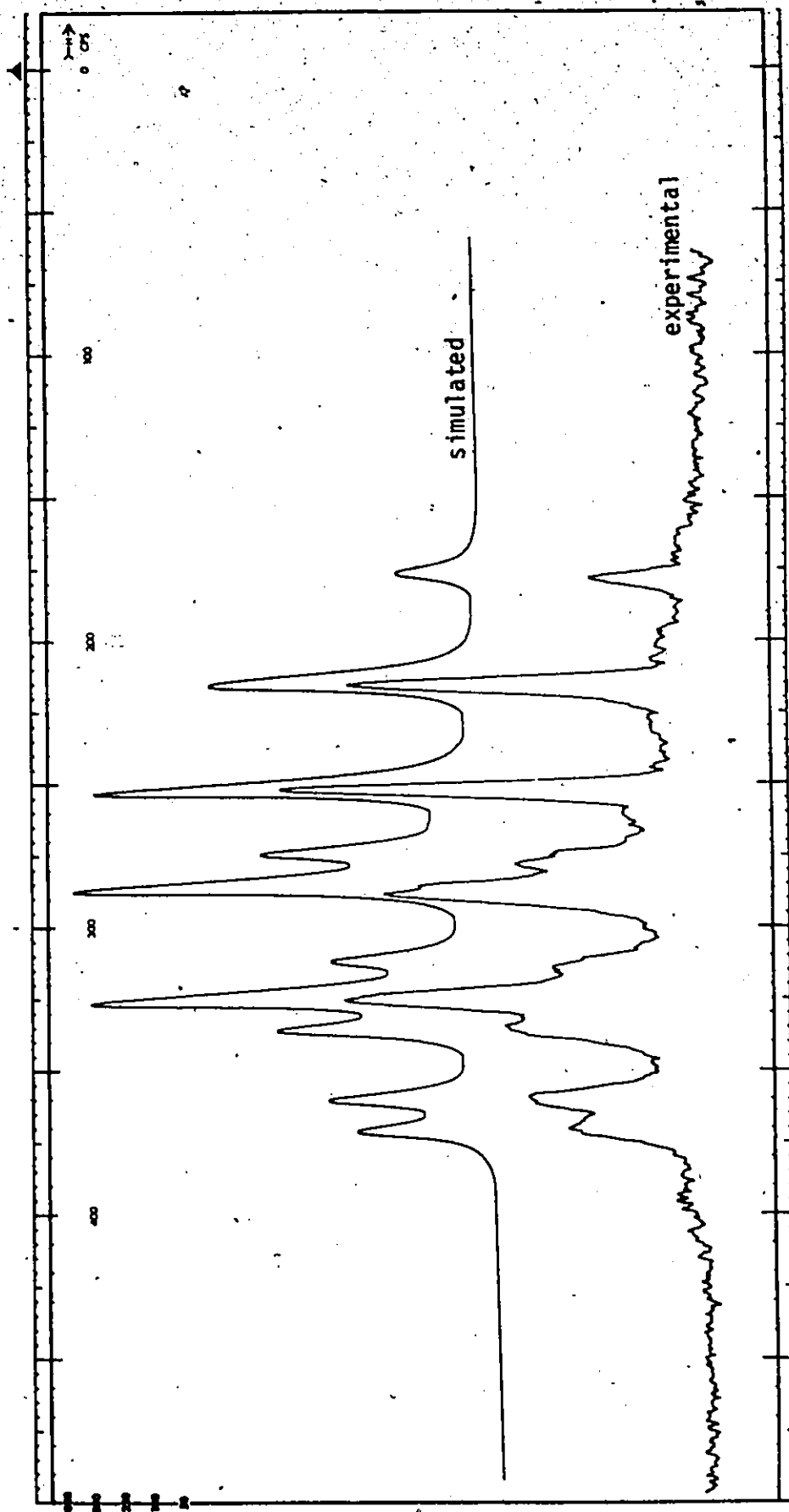


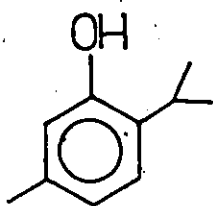
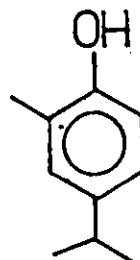
Table 12: ^{13}C nmr Spectra of the Isomeric Phenols 8, 13, 14 and 15.^a

Compound	Chemical Shifts (ppm)						
	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	t-propyl methyls
<u>8</u>	153.3	120.8	130.4	118.3	147.7	112.9	33.6
<u>13</u>	150.7	122.5	127.8	120.0	123.7	133.4	27.2
<u>14</u>	152.2	115.9	131.2	121.5	126.0	136.2	20.8
<u>15</u>	151.8	123.6	129.2	141.4	124.9	114.9	15.9
							33.4
							24.3

a/ at 22.63 MHz as approximately 50% solution in CDCl_3 chemical shifts

increase downfield and are relative to TMS (0.00 ppm).

While the spectroscopic evidence presented above strongly suggests that the structure of this photoproduct is 13, it does not rigorously prove it. Alternative structures 14 and 15 were also considered.

1415

The former can be eliminated because the pmr spectrum of the authentic thymol, 14, Table 13, particularly the pattern of the aromatic protons differs from that observed for 13. 15 is known⁴⁴ but no nmr data are reported. It was synthesized by the procedure of Carpenter and Easter⁴⁴ and its structure was confirmed by ¹³C nmr, Table 12 and pmr, Table 13. The pmr spectrum of 15 showed no similarity in the aromatic region to that observed for 13. Moreover, 15 had a much longer glpc retention time than that of 13 and it is clear that the product isolated from the irradiations of the complexes of 1 is not 15.

Strong supportive evidence for the assigned structure of 13 was obtained by recording the pmr spectrum of protonated 13. It is generally found that when a phenol is unsubstituted at the para position, protonation takes place at this site⁴⁵. Solution of 13 in FSO₃H gave a solution whose pmr spectrum, Table 13, indicated that only one cation was present. The

Table 13: Pmr Spectra^a of Phenols 14, 15, 13 and Protonated 13.

Compound	Chemical Shifts (ppm)						Coupling Constants (Hz)
	O-H	H ₂	H ₃	H ₄	H ₅	H ₆	
<u>14</u>	4.77	6.53	-	6.71	7.07	-	J _{2,4} =1.9, J _{4,5} =7.6
<u>15</u>	4.46	-	6.82	-	6.80	6.52	J _{3,5} =2.1 J _{5,6} =7.8
<u>13</u>	4.24	-	6.92	6.67	6.82	-	J _{3,4} =7.74, J _{4,5} =7.54, J _{3,5} =1.66
¹³ H ^c	-	-	8.22	4.18	8.22	-	2(15, 1.30) ^d

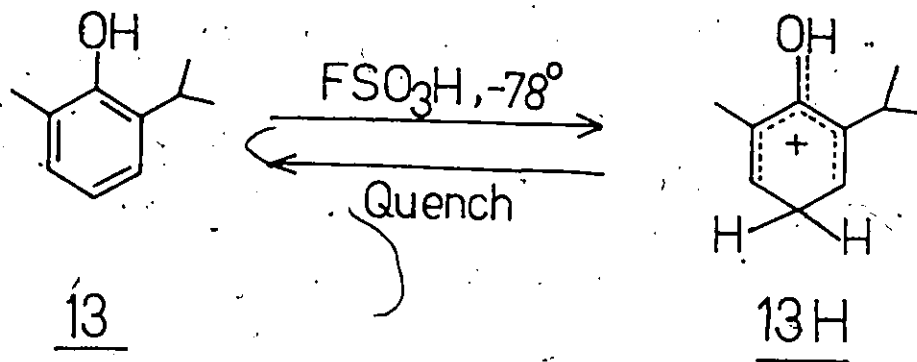
a/ at HA-100 MHz, phenols in CCl₄ (TMS as internal standard)

b/ ± 0.3 Hz

c/ in FS₂O₃H at -50°, tetramethyl ammonium chloride (δ3.10) was used as internal standard.

d/ doublet with J = 7 Hz.

position of the proton resonances of this cation, which were very similar to those of protonated 2,6-dimethylphenol⁴⁶, were entirely consistent with its formulation as 13H. Final proof of the assigned structure of 13



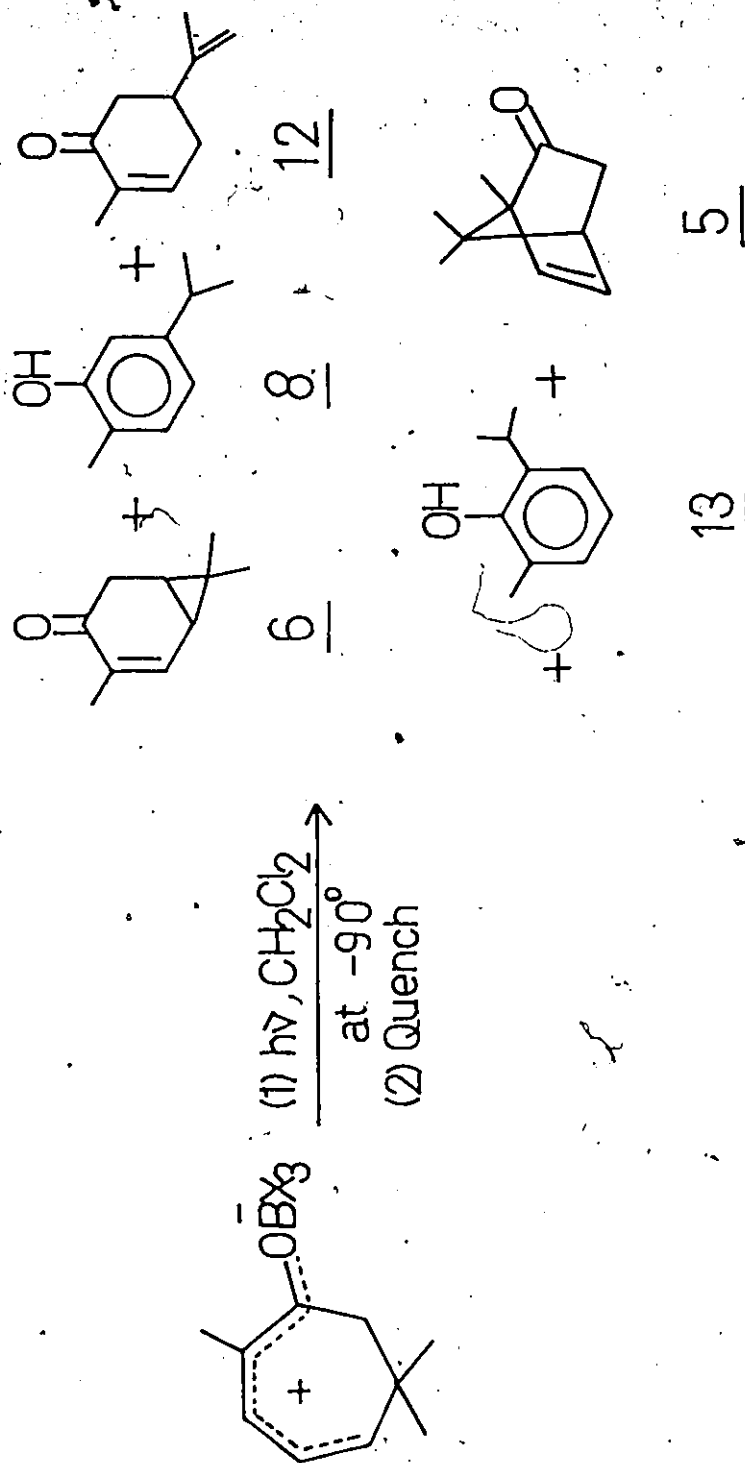
was obtained by preparation of an authentic sample using a similar procedure to that of Sowa⁴⁷.

All the photoproducts had identical glpc retention times to those of the corresponding authentic compounds. The products obtained on the irradiation of the Lewis acid complexes of 1 are summarized in Figure 12.

(ii) Product Distribution with Extensive Conversion of 1-BX₃

Small quantities (10-16 mg) of 1 complexed with the Lewis acids in CH₂Cl₂ were irradiated at -90° with light of wavelength >370 nm for 30-45 minutes. The resulting solutions were quenched with an ether/HCO₃⁻ slurry at -90° and analyzed by glpc. It was observed on the basis of the relative retention times that the recovered oil consisted of 5, 1, 6, 12, 13 and 8. Using cycloheptanone as an internal standard, it was

Figure 12: Products Obtained on Irradiation of Lewis Acid-Eucarvone Complexes.



determined that the total recovered yields of the products and unreacted 1 were above 90%. It might well be expected that there would be some small manipulation loss of material during the quenching and work-up of these reactions and no further non-volatile or other insoluble products were looked for.

Table 14: Product Distribution with Extensive Conversion of the Lewis Acid Complexes of Eucarvone in CH_2Cl_2 .

Lewis Acid	Recovery ^a %	Conversion %	Product Ratio % ^b				
			<u>5</u>	<u>6</u>	<u>12</u>	<u>13</u>	<u>8</u>
BF_3	94	74	1	68	3	10	18
BCl_3	92	83	1	29	22	10	38
BBr_3	95	61	> 0.5	7	25	8	60

a/ total recovery of unreacted 1 plus total products.

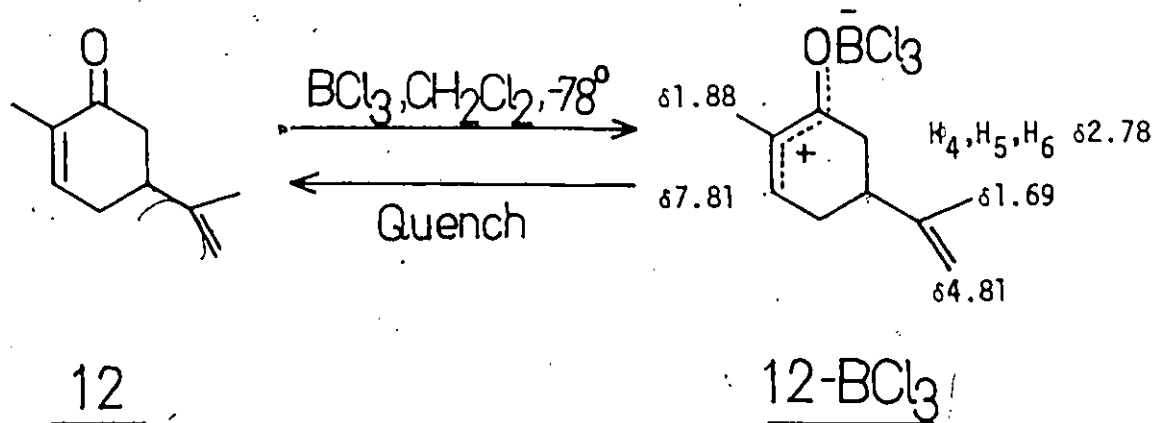
b/ expressed as percentage of total products.

Listed in Table 14 are the observed product distributions as a function of the Lewis acid used. The product ratios were not found to be sensitive to the way the complexes were made. For example, samples of the complexes made either using a high vacuum system, under a N_2 atmosphere or without any special precautions to eliminate water, gave a similar product distribution upon irradiation. It is quite clear from the results in Table 14 that the product ratio is markedly dependent on the Lewis acid used. At this stage it was imperative to establish whether the photo-

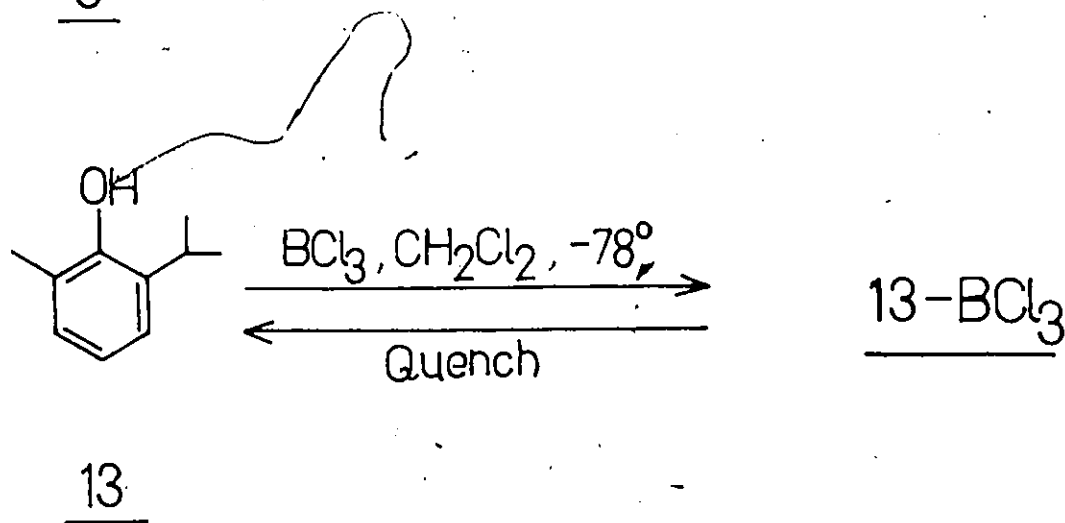
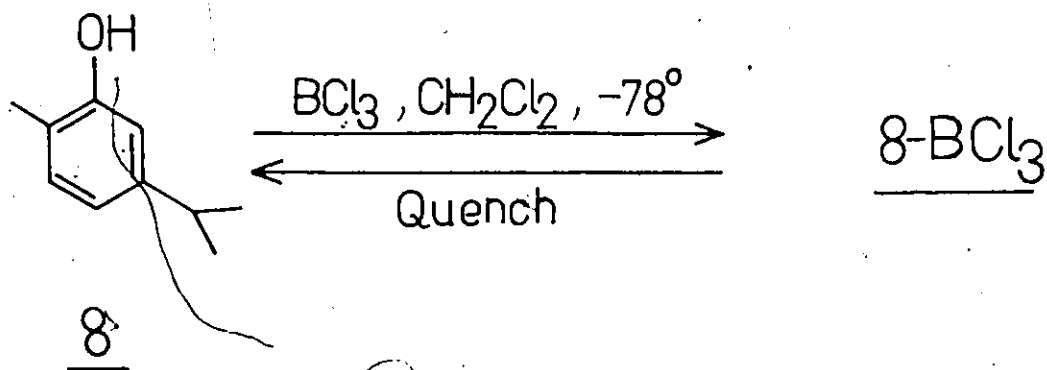
products were all primary products. There are two possible reasons why they need not be: (i) thermal instability of any initial products and (ii) further photochemical reactions of the primary products. Consequently, it was necessary to investigate the thermal and photochemical stabilities of the photoproducts of the $1-BX_3$ complexes and other possible isomeric products which could also have been formed.

(iii) Thermal and Photochemical Stabilities of the BCl_3 Complexes of 12, 8 and 13 in CH_2Cl_2

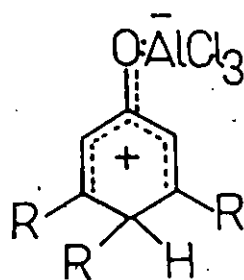
Reaction of 12 with BCl_3 in CH_2Cl_2 at -78° , resulted in the formation of the corresponding complex, 12- BCl_3 . The pmr spectrum of the pale yellow solution of this complex indicated that the Lewis acid was again coordinated to the carbonyl oxygen. The complex was stable at -20° for a long period of time, however it decomposed on standing at room temperature. On irradiation of a solution of the complex at -75° , under similar conditions to those used for the isomerization of $1-BX_3$, no rearrangement could be detected by pmr. 12 could be recovered in good yield by quenching this solution with an ether/ HCO_3^- slurry.



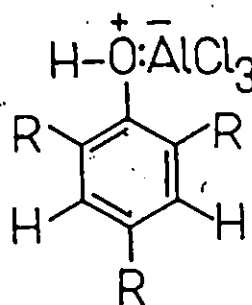
Reaction of phenols 8 and 13 with BCl_3 in CH_2Cl_2 at -78° gave pale yellow solutions whose pmr spectra were quite complicated. Although the pmr spectra of these complexes were not quite reproducible, quenching these solutions at 0° with ether/ HCO_3^- regenerated the phenols 8 and 13, respectively, in good yield. The areas of the resonances attributable to the aromatic protons of the two complexes corresponded to approximately three protons in each case, suggesting that the BCl_3 might perhaps be coordinated to the phenolic oxygen.



Koptyug and Golounin⁴⁸ have reported that phenols substituted in the meta position with a methyl group, react with Al_2Cl_6 to form a "Type 1" complex, in which the phenol has tautomerized to its keto form. They also found that without a meta substituent, phenols reacted with Al_2Cl_6 to form predominantly complexes of the aromatic hydroxy form, which were called "Type 2" complexes.

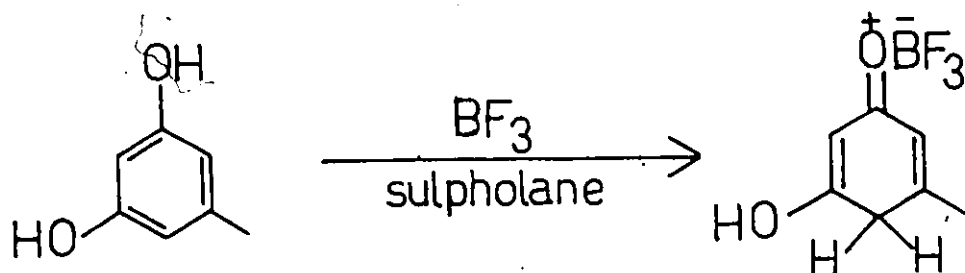
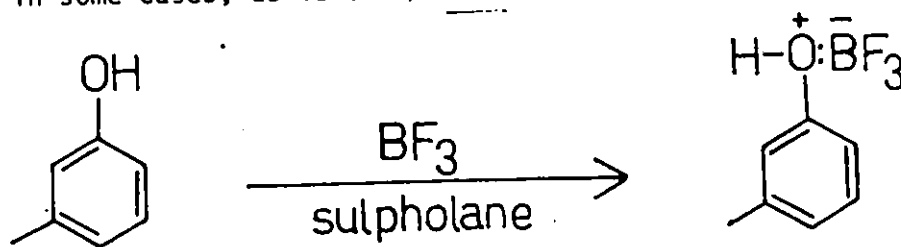


Type 1



Type 2

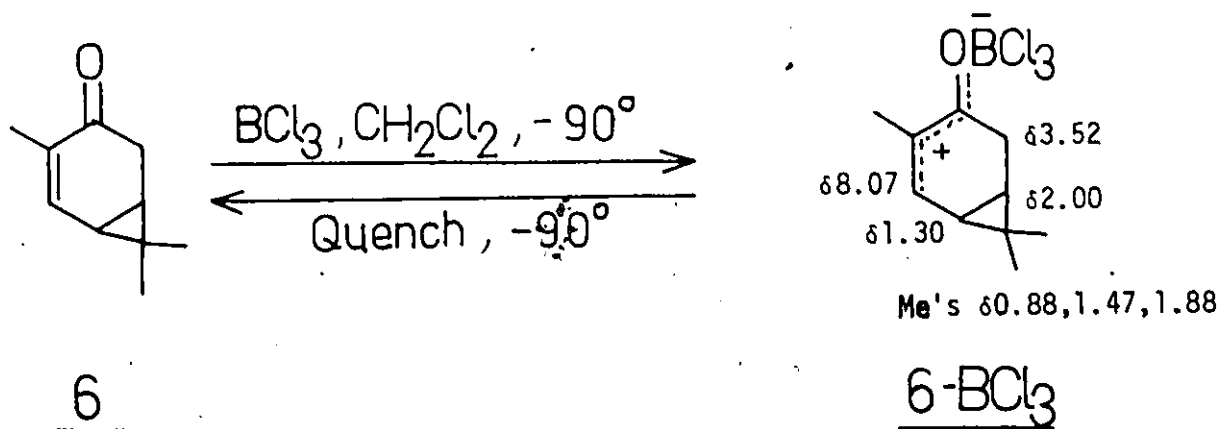
Similarly, Alder and Taylor have studied the reaction of BF_3 with certain phenols and have found that the Lewis acid is always coordinated with the oxygen atom.⁴⁹ Subsequent tautomerization of the initial adduct was found in some cases, as is shown below.



In view of the complicated pmr spectra obtained with 8-BCl₃ and 13-BCl₃, it is not certain what the structure of these complexes are, and probably, a mixture of complexes is being formed. To clarify this question further investigation is needed. These complexes were found to be photochemically stable when irradiated under the conditions used for the isomerization of 1-BX₃.

(iv) Thermal and Photochemical Stabilities of Boron Trihalide Complexes of 6

Compound 6, needed for this study, was obtained by irradiating eucarvone in a FSO₃H/SO₂ mixture in a comparable manner to the procedure described by Childs and Hine¹⁴. Reaction of 6 with BCl₃ at -90° in CH₂Cl₂, resulted in the formation of the corresponding complex, 6-BCl₃. The pmr of this zwitterion, which is very similar to that of protonated 6,¹⁴ clearly showed that the Lewis acid was coordinated to the carbonyl oxygen. 6-BCl₃ was found to be stable at -90°, since careful quenching of this complex at -90° regenerated 6 in high yield. However, at -78° it decomposed slowly to give a solution with a very complicated pmr spectrum. The product of this decomposition could not be characterized. After quenching this resulting decomposed solution with an ether/HCO₃⁻ slurry, no product could be isolated.



Reaction of 6 with BF_3 and BBr_3 proceeded in a comparable manner to that described above to give 6-BF₃ and 6-BBr₃, respectively. The pmr spectra of the BF_3 and BBr_3 complexes of 6 were not recorded. However, on quenching these complexes at -90° , 6 was regenerated in good yield in each case. The thermal stabilities of the BF_3 and BBr_3 complexes of 6 were not checked. All three Lewis acid complexes of 6 were irradiated at -90° , using identical conditions to those described for the photoisomerization of the 1-BX₃ complexes, and in each case two products were formed. The irradiated solutions were quenched and the products were identified as 12 and 8 on the basis of their glpc retention times. The product distributions, determined by glpc, are listed in Table 15.

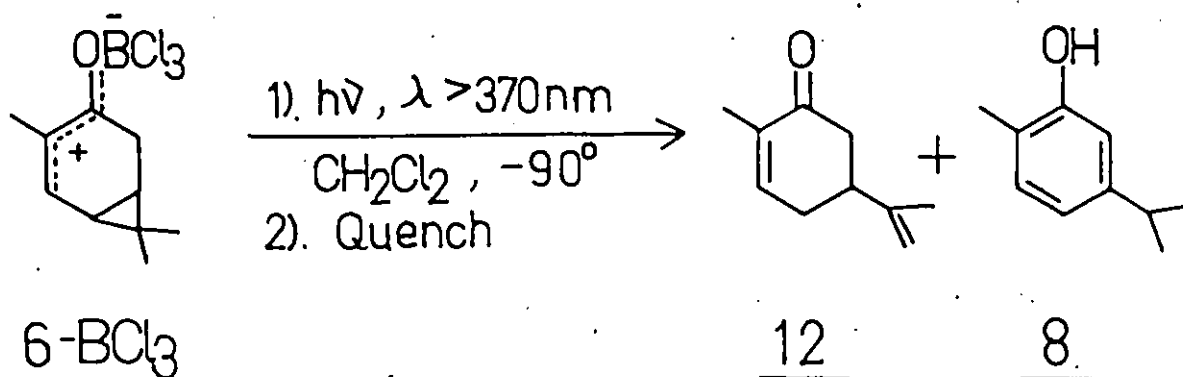


Table 15: Product Distribution Obtained on Irradiation of 6-BX₃ in CH₂Cl₂^a

Lewis Acid	Product Ratio (%) ^b	
	<u>12</u>	<u>8</u>
BF_3	44	56
BCl_3	43	57
BBr_3	60	40

a/ after quenching ; b/ expressed as % of total products.

It would seem that the product formed on irradiation of 6-BX₃ prior to quenching must be 12-BX₃ and 8-BX₃. Mechanistically, the formation of these products is interesting. Possibly, as is shown in Figure 13, a cationic diradical may be involved as an intermediate, generated photochemically from 6-BX₃. The formation of 12-BX₃ could be thought of in terms of a 1,4 hydrogen migration from C₈ to C₁, while 8-BX₃ may arise as a result of 1,2 hydrogen shift from C₅ to C₆.⁵⁰

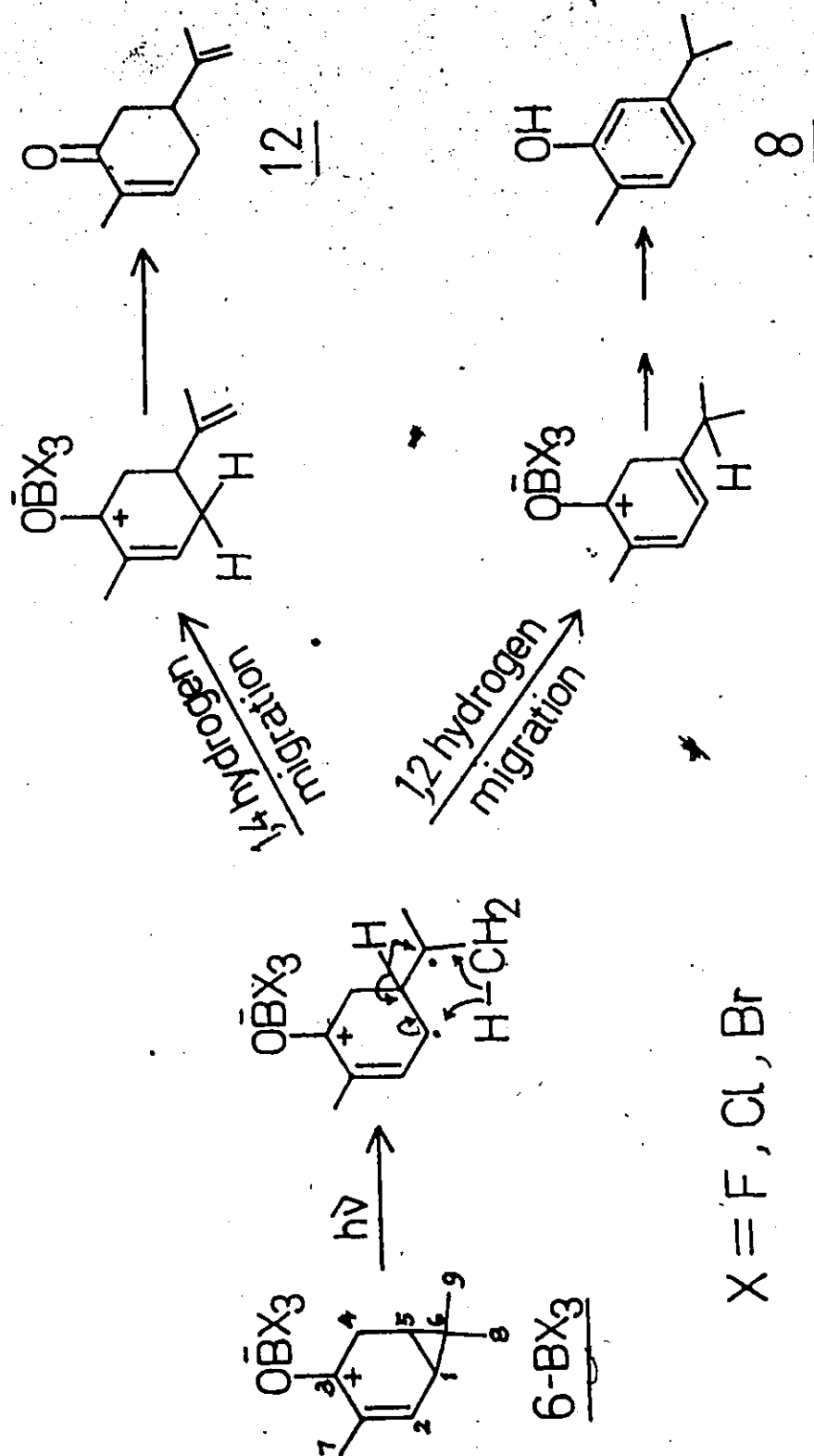
It is interesting to note that the Lewis acid complexes of 6 and protonated 6 appear to undergo different thermal and photochemical isomerizations. 6H was reported by Hine¹⁴ to thermally rearrange in FSO₃H to 8H in high yield at -15°, while as has been shown earlier, 6-BCl₃ decomposed in CH₂Cl₂ at -78°. One possible reason for this difference in the behaviour may perhaps be the polarity of the solvents used and the stabilization of any intermediate or transition state involved in the isomerization of 6H in the highly polar, strong acid medium.

Photochemically, 6H was found to isomerize in FSO₃H to give only 8H, while it has been shown here that 6-BX₃ gives 12-BX₃ and 8-BX₃. One possible explanation for this different photobehaviour could be that, in FSO₃H, 12 may be unstable and rearrange to 8H. To check this the protonation of 12 was examined.

(v) Thermal Stability of Protonated Carvone, 12H

Addition of 12 to FSO₃H at -78° gave a clear yellow solution whose pmr at -60° indicated that more than one cation was present. The pmr spectrum of this acid solution, δ 1.81, 2.04, 2.55-3.4, 8.24, showed some

Figure 13: Proposed Mechanism for the Photoisomerization of the Lewis Acid Complexes of 6.

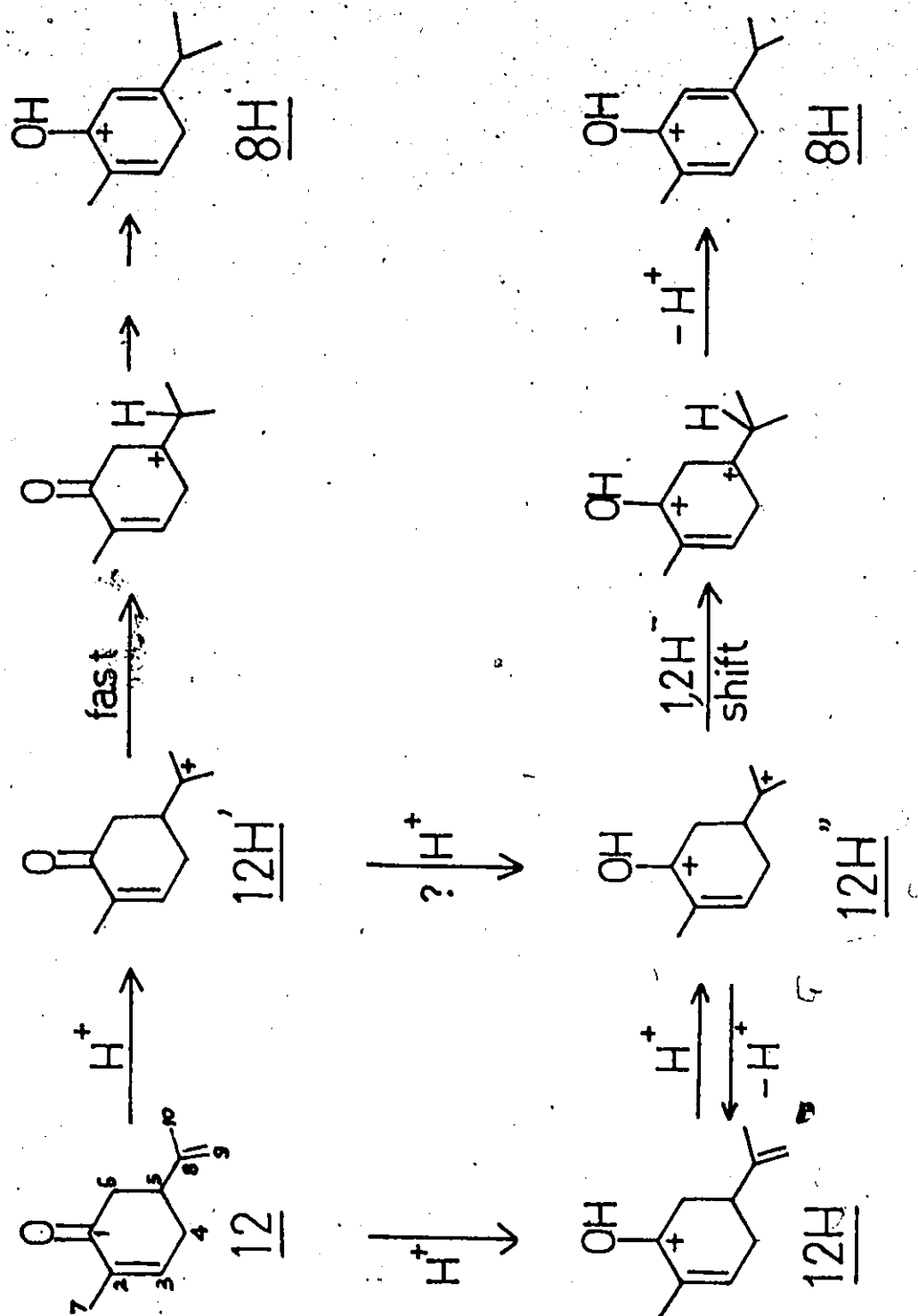


similarity to that of 12-BCl₃, which suggested that O-protonation had occurred to some extent. In addition to these signals, a further set of resonances at δ 1.32, 2.25, 4.06, 7.17 and 8.13 were also observed and the latter corresponded to those found for 8H. The ratio of the two cations formed did not change while the sample was kept at -60° . On warming this sample to -40° , a rearrangement of all the material to 8H was observed. The isomerization could be followed by pmr and it was found to have a half life of some 10 minutes at -40° . No product other than 8H could be detected by pmr after completion of the rearrangement. On quenching this resulting acid solution with an ether/ HCO_3^- slurry, 8 was obtained.

As illustrated in Figure 14, protonation of 12 could occur at two sites, the carbonyl oxygen and the alkene moiety, to yield the respective cations 12H and 12H'. While 12H might be expected to be thermodynamically more stable than 12H', kinetically both could be produced. It would seem that isomerization of 12H' to 8H could be a fast process at -60° and compete with the isomerization of 12H' to 12H. The rearrangement of 12H to 8H could be thought of proceeding via a further protonation of 12H at C_9 to give the dication 12H'', followed by a thermal 1,2 hydride shift from C_5 to C_8 and deprotonation. The involvement of dicationic intermediates in rearrangement of unsaturated ketones has been previously suggested.⁵¹

It is therefore quite possible that 12H is also formed in the irradiation of 6H but that under the reaction conditions it thermally isomerizes to give 8H, the only product detected.

Figure 14: Protonation of Carvone.



(vi) Product Distribution with Low Conversion of 1-BX₃

Since it would appear that 8-BX₃ and 12-BX₃ might not be the primary products of 1-BX₃ but derive from further photochemical reactions of 6-BX₃, attempts were made to minimize, if not eliminate this secondary reaction. The Lewis acid complexes of 1 in CH₂Cl₂ were irradiated under the same conditions as before but for much shorter lengths of time so as to ensure low conversion of 1-BX₃ (less than 5%). The resulting solutions were quenched very carefully at -90° with an ether/HCO₃⁻ slurry and analyzed by glpc. The results of these studies are given in Table 16. With the photoreactions of the BF₃ and BCl₃ complexes of 1, no 12 was now detected and the product distributions were similar in each case. However, with the irradiation of 1-BBr₃, carvone, 12, was still formed and the product ratio was found to be identical to that obtained with higher percentage conversions of 1-BBr₃.

Table 16: Product Distributions with Low Conversion of the Lewis Acid Complexes of Eucarvone in CH₂Cl₂.

X	Recovery ^a %	Conversion %	Product Ratios % ^b				
			<u>5</u>	<u>6</u>	<u>12</u>	<u>13</u>	<u>8</u>
F	94	5	1	69	n.d. ^c	10	20
Cl	95	4	1	69	n.d. ^c	10	20
Br	94	4	>0.5	7	25	8	60

a/ total recovery of unreacted 1 plus all products.

b/ expressed as relative percent, ±2%.

c/ not detected <0.5%.

It would appear from the results given in Table 16, that 12-BX₃ (12) could be a direct photoproduct of 1-BBr₃ but not 1-BF₃ and 1-BCl₃. However, a comparison of the relative rates of photoisomerizations of the complexes of 1 and 6 gives some further insight into the possible origin of the products. A comparison of the rates of photoisomerization of 1-BX₃ and 6-BX₃ was made by determining the amount of 1-BX₃ reacted per unit time as compared to that of 6-BX₃. This was done by irradiating at -90°, known amounts of 1-BX₃ or 6-BX₃ for known periods of time. With the apparatus we had available, these irradiations had to be carried out consecutively and could thus be susceptible to fluctuation in the intensity of the light source. To minimize this, each irradiation was carried out twice and the results shown in Table 17 were found to be reproducible.

Table 17: Comparison of the Relative Rates of Photoisomerization of the Lewis Acid Complexes of 1 and 6 in CH₂Cl₂.

Lewis Acid	Compounds	Initial ^a Amount (mg)	Irradiation Time (min)	Conversion ^b %	Amount ^c Isomerized (mg)	Rate mg/min
BF ₃	<u>1</u>	11	45	74	8.1	0.18
	<u>6</u>	13.3	20	15	2.0	0.10
BCl ₃	<u>1</u>	12	30	83	10	0.33
	<u>6</u>	13.1	30	35	4.6	0.15
BBr ₃	<u>1</u>	15.8	40	61	9.8	0.25
	<u>6</u>	13	10	70	9.1	0.91

a/ Initial weight of ketone used.

b/ Estimated by glpc.

c/ Calculated on the basis of percent conversion.

The results in Table 17 showed that the rate of conversion of 6-BF₃ was rather slow compared to that of 1-BF₃. Hence, for short irradiation, it would not be expected to compete with the primary isomerization of 1-BF₃. The same argument seems to hold for the BCl₃ complexes of 1 and 6. On the contrary, 6-BBr₃ isomerized much more rapidly than 1-BBr₃. Its rate of conversion was almost 4 times as fast as that of 1-BBr₃. It is then possible that once 6-BBr₃ is formed by the isomerization of 1-BBr₃, it may be further reacted to give 12-BBr₃ and 8-BBr₃. However, in view of the uncertainty of the absorption maxima of 6-BBr₃ and that 1-BBr₃ being the predominant species would be absorbing most if not all of the incident light, it is still not clear whether 12-BBr₃ is a primary photoproduct.

A comparison of the product distributions obtained in the irradiations of the BX₃ complexes of 1 with that of protonated 1, suggests a parallel between the photochemistry of 1-BF₃, 1-BCl₃ and 1H. 6 and 8 were formed in similar yields in the isomerizations of 1-BF₃, 1-BCl₃ and 1H. However, the Lewis acid complexes differ from the protonated systems in the formation of phenol 13 (13-BX₃) and the norbonenone 4 (4-BX₃). Protonated 13 (13H) was stable in FSO₃H and would have been observed if it had been formed in the photoisomerization of 1H. To establish whether 4-BCl₃ would have been observed if it had been formed photochemically, the complexation of 4 and its thermal product in FSO₃H, 9, were investigated.

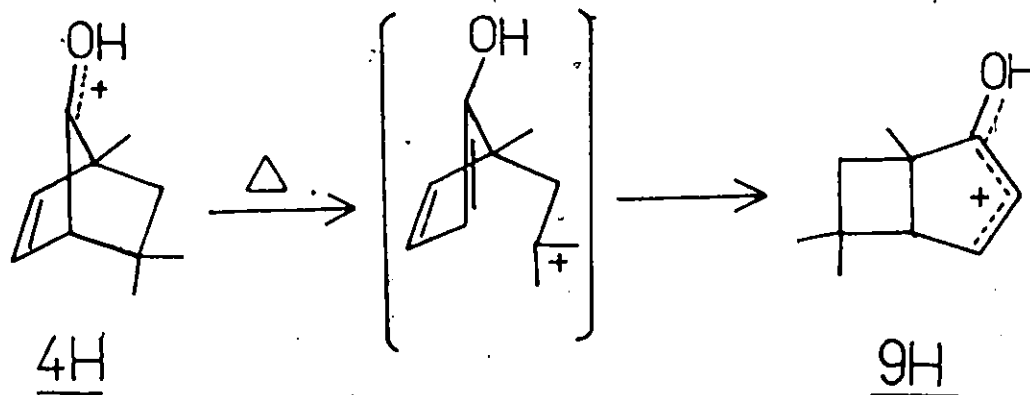
(vii) Thermal and Photochemical Stabilities of the BCl₃ Complex of 4

Compound 4 needed for this study, was obtained by the irradiation

of 1 in 50 % acetic acid according to the procedure of Hurst and Whitham¹⁰. Identification of this compound was made on the basis of its pmr, Table 18, and ir spectra in comparison to those previously reported.

Addition of 4 to BCl_3 in CH_2Cl_2 at -78° gave a yellow solution whose pmr, Table 18, was very similar to that of the protonated 4, indicating that the 4-BCl₃ was formed. On quenching this solution with ether/ HCO_3^- , 4 was regenerated in high yield. The complex was thermally stable at -15° for 2 hours but decomposed at room temperature. Photochemically, it was stable to rearrangement when irradiated under identical conditions to those used for the isomerizations of 1-BX₃.

It was rather surprising that 4-BCl₃ was so stable in comparison to 4H, which quantitatively isomerized to 9H in FSO_3H at -55° ($t_{1/2} = 10-15 \text{ min}$).^{8a}



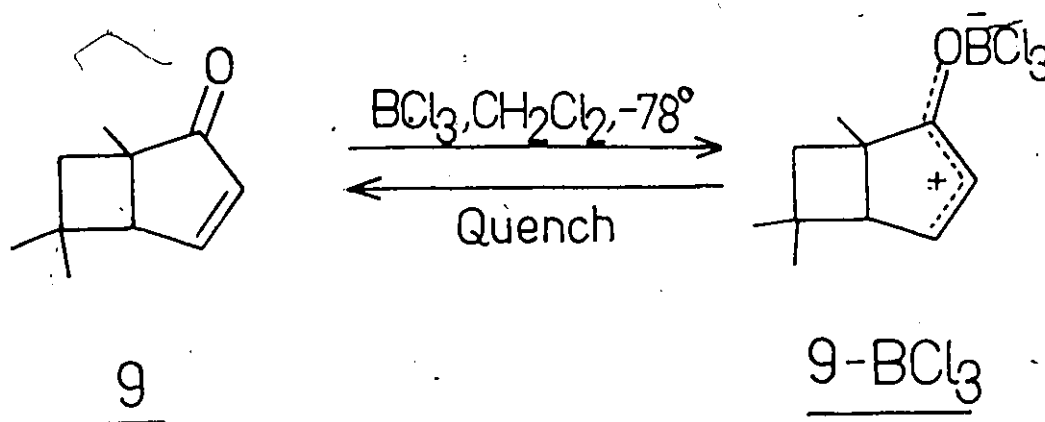
The difference in the behaviour of 4-BCl₃ and 4H may be due to the polarity of the solvent used and the consequent stabilization of the intermediate or transition state involved in the isomerization. Another possible reason may perhaps be the difference in the charge distributions in 4-BCl₃

and 4H. In the case of 4H, there may be more positive charge developed on the carbonyl carbon than in the case of 4-BCl₃, where a greater fraction of the positive charge resides on the carbonyl oxygen.

(viii) Reaction of Bicyclo [3.2.0] Heptenone, 9, with BCl₃

9 was obtained by irradiating 1 in a FSO₃H/SO₂ mixture in a comparable manner to that described by Hine.¹⁴

Reaction of 9 with BCl₃ at -78° resulted in the formation of 9-BCl₃ whose pmr, Table 18, was very similar to that of protonated 9. Quenching this solution at -45° with ether/HCO₃⁻, recovered 9 in good yield. The thermal and photochemical stabilities of 9-BCl₃ have not been examined.



It was quite clear that 13-BCl₃ did not derive from 4-BCl₃, either thermally or photochemically. Moreover, 13-BX₃ is formed in consistent amount in the irradiations of 1-BX₃ regardless of the length of irradiation time. It would thus seem likely that 13-BX₃ is a primary photoproduct of the Lewis complexes of 1.

Table 18: Pmr Spectra of Neutral, Protonated and BCl_3 Complexes of 4 and 9.^a

Compound	Chemical Shifts (ppm)						Coupling Constants (Hz) ^b
	H ₂	H ₃	H ₄	H ₅	H ₆	H ₇	
<u>4</u>	6.38	6.38	2.40	-	1.10	-	1.17, 1.07, 0.90 $J_{2,3} = 3.5$
<u>4H</u> ^c	6.70	6.70	3.29	-	1.96 1.61	-	1.40, 1.17, 1.06 $J_{2,3} = 2.7$ $J_{6,6'} = 12.2$
<u>4-BCl₃</u> ^d	6.67	6.67	3.68	-	1.67 1.60	-	1.24, 1.10, 0.92 $J_{2,3} = 2.5$ $J_{6,6'} = 10$
<u>9</u>	-	6.15	7.45	2.62	-	1.70	1.33, 1.20, 0.88 $J_{3,4} = 5.5$ $J_{4,5} = 3.0$
<u>9H</u> ^c	-	7.20	9.08	3.50	-	2.42 1.86	1.44, 1.42, 0.91 $J_{3,4} = 5.5$ $J_{4,5} = 2.5$ $J_{7,7'} = 13.0$
<u>9-BCl₃</u>	-	7.63	8.60	3.34	-	2.25 1.76	1.42, 1.40, 0.90 $J_{3,4} = 6.0$ $J_{4,5} = 2.0$ $J_{7,7'} = 12.5$

a/ 100 MHz spectra, ketones in CCl_4 (TMS as internal reference, δ 0.00) at +37°. Complexes in CH_2Cl_2 at -50° with CH_2Cl_2 (δ 5.30) as internal reference.

b/ ± 0.3 Hz.

c/ Data taken from reference 8a

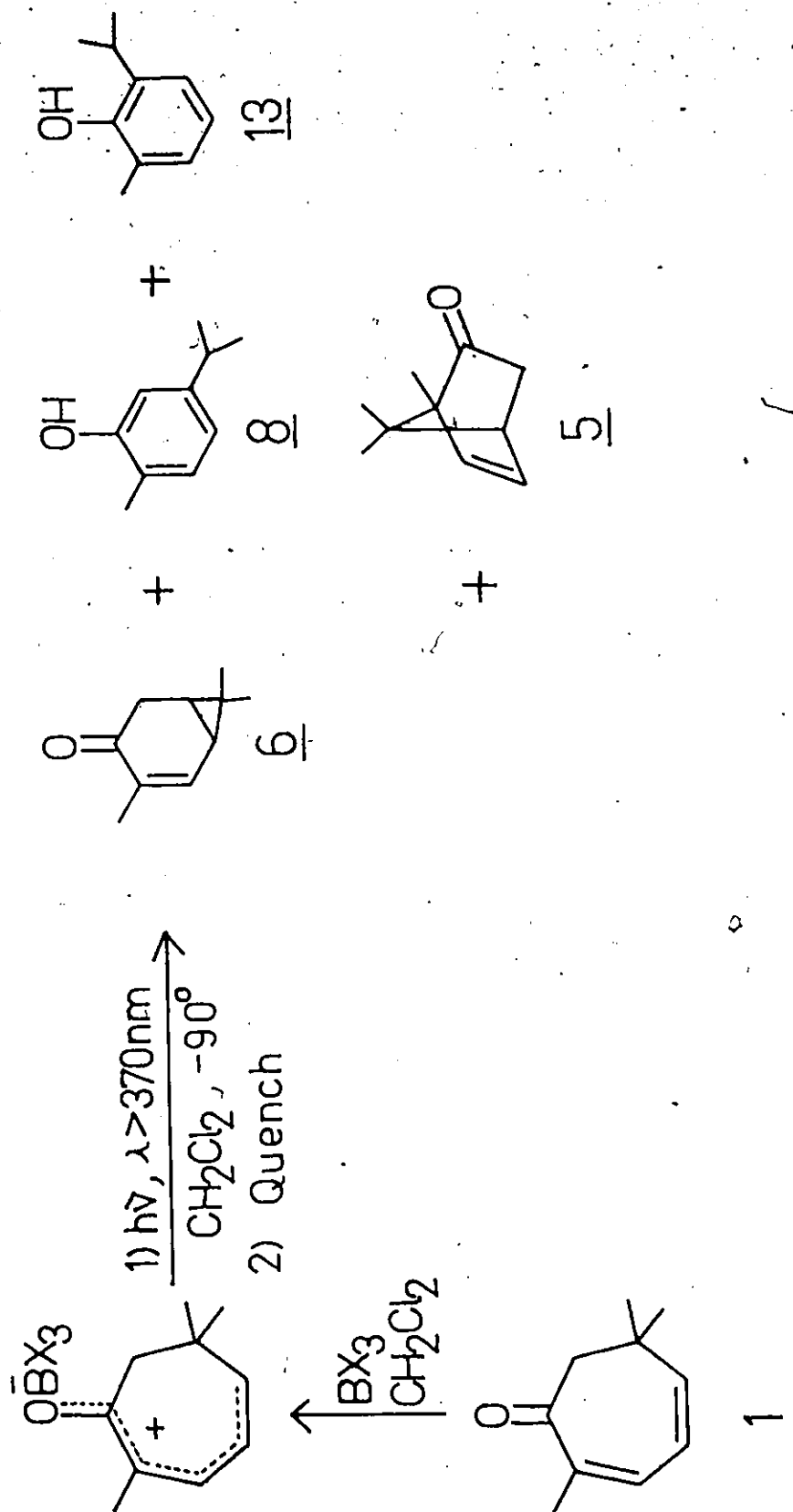
d/ 60 MHz spectrum.

It has not been determined whether 5 is an initial photoproduct. However, it appeared to be so, since it was present in similar amounts in all irradiations of the Lewis acid complexes of 1.

In summary, it would appear that 5, 6, 13 and 8 are all primary photoproducts of the boron trihalide complexes of eucarvone, Figure 15. The possibility that 12 (12-BBr₃) is also a direct photoproduct of 1-BBr₃ cannot be completely ruled out.

One factor which could be largely negating the effect of the progressive introduction of a heavy atom in these boron trihalide complexes of eucarvone is the solvent used. Methylene chloride, CH_2Cl_2 , which is present in considerable excess, contains two chlorine atoms and it is conceivable that any intramolecular heavy atom effect is being swamped by the presence of an intermolecular interaction between solute and solvent. Consequently, these photoreactions were re-examined with solvents which contained no heavy atom substituents.

Figure 15: Primary Photoproducts of Eucaryone-Lewis Acid Complexes in CH_2Cl_2 .

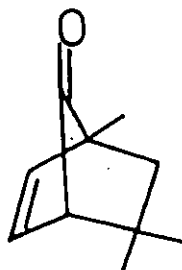


4. Solvent Effect Upon Product Distribution

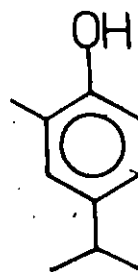
Table 19 lists the results of a study of the effect of solvent changes on the distribution of products resulting from the irradiation of 1-BX₃ in solvents which just contained C, H, F and no other heavier elements. Photoisomerizations of the degassed solutions of the complexes were carried out to less than 5% conversion of 1-BX₃ to minimize the formation of secondary products. The products were analyzed by glpc after quenching the reaction mixtures.

As the results in Table 19 show, the fluorinated solvents had no appreciable effect on the product distribution for the BF₃ and BCl₃ complexes of 1 but had a marked influence on that obtained with 1-BBr₃.

Three additional products were obtained upon irradiation of 1-BBr₃ in CH₃CH₂F and CH₃CHF₂. Two of these were identified as 4 and 15 on the basis of a comparison of their glpc retention times with those of authentic compounds. The identification of the other photoproduct, which had a different retention time to that of any of the photoproducts of 1, was not pursued.



4



15

It is not clear if 15-BBr₃ is a primary photoproduct of 1-BBr₃ in the fluorinated solvents. The irradiation of 6-BBr₃ in these solvents may

Table 19: Solvent Effect Upon the Product Distribution on the Irradiation of α -1-BX₃ Complexes.^a

Solvents	BX ₃	Product Distribution % ^b							Unidentified
		<u>4</u> ^c	<u>5</u>	<u>6</u>	<u>13</u>	<u>8</u>	<u>12</u>	<u>15</u> ^c	
CH ₂ Cl ₂	BF ₃	-	1	69	10	20	-	-	-
	BCl ₃	-	1	69	10	20	-	-	-
	BBr ₃	-	>0.5	7	8	60	25	-	-
CH ₃ CH ₂ F	BF ₃	-	1	69	10	20	-	-	-
	BCl ₃	-	1	70	10	19	-	-	-
	BBr ₃	2	3	43	7	19	12	6	8
CH ₃ CHF ₂	BF ₃	-	1	74	9	16	-	-	-
	BCl ₃	-	1	72	8	19	-	-	-
	BBr ₃	2	3	42	5	13	12	4	19

a/ Irradiated at -90°, $\lambda > 370$ nm.

b/ Expressed as relative percent, $\pm 2\%$.

c/ Identified on the basis of relative retention time.

cast further light as to the possible origin of 15-BBr₃. However, this experiment has not yet been attempted.

It must be remembered that 4 was not detected on the irradiation and subsequent quenching of 1-BBr₃ when CH₂Cl₂ was used as the solvent. One possible explanation is that 4-BBr₃ may indeed arise from a triplet state of 1, as formerly suggested by Childs and Hine. When CH₂Cl₂ is used as the solvent, the external heavy atom (chlorine) which is present in high concentrations may have increased the rate of intersystem crossing of T₁ → S₀ to the point where the formation of 4-BBr₃ cannot compete with the decay of the triplet.⁵²

Interestingly, 4 was not detected on the irradiation and quenching of 1-BF₃ and 1-BCl₃ in any of the solvents used. Even in the case of 1-BBr₃, very little 4-BBr₃ is produced as compared to the amount of 4H obtained on irradiation of 1H.

5. Quenching Studies

To further probe for the involvement of a triplet excited state in the photoisomerization of 1-BX₃, several experiments were performed with these Lewis acid complexes in both CH₂Cl₂ and CH₃CHF₂ using cyclohexa-1,3-diene as a triplet quenching agent. The choice of quenching agent was not unlimited in that it had to be stable to any possible reaction with the excess BX₃ present in the solution, soluble at low temperatures in the solvent used, not absorb any of the incident light and have a lower triplet energy than 1-BX₃.

Photoisomerizations of the degassed solutions of the Lewis acid complexes of 1, containing cyclohexa-1,3-diene, at -90° with light of $\lambda > 370$ nm, were carried out to less than 5% conversion of 1-BX₃. The results of this study are shown in Table 20.

If one or another of the products of the photoisomerization of 1-BX₃ had originated from a quenchable triplet state, then a change in the product distribution would be anticipated. As can be seen from a comparison of the results given in Tables 19 and 20, the product distribution obtained on irradiation of 1-BX₃ was not altered when cyclohexa-1,3-diene was added to the solutions. However, this failure to detect any quenching cannot be taken to imply that triplet states are not involved in these photoisomerizations. In particular, it is possible that the complexation of 1 with the Lewis acids may have lowered the energy of the triplet excited state of 1 to a point where energy transfer to cyclohexa-1,3-diene ($E_T = 54$ kcal/mole)⁵³ is endothermic. We can get an idea of the triplet energy of 1-BX₃ from related work on benzophenone.

Table 20: Effects of Cyclohexa-1,3-Diene Upon Product Distribution
Obtained on Irradiation of the 1-BX₃ Complexes.^a

Solvent	Lewis Acid	Product Distribution % ^b				
		<u>5</u>	<u>6</u>	<u>12</u>	<u>13</u>	<u>8</u>
CH ₂ Cl ₂	BF ₃	1	70	-	10	19
	BCl ₃	1	69	-	10	19
	BBr ₃	trace	7	25	8	60
CH ₃ CHF ₂	BF ₃	1	74	-	9	16
	BCl ₃	1	73	-	8	18

a/ In all cases, the solution was 0.0123 M in cyclohexa-1,3-diene. Reactions were carried out to <5% completion.

b/ Expressed as relative percent, $\pm 2\%$.

Leermakers reported that the near edge of the phosphorescence band of benzophenone shifted from 385 nm in ethylene-glycol-water to 432 nm in 98% H_2SO_4 .¹⁶ Using the relationship shown in the equation below, one may calculate that the energy of the triplet state has been reduced by some 8 kcal/mole.⁵³

$$E = \frac{2.86 \times 10^5}{\lambda(\text{\AA})} \text{ (kcal/mole)}$$

If we assume that a corresponding decrease could occur with eucarvone and that complexation with boron trihalides would give a similar energy lowering, then the triplet energy of l-BX_3 would be expected to be $[(61 \pm 1) - 8] = 53$ kcal/mole. While this estimate is very crude, this value is comparable to the triplet energy of the diene. In order to observe quenching, the energy of the donor must be at least 3 kcal/mole higher than that of the acceptor.²⁴

One of the obvious experiments that should be done is to find a triplet quencher that has a triplet energy of some 50 kcal/mole or less. However, as was pointed out at the outset of this section, the choice is not unlimited. Molecular oxygen does not seem to have any effect on the product distribution obtained in the irradiation of these complexes.

6. Possible Mechanisms for the Formation of Products

The formation of 6H from 1H must involve the rupture of the C_6-C_7 bond and bond formation between C_6 and C_4 , and C_2 and C_5 .^{8a} This process could occur in stepwise or concerted fashion, as is illustrated in Figure 16. Since the production of bicyclo [4.1.0]-heptenones occurred only in polar media¹³ and did not occur in the photoisomerization of cyclohepta-2,4-dienones unsubstituted at C_6 , Hine suggested that the formation of 6 or 6H did not proceed in a concerted fashion.^{8a}

The open chain, delocalized cation, 17H was disfavoured by Hine as an intermediate since no protonated vinyl cyclopentenone, which would be the expected product obtained from such an open chain intermediate⁵⁴⁻⁵⁶, was detected in the irradiations of 1H. Hine suggested that the formation of 6H from 1H involved only the intermediate 16H.

In view of the similarities in the spectral properties, charge delocalization and the photoproducts of 1H and 1-BX₃ complexes, it is felt that the photoproducts were formed in a similar manner. The formation of 5-BX₃, 6-BX₃, 8-BX₃ and 13-BX₃ may involve the intermediate 16-BX₃, as illustrated in Figure 17.

The recent results of Hart⁹ would suggest that the formation of the intermediate 16-BX₃ could be thought of as involving a 1,2 alkyl shift of C_7 to C_5 at some stage during, or after, a light-induced cis/trans isomerization of 1-BX₃. The formation of 6-BX₃ may involve the subsequent formation of the C_4-C_8 bond, while the formation of the isomeric phenols could proceed through the intermediate 18. This intermediate could result from

Figure 16: Stepwise and Concerted Mechanism for the Formation of 6H
Suggested by Hine.

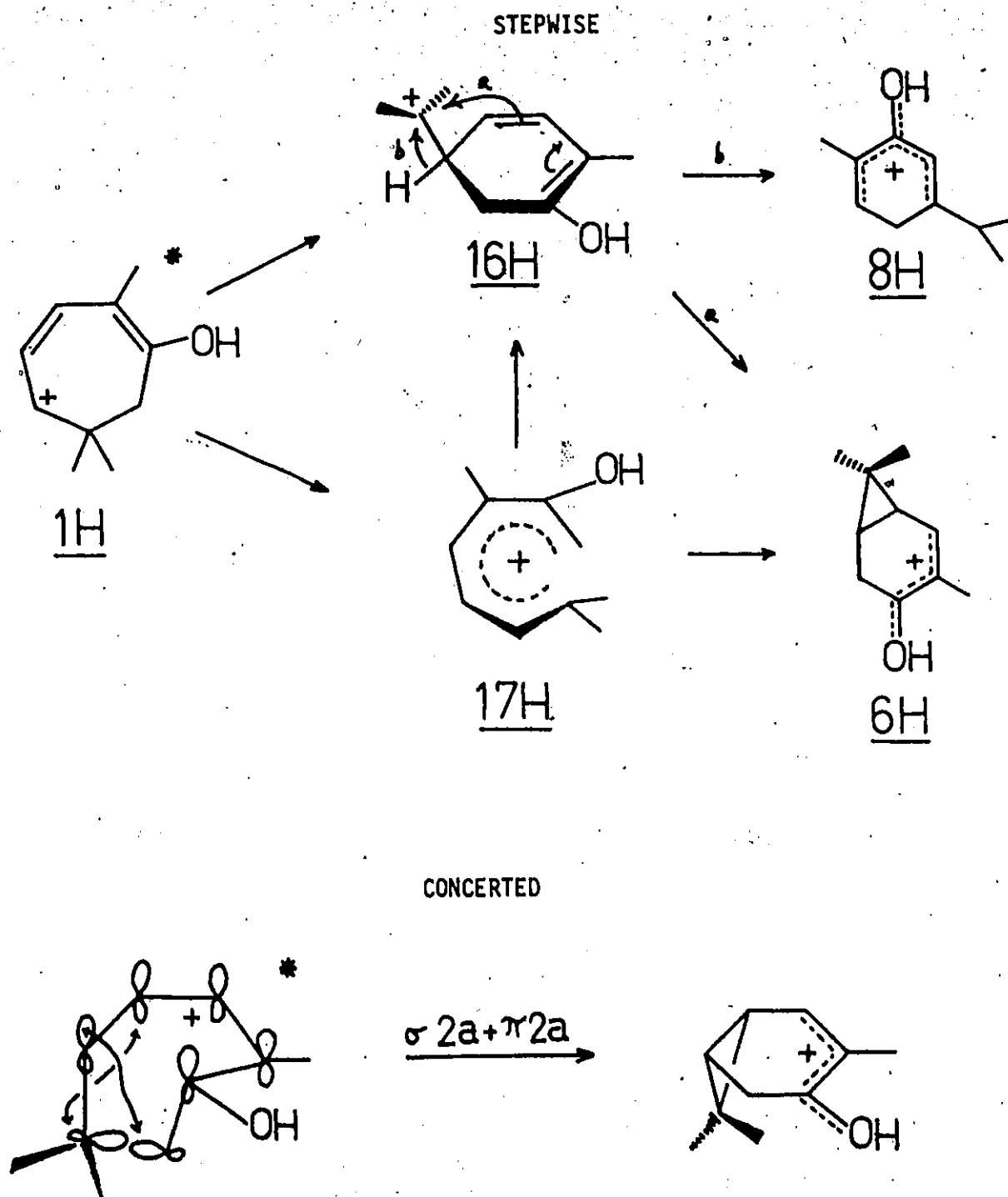


Figure 17: Possible Mechanistic Scheme for the Production of Primary Products.

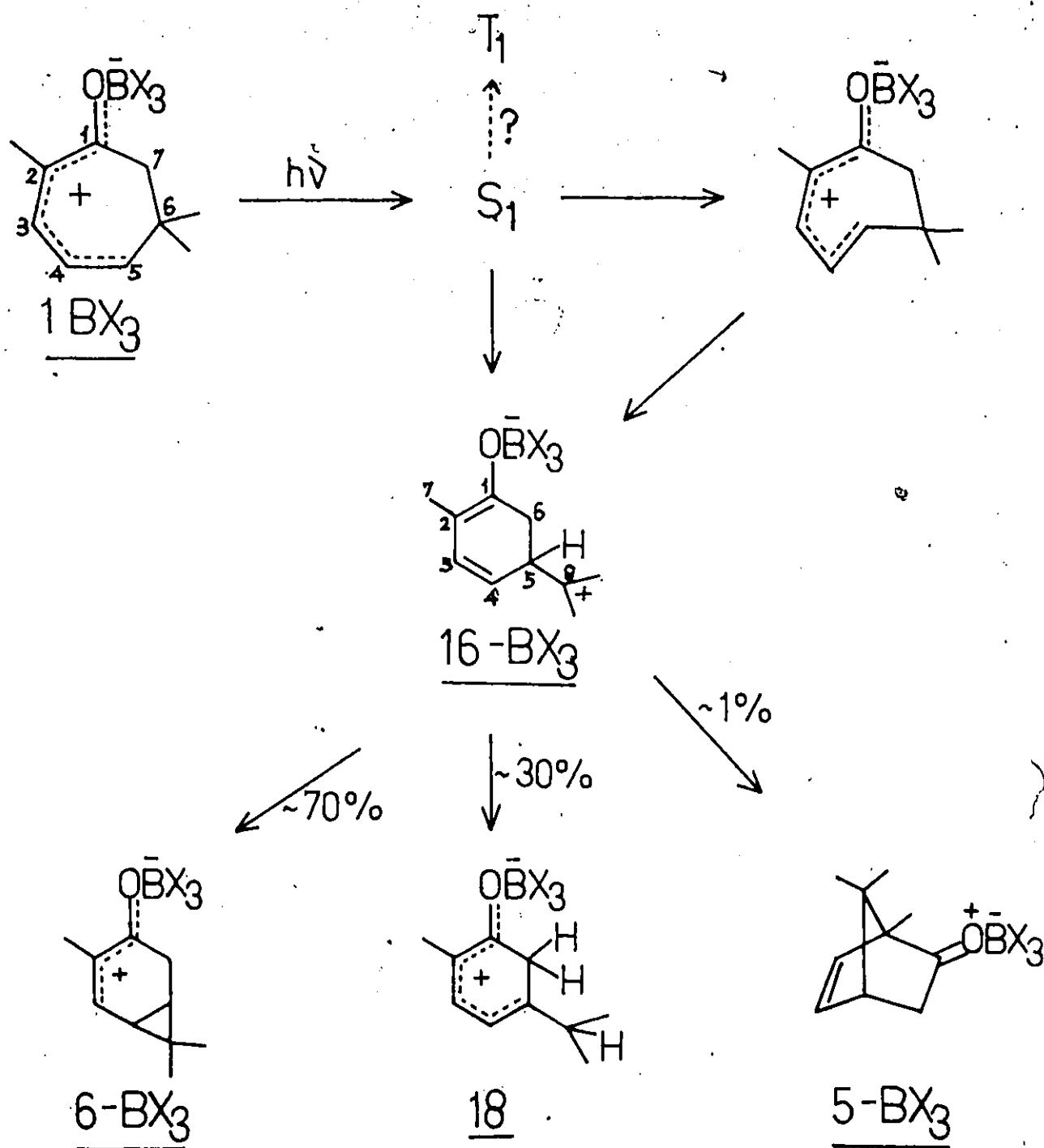
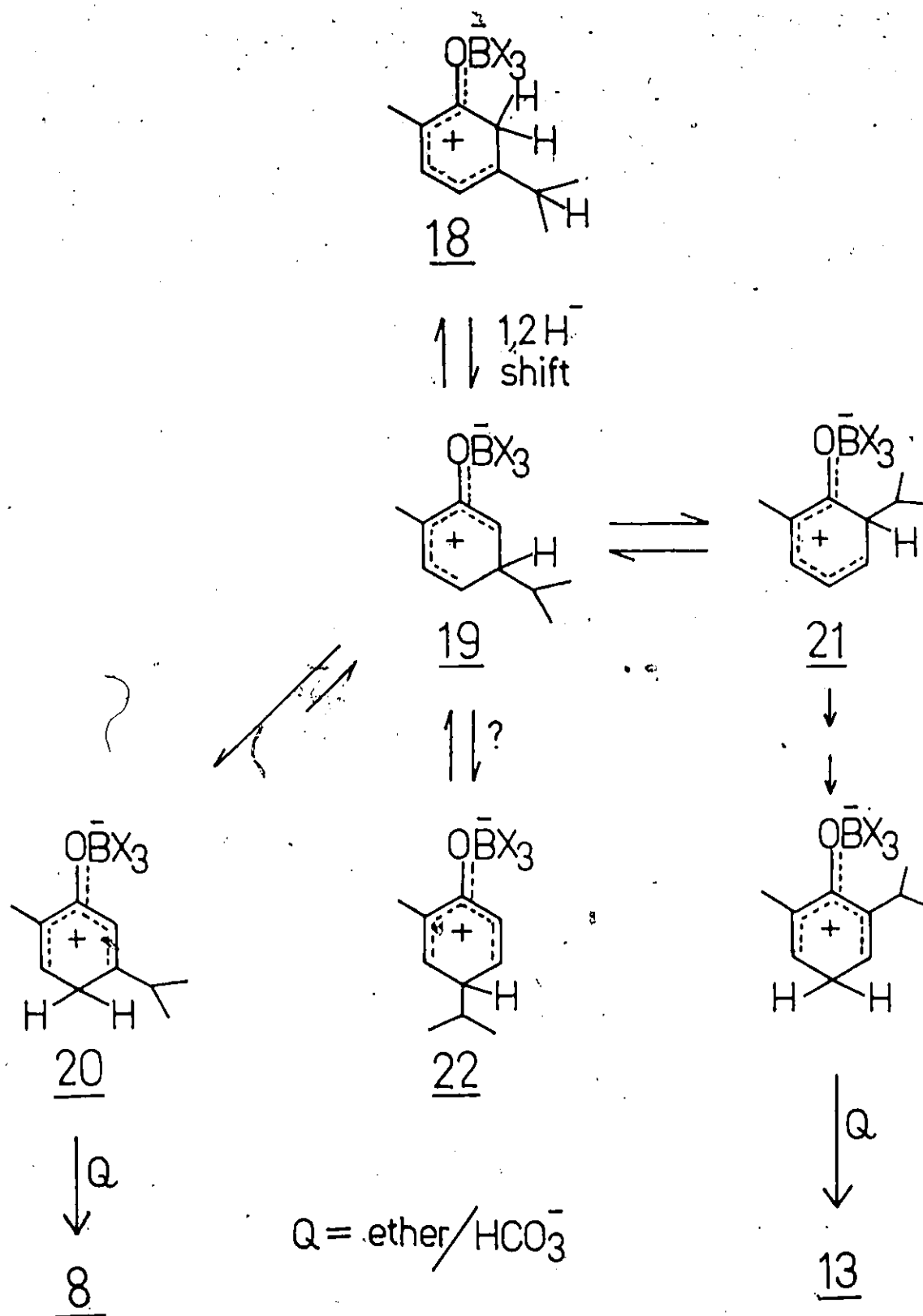
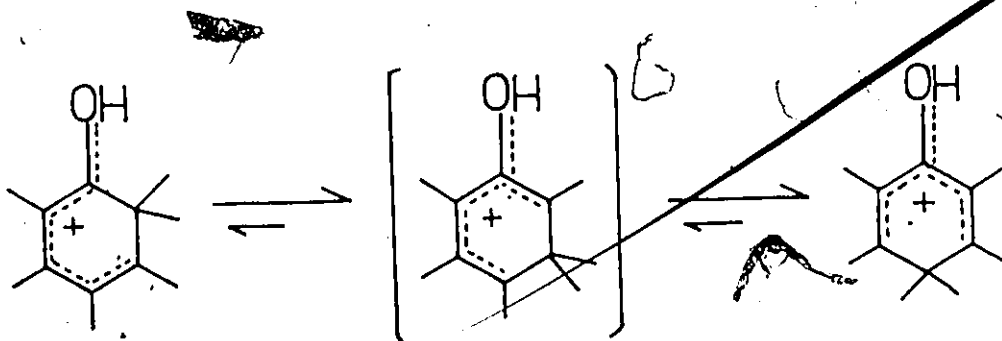


Figure 17 (continued)



a 1,2 hydride shift from C₅ to C₈ of 16-BX₃ as shown in Figure 17.

While 18 would be expected to give 8 on quenching of the CH₂Cl₂ solution of the complexes, it is probable that it would rearrange to give thermodynamically more stable products. For example, it is known that protonated 2,3,4,5,6,6-hexamethylcyclohexa-2,4-dienone is thermodynamically less stable than, and rearranges to the corresponding symmetrical protonated dienone.⁵⁷

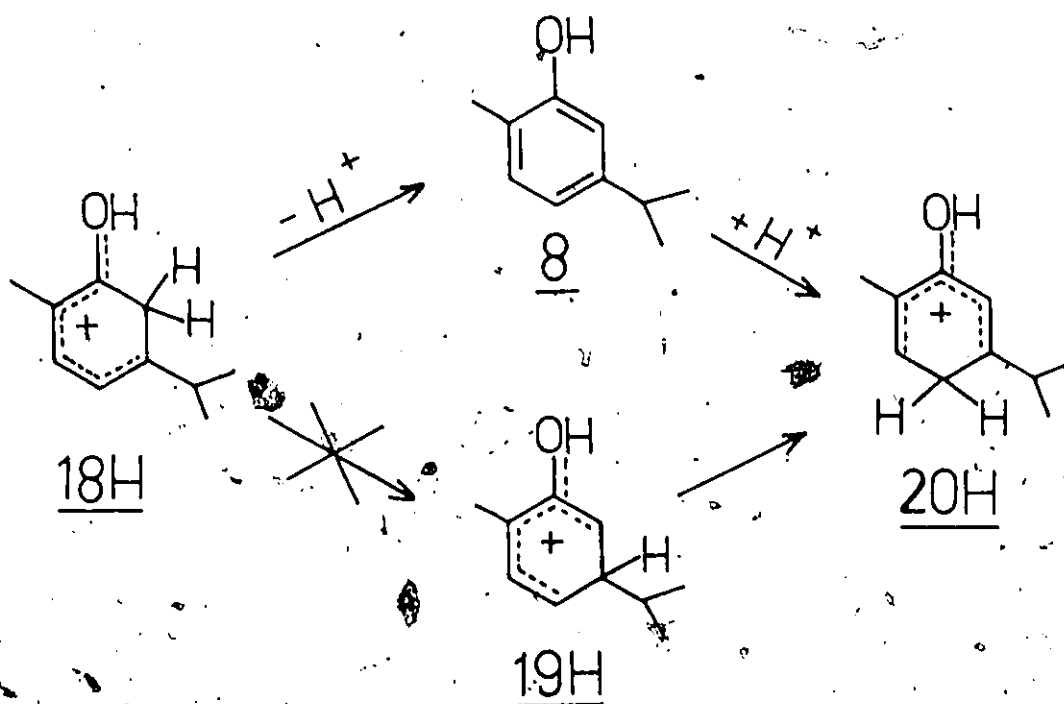


The occurrence of a 1,2 (or 1,6) hydride shift with 18 would give 19 and a further hydride shift would give 20. By analogy with the protonation of 8, 20 would be expected to be more stable than 18 and would give 8 on reaction with ether/HCO₃⁻.¹⁴

Isopropyl groups are known to be capable of readily undergoing 1,2 migrations in cationic systems.⁵⁸ A competing reaction of 19 would be isopropyl migration to give either 21 or 22. As is indicated in Figure 17, 21 could ultimately lead to a complex which on quenching would give 13. From all that is known about cations such as 19^{59,60}, migration of isopropyl to C₄ would be expected to compete with migration to C₆. However, the product expected on quenching, 15, was not found

in the photoisomerizations of 1-BF₃ and 1-BCl₃, and only detected in the irradiation of 1-BBr₃ in CH₃CH₂F and CH₃CHF₂. Even in this latter case it will be remembered that there was some doubt as to whether 15 was a primary product. It is not completely clear at this stage why 15 is not detected as a product of these isomerizations. One possible explanation, which has not been tested, is that 15-BX₃ is thermodynamically unstable and reverts back to 19 and thence 20 and 21.⁶⁰

It is interesting that protonated 13 (13H), is not a product of the photoisomerization of 7H. This would possibly be the result of an intermolecular mechanism being involved in the isomerization of 18H to 20H, rather than an intramolecular process involving a cation such as 19H.⁶¹ There is ample precedent for intermolecular hydride shifts occurring with benzenonium ions in media such as FSO₃H.⁶²



CONCLUSIONS

1. The results presented in this thesis have demonstrated that the photoisomerizations of the Lewis acid complexes of unsaturated ketones can indeed be studied and that such irradiations can lead to clean isomerization reactions.
2. The photoisomerizations of the BF_3 and BCl_3 complexes of eucarvone are quite similar to those found for protonated eucarvone. In view of this similarity, it would seem, as was suggested by Hine, that the photoproducts are derived from a singlet state.
3. The BBr_3 complex of eucarvone is a more complicated system in view of the extreme sensitivity of one of the products to further photoisomerization. Moreover, additional products are formed to those found with the irradiation of l-BF_3 and l-BCl_3 . However, at this stage it cannot be stated positively whether a triplet excited state is involved in the photoisomerizations of l-BBr_3 .
4. The results of this study also show that the photo-behaviour of protonated eucarvone may be more complicated than was previously thought, especially in the products formed in the irradiation of 6H .
5. The study of photoisomerization of the Lewis acid complexes of eucarvone is complicated by the large array of products that are formed. It would probably be better to investigate a simpler system with a view to developing suitable techniques to glean information about the multi-

plicity of the excited states involved in the photoisomerization of complexed or protonated ketones.

EXPERIMENTAL SECTION

1. Instrumental

Pmr spectra were obtained on Varian HA-100, A-60 and T-60 spectrometers, the first two being equipped with variable temperature probes. Probe temperature was measured with a copper constantan thermocouple connected to a standardized potentiometer. Carbon-13 nmr spectra were measured by the pulsed Fourier transform technique on a Bruker WH90 spectrometer. The Pmr chemical shifts in CCl_4 were referred to internal TMS (δ 0.00); those in FSO_3H and of the boron trihalide-complexes to internal CH_2Cl_2 (δ 5.30). The ^{13}C chemical shifts of neutral compounds in CDCl_3 were recorded relative to internal TMS (δ 0.00) while those of the Lewis acids-complexes to internal CDCl_3 (δ 77.21). Infrared spectra were obtained on a Perkin-Elmer Model 337 grating spectrophotometer using NaCl cells. The 1601 and 1028 cm^{-1} bands of polystyrene were used to calibrate the spectra. Ultraviolet spectra were recorded with a Cary 14 spectrometer. Varian Aerograph 204 (analytical) and Aerograph A-90-P3 (preparative) gas chromatographs were used. Helium was used as a carrier gas at 50-60 ml/min. Several glpc columns were employed and these are subsequently referred to by a letter code: Column A, 10 ft. x 1/8 in. 20% carbowax 2000 M on chromosorb W, 60-80 mesh; Column B, 10 ft. x 1/4 in. 15% SE 30 on chromosorb W, 60-80 mesh; Column C, 13 ft. x 1/4 in. 20% carbowax 2000 M on chromosorb W, 60-80 mesh.

2. Reagents

FSO_3H (Allied chemicals) was distilled first from sodium fluoride

(1 gm for 400 ml) and then (without NaF) through a 12" glass column. It was stored in 1 ml aliquots in sealed glass ampoules. Reagent grade methylene chloride was purified by the procedure of Wood and Jones.⁶³ Reagent grade chloroform was purified⁶⁴ by washing with concentrated H_2SO_4 , dilute NaOH and finally three times with distilled water. It was then dried over K_2CO_3 and redistilled twice from P_2O_5 , b.p. 61° . Acetic acid was refluxed with acetic anhydride and distilled, the fraction boiling at 118° being collected. n-Pentane was purified by treatment with fuming H_2SO_4 and distilled, b.p. 35° - 36° .^{8a} Diethyl ether, spectral-grade carbon tetrachloride, sulfur dioxide and the boron trihalides were used as supplied.

3. General Techniques

(i) Protonation

Method A - Protonations were carried out by slowly adding precooled (-78°) FSO_3H (~ 0.5 ml) to a dry nmr tube which contained the cation precursor (ca. 20 mg) and which was kept in a dry-ice-acetone bath. Solution was effected by agitating the sample with a precooled (liquid N_2) 2 mm quartz rod.

(ii) Quenching of the Acid Solution

Method B - The acid solution of the cation was added dropwise to a rapidly stirred suspension of sodium bicarbonate (5 g) in ether (25 ml) kept at -78° . Upon warming to 0° , ice water (5 ml) was added, the mixture was stirred and filtered under suction. The organic layer was washed

with brine solution until neutral to litmus and then dried (MgSO_4). The products were recovered by careful evaporation of the solvent at atmospheric pressure through a 6" Vigreux column and analyzed by vapor phase chromatography.

(iii) Preparation of Complexes

Method C - Vacuum Line Technique

The ketone or phenol (10-20 mg) to be complexed was weighed into a nmr tube which was then attached to a high vacuum line and evacuated. The tube was cooled with liquid N_2 and the appropriate solvent, e.g. CH_2Cl_2 (~1.0 ml), was distilled into it. This mixture was warmed to room temperature to allow the compound to go into solution, cooled once more with liquid N_2 and evacuated. A known amount of the desired boron trihalide was condensed directly from a calibrated volume into the tube. The resulting mixture was warmed until the solvent melted to allow reaction with the Lewis acid (e.g. -78° with CH_2Cl_2 as solvent). The nmr tube was sealed under vacuum.

For complexes which are not stable at -78° , the mixture was only allowed to warm up to $\sim -95^\circ$ (liquid N_2 -toluene bath) and the nmr tube again sealed under vacuum.

Method D - For Complexes Which Were Relatively Stable at -78°

The complex was formed by slow dropwise addition of the precursor dissolved in the appropriate solvent, e.g. CH_2Cl_2 (20 mg in ~0.5 ml), along the inner wall of a nmr tube containing the Lewis acid (BF_3 or BCl_3 , ca. 25 mg) and kept at -78° . During the addition, a slow stream of N_2 was passed into the

nmr tube to minimize the absorption of moisture from the air. The solution of the complex was mixed by agitation with a precooled 2 mm quartz rod.

Method E - For Complexes Which Were Relatively Unstable at -78°

The complex was formed as above except that the nmr tube containing the Lewis acid precooled to a temperature below -90° (liquid N_2 -toluene bath).

Method F - For U.V. Measurements

The complexes were prepared as described in Method C except that a 200 ml reaction flask equipped with a stirrer bar and fitted with a side arm leading to a 2 mm quartz cuvette was used. CH_2Cl_2 was used as the solvent. After the complex was formed, the flask was detached from the vacuum line and placed in a sufficiently large Dewar vessel containing a dry-ice-acetone mixture, so that the side arm with the quartz cuvette could also be cooled to -78° . Some of the solution was transferred into the cuvette by tilting the flask and the cuvette was sealed under vacuum.

(iv) Quenching of Complexes

Method G - A mixture of $NaHCO_3$ (0.5 g) in ether (25 ml) was stirred and cooled to -90° in a liquid N_2 -toluene bath. A precooled 2 mm quartz rod (in liquid N_2) was inserted into the nmr tube and the solution stirred while some of the precooled ether/ HCO_3^- slurry (ca. 2 ml) was slowly added dropwise down the wall of the nmr tube. The quenched solution was quickly transferred into the remaining ether/ HCO_3^- solution. Upon warming to 0° , ice water (5 ml) was added to the ether slurry, the mixture swirled and filtered under suction. The organic layer was washed with brine until neutral (litmus) and dried ($MgSO_4$). The products were worked up as in Method B and analyzed by glpc.

(v) Determination of Product Ratios

These were determined by analytical glpc. The areas of the appropriate peaks were measured either by triangulation or cutting and weighing the peaks of the original trace or its photocopy. An internal standard, cycloheptanone, was used to calibrate the detector for several of the products to ensure that all had identical detector responses. This was done by injecting a preweighed amount of cycloheptanone into a mixture of known amounts of eucarvone (1), carvone (12), and carvacrol (8). The mixture of these 4 compounds was analyzed by glpc. This experiment was repeated several times with different amounts of each compound and the detector was found to give identical response for each compound. The results of all analyses were reproducible to $\pm 2\%$ and the average of 2 or 3 injections is quoted in the various tables.

(vi) Photochemical Experiments

With the eucarvone complexes, several separate irradiations were performed. The first set of experiments was used to determine the length of time required for photochemical isomerization. Having achieved this, a second set was carried on preparative scale to identify the photoproducts. Subsequent experiments were conducted in a more quantitative manner to examine the product stability and any change in product ratios with irradiation time.

Method H - Irradiation of Protonated Ketones or Complexes at Low Temperature.

All irradiations were performed on samples contained in clear, thin walled nmr tubes which cut off light at wavelengths < 260 nm. The cooling

system, which is capable of maintaining a constant temperature over a range of -95° to -55° , has been previously described.^{8a,60} The temperature of the sample was measured with a copper constantan thermocouple connected to a standardized potentiometer. To avoid corrosion of the wire, the thermocouple was covered with a glass tube before it was inserted into the sample. When the light source was switched on, the temperature of the sample increased by about 5° .

Light Source - The light from a Phillips Sp-500 high pressure lamp was passed along a highly polished aluminum tube, through a glass filter, and focussed by a semi-cylindrical quartz lens upon the sample. A Corning #3850 filter was used in all irradiations and this cut off light at wavelengths less than 370 nm.^{8a}

4. Synthesis of Ketones and Phenols

(i) Eucarvone, 1, was prepared in 70% yield from carvone (Eastman) by the procedure of Corey and Burke.⁶⁵ The spectral properties of this material were identical to those reported earlier.⁶⁶

(ii) Bicyclo [4.1.0] heptenone, 6, and Bicyclo [3.2.0] heptenone, 9, were obtained by irradiating eucarvone, 1, in a $\text{FSO}_3\text{H}/\text{SO}_2$ mixture in a comparable manner to that described by Hine.¹⁴ It was found that 6 was not stable for long periods of time when dissolved in the ether obtained directly from the work up procedure (it reacted slowly to give two compounds as indicated by glpc analysis). When purified n-pentane was used to replace the ether in the final work up step, no such instability was found. 6 and 9

had identical properties to those previously reported.^{13,14}

(iii) Norbornenone, 4, was prepared by irradiating eucarvone,¹ in 50% acetic acid using the procedure of Hurst and Whitham.¹⁰ It was collected by preparative glpc (Column C). Its spectral properties were identical to those reported earlier.^{10,14}

(iv) 2-methyl-6-isopropylphenol, 13, was prepared from o-cresol in a comparable manner to that described by Sowa.⁴⁷ BF_3 (2.4 g) was passed into a mixture of isopropyl alcohol (6 g, 0.1 mole) and o-cresol (10.8 g, 0.1 mole). The mixture was heated under reflux for 1 hour. The reaction was cooled, the upper layer collected and then distilled at 0.5 mm. The fraction boiling between 30° and 50° was collected, dissolved in benzene (60 ml) and extracted with 15% aqueous potassium hydroxide solution (2 x 60 ml). The combined aqueous layers were acidified with dilute hydrochloric acid and the phenols extracted into benzene (60 ml). The benzene layer was dried (MgSO_4) and the solvent removed in vacuo to give an oil (5 g). Glpc analysis (Column C) showed three compounds to be present and these were collected and analyzed by pmr. The last two were each shown by pmr to have two isopropyl groups present and they were not further identified. The first peak was shown to be 2-methyl-6-isopropylphenol by spectroscopic means. Pmr Table 11; ir (CCl_4) 3690, 3090, 3000, 2900, 1460, 1375, 1300, 1220, 1169, 1119, 1068, 965, 930, 910, 630, 600, 580, 550 cm^{-1} ; ^{13}C nmr Table 12.

(iv) 2-methyl-4-isopropylphenol, 15, was prepared from p-isopropylphenol by the four-step procedure outlined by Carpenter and Easter.⁴⁴ Pmr Table 13, ^{13}C nmr Table 12.

5. Photochemical Experiments

(i) Photoisomerization of Protonated Eucarvone in FSO_3H

Samples of 1H (25 mg) in FSO_3H (0.5 ml) were irradiated in nmr tubes at -75° for about an hour according to Method H. The resulting acid solutions of the products were quenched as described in Method B. Analysis of the products by glpc on Column A showed 4 (11%), 6 (72%), and 8 (17%) to be present.

(ii) Photoisomerization of Protonated Eucarvone in $\text{FSO}_3\text{H}/\text{SO}_2$

Samples containing equal concentrations of 1H (20 mg) in FSO_3H and a $\text{FSO}_3\text{H}/\text{SO}_2$ mixture were irradiated for the same length of time at -75° as described in Method H. The solutions were quenched (Method B) and analyzed by glpc, Column A. The results are shown in Tables 2 and 3.

(iii) Preparative Scale Irradiation of Eucarvone- BCl_3 Complex in CH_2Cl_2

Compound 1 (200 mg) in CH_2Cl_2 (2 ml) was reacted with BCl_3 as described in Method C and irradiated (Method H) at -90° for four to five hours. The progress of the reaction was monitored by pmr. The photoproducts were quenched at -90° with ether/ HCO_3^- as described in Method G. The oil obtained was separated by glpc (Column B) to give compound 1 and five other products. Enough of each was collected for spectroscopic identification. The following compounds were isolated: 5, pmr Table 11; ir (CCl_4) 3000, 2800, 1740 cm^{-1} ; 6, pmr Table 11; ir (CCl_4) 3015, 2950, 2930, 1665, 1390, 1285, 1250, 1120, 1050 cm^{-1} ; 12, pmr Table 11, ir (CCl_4) 3000, 2950, 2900, 1700, 1670, 1640, 1440, 1350, 1270, 1128 (CS_2), 930, 810 cm^{-1} ; 13, pmr Table

11, ^{13}C nmr Table 12; ir (given in previous section); 8, pmr Table 11, ir (CCl_4) 3600, 2960, 2930, 1300, 1230, 1172, 1115, 995, 938, (CS_2) 860, 812, 712, 694, 638 cm^{-1} , ^{13}C nmr Table 12.

(iv) Low Temperature Irradiation of Eucarvone-Boron Trihalide Complexes

✓ Samples of 1 (10-19 mg) in CH_2Cl_2 (~0.5 ml) were reacted with the boron trihalides as described in methods C or D and irradiated in nmr tubes at -90° for 2 to 45 minutes (Method H). The resulting solutions were quenched at -90° with ether-bicarbonate solution as described in Method G. Analysis by glpc on Column A showed compounds 5, 1, 6, 12, 13 and 8 to be present. The product distributions are given in Tables 14 and 16. The relative retention times of these materials are given in Table 21.

6. Control Experiments

(i) Thermal Stability of the Lewis Acid-Complexes of Eucarvone

Samples of 1 (ca. 20 mg) in CH_2Cl_2 (ca. 0.5 ml) were reacted with each boron trihalide (Method C). The resulting solutions were examined by pmr at temperatures between -50° and room temperature ($+37^\circ$). The probe temperature was increased by increments of 20° until room temperature was reached. No changes in the pmr spectra (Table 5) of the three Lewis acid complexes of 1 were detected at room temperature. The solutions of the complexes were quenched with ether/ HCO_3^- (Method B), and 1 was regenerated in high yield (98%) in each case.

Table 21: Glpc Retention Times of the Photoproducts (After Quenching)
of III and 1-BX₃ Relative to 1.^a

Compounds	Relative Retention Times (min)
<u>1</u>	1
<u>4</u>	0.46
<u>5</u>	0.76
<u>6</u>	1.55
<u>8</u>	11.17
<u>9</u>	0.90
<u>12</u>	1.94
<u>13</u>	4.48
<u>18</u>	10.69

a/ Column used: 20% carbowax (Column A)

Column temperature: 155°.

Flow rate: 60 ml/min.

(11) Thermal Stability of the BCl_3 Complexes of Eucarvone Photoproducts in CH_2Cl_2

Compounds 6, 12, 13 and 8 (ca. 25 mg) were individually dissolved in CH_2Cl_2 (ca. 0.5 ml) and reacted with BCl_3 according to Methods C, D and E. The resulting solutions were examined by pmr at temperatures between -90° and room temperature ($+37^\circ$). The probe temperature was increased from the lowest value by increments of 15° until either an isomerization was observed or room temperature was reached.

At -50° , the BCl_3 complexes of 13 and 8 each exhibited a complex and irreproducible pmr spectrum. The solutions of these complexes were quenched with ether/ HCO_3^- at -78° (Method B) and 13 or 8 respectively were recovered in high yield.

When the solutions of 13-BCl₃ or 8-BCl₃ were warmed to room temperature, no change in their pmr spectrum was detected. The solutions of 13-BCl₃ or 8-BCl₃ after being warmed to room temperature were quenched at 0° (Method B) and the original phenols, 13 or 8, were regenerated.

At -50° , the pmr spectrum of 12-BCl₃ showed signals at δ 7.81, 4.81, 2.78 (broad), 1.88 and 1.69. This complex was stable at -15° but decomposed at room temperature as indicated by a change in its pmr spectrum. At room temperature, its pmr spectrum showed only two broad signals at δ 4.65 and 1.70.

6-BCl₃ was unstable at -78° . It slowly decomposed as indicated by the change of color from yellow to reddish brown. Its pmr spectrum at -50° was different from that at -90° (see text) and showed signals at δ 8.03, 6.68 (broad), 2.73 (broad), 2.08, 1.93, 1.52 (broad), 1.32, 1.20,

1.05, 0.77. Nothing could be recovered upon quenching solutions of 6-BCl₃ (Method B) after it had decomposed.

(iii) Photochemical Stability of the BCl₃ Complexes of Eucaryone Photo-products in CH₂Cl₂

The products 2, 13 and 8 (ca. 20 mg) were each reacted with BCl₃ in CH₂Cl₂ according to Method C. The resulting complexes were irradiated at -90° as described in Method H. The progress of the irradiation was checked by pmr. A complex was considered as photochemically "stable" if its pmr spectrum did not change on irradiation for more than two hours. The irradiated solutions were quenched with ether/HCO₃⁻ (Method B) and the recovered materials were either identified by their pmr spectra or by their glpc retention times (Column A).

The BCl₃ complexes of 12, 13 and 8 were found to be photochemically stable under the irradiation condition.

(iv) Low Temperature Irradiation of Boron Trihalide-Complexes of 6 in CH₂Cl₂

Samples of 6 (10-16 mg) in CH₂Cl₂ were reacted with each boron trihalide at -90° (Method C or E). Each complex solution was then quenched at -90° with ether/HCO₃⁻ (Method G) and 6 was recovered in 95% yield in each case as indicated by the glpc analysis.

Samples of known amounts of 6-BF₃, 6-BCl₃ and 6-BBr₃ were irradiated at -90°, as described in Method H, for known lengths of time (the light source was switched on an hour before the commencement of any irradiation). The irradiated solutions of the complexes were quenched with ether/HCO₃⁻ (Method G)

to give an oil in each case. The oil obtained was analyzed by glpc (Column A) which showed that two products were present. The retention times of the products were identical to those of 12 and 8. The product ratios are given in Table 15. The relative rates of the photochemical reactions of 6-BX₃ were obtained by calculating the amount of 6 converted per unit time and are given in Table 17.

(v) Protonation of Carvone, 12

Carvone, 12 (ca. 25 mg), was protonated in FSO_3H at -78° using the procedure described in Method A. The resulting solution was examined by pmr. At -60° , its pmr spectrum showed signals at δ 1.81, 1.32, 2.04, 2.25, 2.55-3.4, 4.06, 7.17, 8.13 and 8.24. On warming the acid solution to -40° , the pmr spectrum only showed signals at 1.32, 2.25, 3.06, 4.06, 7.17 and 8.13. When the probe temperature was raised to -20° , no further change in the pmr spectrum could be detected. The resulting solution was quenched at 0° (Method B) and the pmr spectrum of the resulting product showed that only 8 was present.

(vi) Thermal and Photochemical Stability of 4-BCl₃

Samples of 4 (25 mg) in CH_2Cl_2 were reacted with BCl_3 according to Method E. The resulting complex was examined by pmr (Table 18) and found to be thermally stable up to -20° . It decomposed at room temperature as indicated by the change in pmr spectrum.

On irradiation of the complex at -75° (Method H) for 3 hours, no change in the pmr spectrum could be detected. The solution was quenched

(Method B) and gave back the original compound as indicated by pmr and glpc analysis.

(vii) Complexation of Bicyclo [3.2.0] Heptenone 9 with BCl_3

Ketone 9 (ca. 20 mg) was reacted with BCl_3 at -78° (Method C) and the resulting complex was examined by pmr at -50° (Table 18). On quenching the solution at -45° (Method B), 9 was regenerated in high yield.

7. Quenching Studies on Lewis Acid Complexes of 1 With Cyclohexa-1,3-Diene

Samples of 1 (10-14 mg) dissolved in CH_2Cl_2 or CH_3CHF_2 (ca. 0.5 ml) were reacted with the appropriate Lewis acids at -78° according to Method C. Cyclohexa-1,3-diene (1 mg) was added in each case. The resulting solutions were irradiated at -90° (Method H) for less than five minutes. The solutions were then each quenched with ether/ HCO_3^- (Method G) and analyzed by glpc, Column A. The results are shown in Table 20.

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