LEWIS ACID CATALYSED PHOTOCHEMISTRY
OF CARBONYL COMPOUNDS

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By

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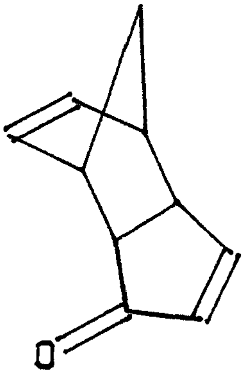
ABSTRACT

This thesis describes an investigation into the effects of Lewis acid complexation on the photochemistry of α,β unsaturated carbonyl compounds.

Initial studies involved the use of Nuclear Magnetic Resonance (NMR) and Ultraviolet (UV) spectroscopy in examining Lewis acid modification of the photostationary state for E/Z isomerization of various acyclic enones. The results obtained provide a good understanding of the origin of the perturbation of the photostationary state of these systems. In the course of these investigations, the question also arose as to the possible effects of complexation upon the photochemistry of cyclic enone systems where E/Z isomerization cannot occur, particularly whether this would catalyze [2+2] cycloadditions to the enone carbon/carbon double bond. Lewis acid complexed enones are widely used as activated dienophiles in Diels Alder reactions, and have been recently reported to serve as activated 'enophiles' in a photochemical dimerization of coumarin.

The examination here is focused upon endo-tricyclo [5.2.1.02,6] deca-4,8-dien-3-one.



Reported here is a detailed investigation of the photochemistry of the $AlEtCl_2$ complex of this compound, and the results are interpreted mechanistically. The reaction gives rise to a single product which reaches a photostationary state with the reactant complex. The isomerization is formally a [1,3] sigmatropic shift involving the isolated double bond. It seems likely however, to proceed by the formation of an allyl cation intermediate.

To my loving wife Irene,

she puts up with so much.

And to my parents,

without whose sincere cooperation

this author would not be possible.

Acknowledgments

I wish to extend my sincere appreciation to Professor R.F. Childs for his continual guidance, encouragement, and critical appraisal during the course of this work.

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Finally, thanks are due to Ms. Carol Rogerson, Mr. Brian Sayer, and Mr. Ian Thompson for their assistance in the recording of NMR spectra.

Table of Contents

List of Tables

List of Figures

It can justly be said that science and technology today are mainly engaged in making the rich countries richer and the strong countries stronger.

Abba Eban

Foreign Minister of Israel

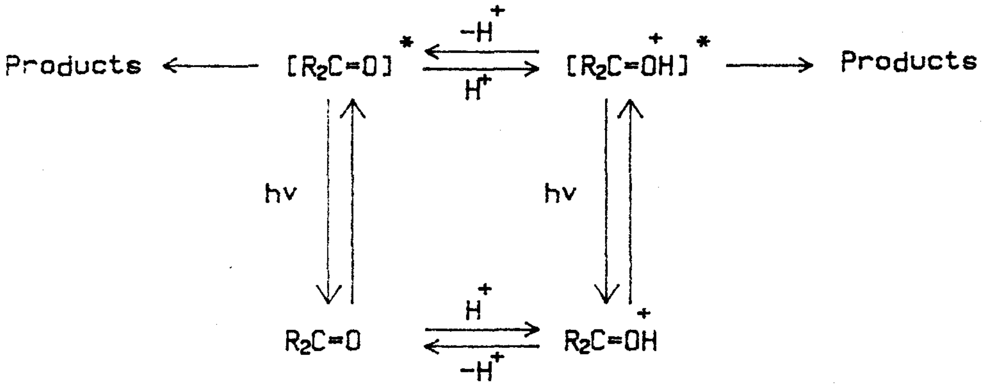
CHAPTER 1

INTRODUCTION

INTRODUCTION

1) Photochemistry of Protonated Enones

The photochemistry of oxygen protonated carbonyl compounds has begun to receive serious attention only in the last decade or so. Prior to this, very few reports of acid involvement in photochemical reactions appear in the literature. In many of these early examples, such as the acid catalysed photoinduced ring closure of substituted naphthofuranones described by Barton and co-workers,[1] involvement of the acid takes place only subsequent to excitation, and it is the excited state which becomes protonated. In principle, the desired protonated excited state can be reached regardless of whether protonation takes place prior to or subsequent to excitation. Since the former route results in a modification of the light absorbing properties of the chromophore however, most of the more recent attention has been focused on photoexcitation of the 'already' protonated species.[2]



Simple protonated enones typically have pK_a values in the -3 to -4 range on the H_A scale, and are thus essentially completely protonated in 100% sulphuric acid.[3] Enones possessing greater degrees of conjugation are even more basic owing to their enhanced ability to delocalize the positive charge introduced into the system upon protonation.[4]

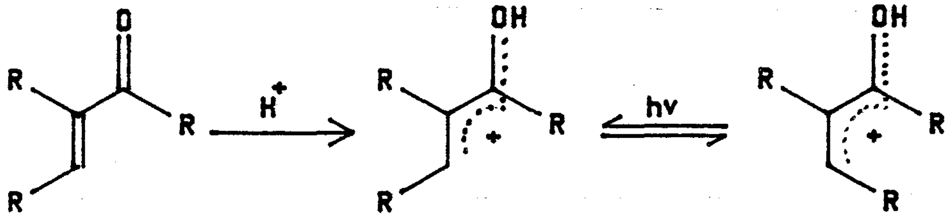
Although sulphuric acid is a cheap and readily available solvent, transparent to 200 nm, it suffers from the disadvantages of being quite viscous, and having a relatively high melting point of +10.4°C. Many protonated enones are unstable at ambient temperatures, necessitating the use of low temperatures in their study. Fluorosulphuric acid, FSO_3H, has emerged as the solvent of choice. It has a very low viscosity and a melting point of -88.98°C which makes it eminently suitable for low temperature work, it possesses the necessary transparency, and is also much more acidic, $H_o(H_2SO_4) = -11.93$; $H_o(FSO_3H) = -15.07$.[5]

Solutions of the protonated enones are easily obtained by dissolution of the appropriate compound in the strong acid medium, and the compounds and/or photoproducts can be recovered in high yield following neutralization. These systems have been extensively studied by a wide range of spectroscopic techniques, including ^1H and ^{13}C NMR, as well as absorption and emission spectroscopy.

Unsaturated carbonyl compounds exhibit both n,π^* and π,π^* bands in their absorption spectra. The former is usually very weak and occurs at lower energy than the π,π^* absorption. The n,π^* band is shifted to shorter wavelength with increasing solvent polarity. The much more intense π,π^* band is normally found at higher energy and is shifted to longer wavelength as the polarity of the medium is increased.[6] When the compound is fully protonated in a strong acid, the red shifted π,π^* band often completely obscures the less intense blue shifted n,π^* band.[7] Two of the nonbonding n-electrons of the carbonyl oxygen are now bound by protonation, causing the absorption band corresponding to the lowest energy transition to be very intense and of π,π^* character.[8]

Calculations show that the π,π^* states of enones can reach an energy minimum by twisting about the carbon/carbon double bond, allowing subsequent radiationless decay to both E and Z isomers.[9] They further show the energy barrier to rotation about the single bond connecting the carbonyl carbon to the double bond to be raised, thus intramolecular cyclizations or similar reactions which require an s-cis conformation of the excited enone could only occur from the π,π^* state if the enone system were reasonably close to an s-cis configuration upon excitation.

Since protonation raises the energy of the n,π^* state, one might expect any photoreactions of enones which are believed to proceed via n,π^* states, such as γ-hydrogen abstractions, not to occur in protonated systems.[10] Conversely, reactions able to proceed via π,π^* states, such as E/Z isomerizations, might reasonably be expected to operate quite efficiently. For example, simple alkyl substituted acyclic enones typically possess an intense π,π^* absorption band in the neighborhood of 220 nm. Upon protonation, the absorption maximum is usually shifted to about 250 nm.[4] These cations undergo efficient E/Z isomerization upon irradiation. Often low temperatures are necessary to prevent the thermal reversion of the Z to the thermodynamically more stable E isomer.



The mixture reached upon prolonged irradiation is referred to as the photostationary state. Some examples of protonated enone photostationary states are given in Table 1.[11]

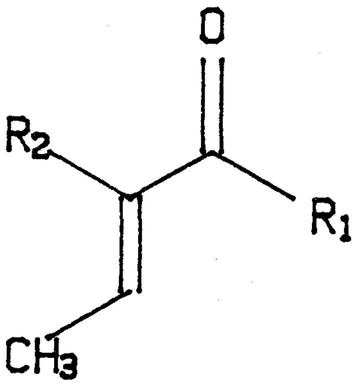
The above irradiations were also carried out in FSO_3D. That the ^1H NMR spectra of irradiated solutions showed no deuterium incorporation into the system suggests that these simple protonated enones do not undergo any photochemical enolization or γ-hydrogen abstraction reactions.

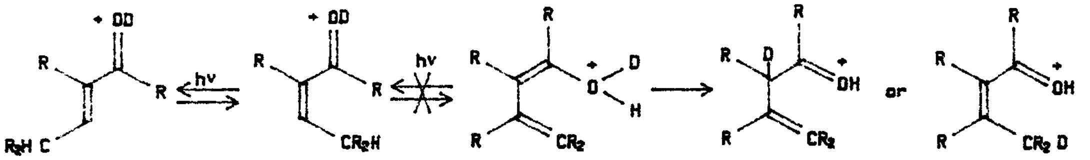
Table 1.[a] UV Spectra[b] and Photostationary State Compositions of some Simple Fully Protonated Enones

Compound	UV Spectra		Composition	
	λ_{max} (nm)	ϵ_{max} (ℓ mol^{-1} cm)	%E	%Z
$R_1=R_2=H$	258	4.37×10^4	46	54
$R_1=CH_3$, $R_2=H$	261	3.01×10^4	55	45
$R_1=H$, $R_2=CH_3$	278	4.68×10^4	26	74
$R_1=R_2=CH_3$	276	1.62×10^4	41	59
$R_1=OH$, $R_2=H$	236	4.08×10^4	58	42

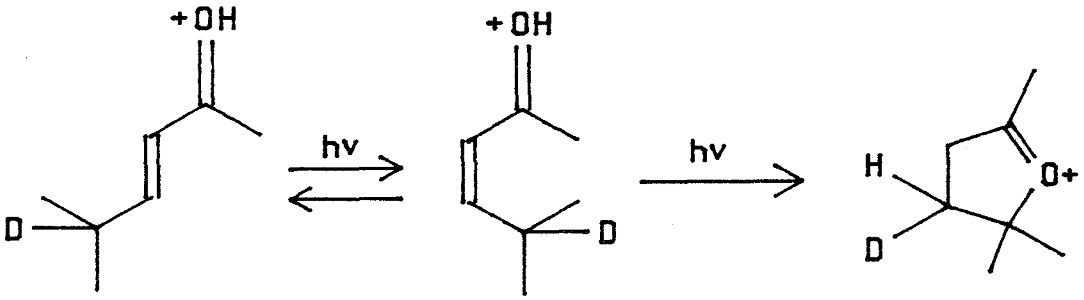
[a] Data presented here appeared originally in reference 12.

[b] UV data for E isomer, recorded in FSO_3H.

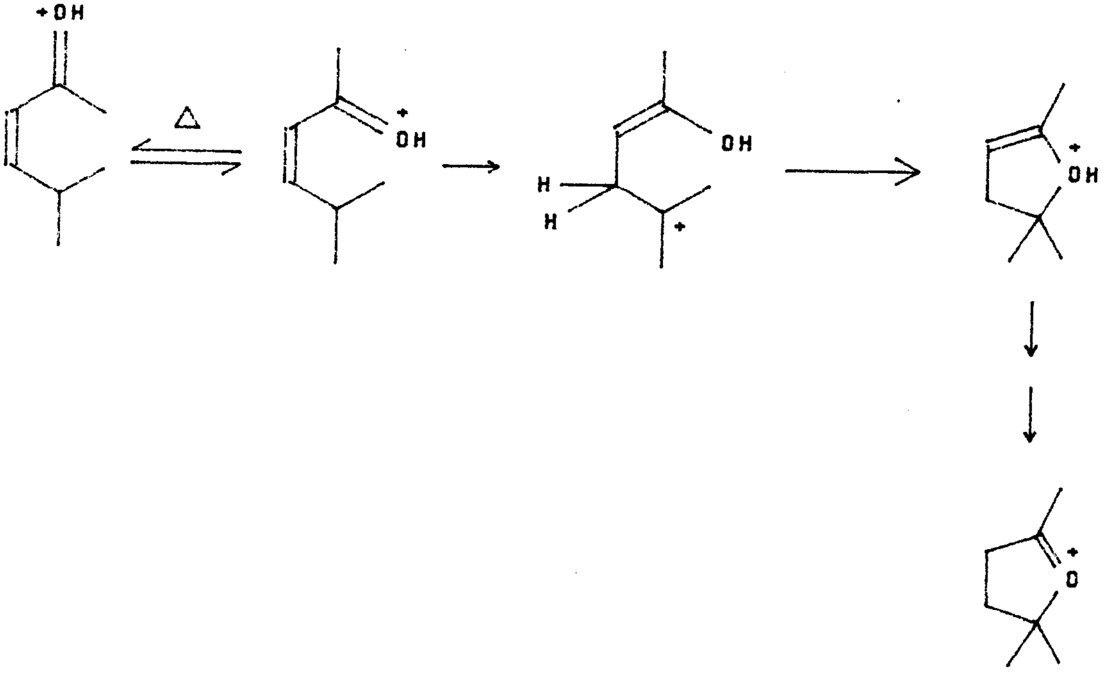




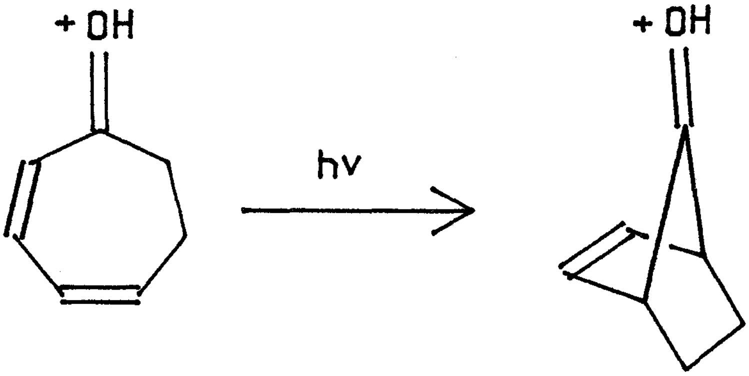
While photoinduced γ-hydrogen abstraction reactions do not occur with protonated enones, when the γ-carbon is potentially a relatively stable cationic site, a different type of photochemical hydrogen migration has been shown to occur. This was demonstrated with studies of protonated 5-methylhex-3-en-2-one.[12] This compound undergoes efficient E/Z isomerization under the previously described conditions as expected, however the slower formation of a third compound is observed.



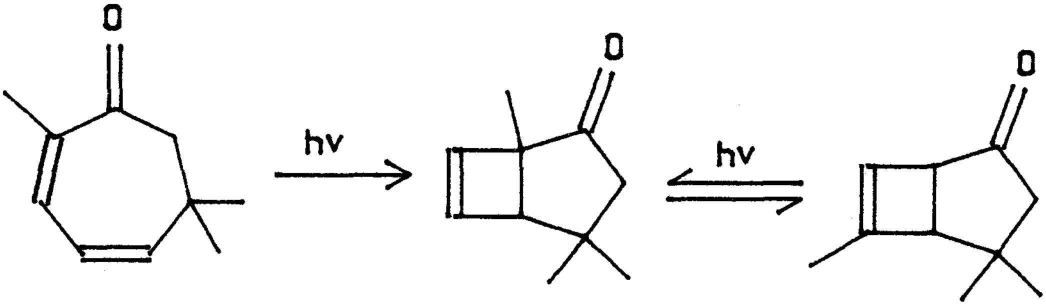
The final product in this reaction was shown to arise from a photochemically induced cyclization. Deuterium incorporation at C-5 shows the cyclization is accompanied by a photochemical 1,2 hydride shift. The results of the labelling experiment are consistent with the mechanism shown below. A 1,5 shift (photoenolization mechanism) would lead to deuterium loss to the solvent. The twisting that occurs upon π,π^* excitation would lead to a localization of positive charge at C-4, since the p-orbital at that carbon would no longer be conjugated to the rest of the π system. The subsequent hydride shift from C5 to C4 results in the formation of a more stable tertiary carbocation.



Studies on the photoisomerization of protonated enones have been extended to dienones as well. Protonated 2,4-cycloheptadienone has been shown on irradiation to give protonated 7-norbornenone.[13]

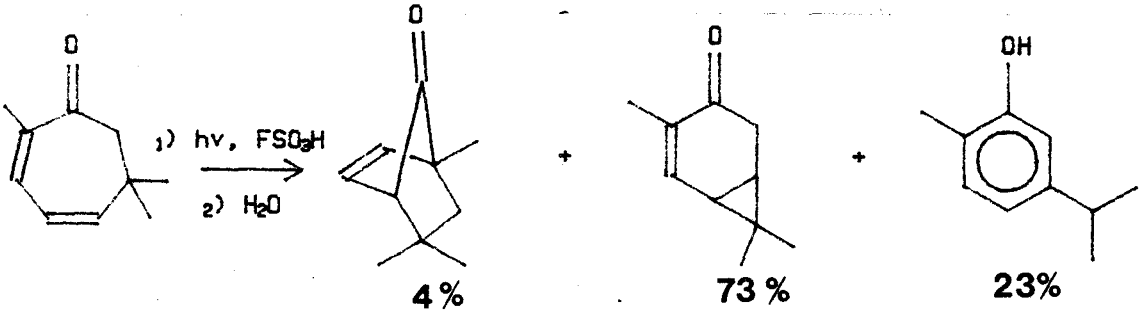


The photoreaction of protonated 2,4-cycloheptadienone would appear to proceed via a 1,5 bonding interaction in the excited state followed by a thermally induced 1,2 shift. This stands in marked contrast to the photoreaction of neutral 2,4-cycloheptadienone, which reacts photochemically in the same manner as does its methyl substituted analogue, the naturally occurring eucarvone. This compound has been the subject of numerous investigations,[14] and has been shown to undergo a light induced transformation to give two isomeric bicyclic ketones, one being a secondary photoproduct derived from the other.

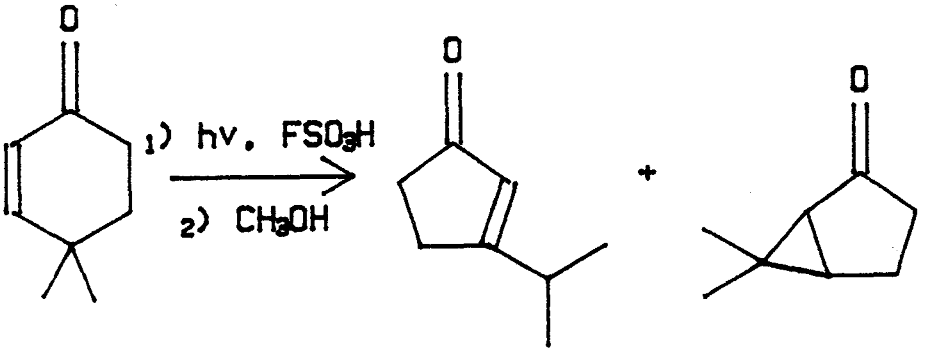


The reaction is readily understood as an electrocyclic reaction, followed by a reversible Norrish Type I cleavage of the product, establishing a photostationary state between the two bicyclic isomers.

The addition of methyl groups to a cycloheptadienone somewhat alters the photoproducts which can be obtained when the compound is protonated. Although 1,5 bonding still occurs, with two methyl groups in the 6 position this is now only a minor reaction pathway.[15]

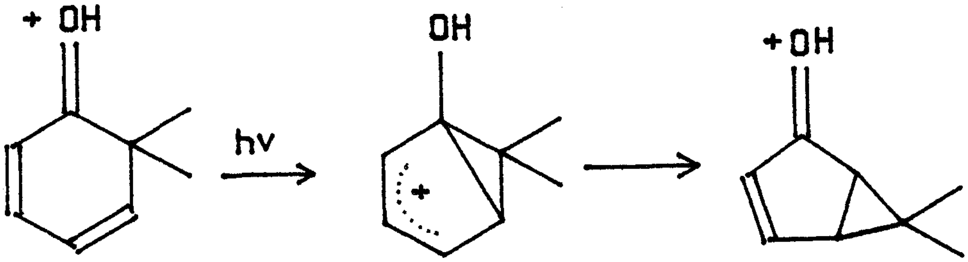


Interestingly, the excitation of protonated eucarvone to give its two most abundant photoproducts exactly parallels that of protonated 4,4-dimethylcyclohex-2-enone.[16]

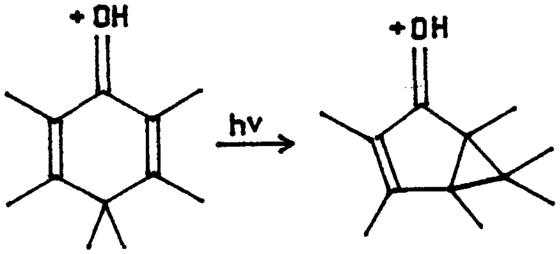


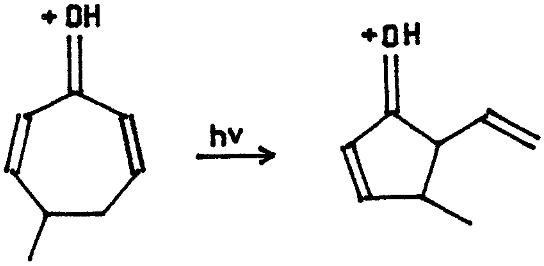
The presence of a geminal dialkyl group adjacent to the unsaturated chromophore appears to be necessary for this type of reaction.

A comparable 1,5 bonding reaction of a protonated dienone has also been observed with cyclohexadienones, as is shown below. In this case the initially formed intermediate rearranges by way of a thermally allowed cyclopropyl migration.[17]



The cross conjugated protonated cyclohexadienones also undergo a photoinduced ring closure on irradiation, however protonated cross conjugated cycloheptadienones undergo a different type of photoreaction.[18]

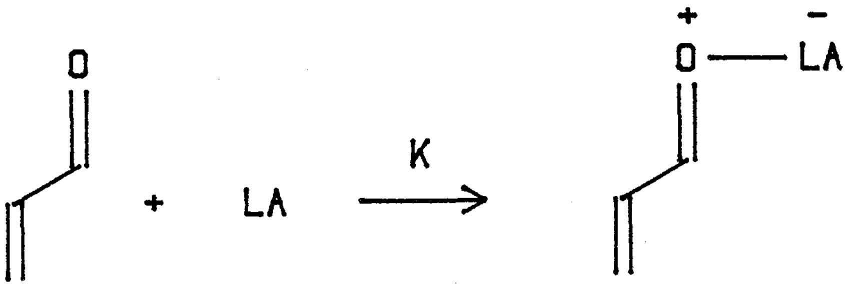




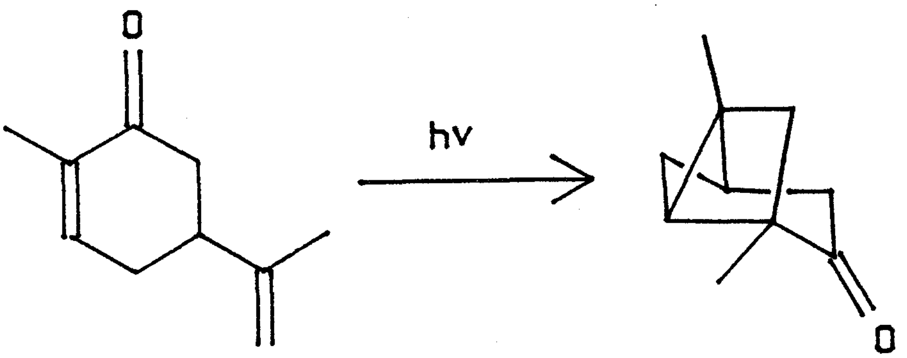
The photochemistry of protonated carbonyls has given rise to many useful reactions, however not all substrates can be handled in these strong acid media. There is the primary requirement that there be no thermal reactions induced by the acid, at least not at suitably low temperatures. Strong acids such as FSO_3H are sufficiently acidic to protonate an isolated double bond, thus often where hydrogen migrations can extend conjugation (within the limitations of Brett's rule), such will occur. There are also practical difficulties involved in working with FSO_3H. It is an extremely hazardous substance, producing very painful burns upon contact with skin or mucous membranes. Since it is seldom available in any form other than technical grade, distillation under an inert atmosphere must be performed if the acid is to be obtained with the necessary chemical and optical purity. Its reactivity with atmospheric moisture and subsequent release of gaseous HF require that it be stored in sealed glass ampules, and precludes any extensive handling of the acid outside of a controlled atmosphere. For such reasons, an increasing amount of attention is being devoted to the use of solid acids such as Nafion, a perfluorinated acid resin with the acid functionalities being $-(OCF_2CF(CF_3)_n-CF_2CF_2SO_3H$ side chains attached to a perflourocarbon backbone. When used in its 'anhydrous' form, Nafion is a strong acid ($H_o < -6$) and possesses the necessary UV transparency.[19] Solid acids usually require treatment at elevated temperature and reduced pressure to remove solvating surface adsorbed water, thus they also require handling and storage in a controlled atmosphere. Solid acids offer considerable preparative and cost advantages however, in that they can be removed from the reaction mixture by simple mechanical means such as filtration, and are easily reconverted to the acid form for subsequent use. Homogeneous acids require neutralization prior to product isolation. Solid acids are also very attractive because they are virtually nonhazardous.

2) Complexation of Enones to Lewis Acids

The origin of the changes in the light absorbing properties of enones in superacid solvent lies in the change in the electron distribution in both the ground and excited states when the system is protonated. Many Lewis acids are strong enough to complex with the oxygen of an enone in a variety of weakly coordinating solvents, and can bring about equivalent changes of the properties of the enone when the two are mixed together in solution. The question arises therefore, as to what effects Lewis acid complexation of an enone might have on its photochemistry, and how the modified reactions might compare to the analogous protonated systems.



Enones complexed to Lewis acids such as $SnCl_4$ have been used as activated dienophiles in Diels Alder reactions for some time.[20] According to frontier molecular orbital theory, complexation lowers the energy of the enone LUMO (lowest unoccupied molecular orbital), thereby lowering the transition state for the reaction.[21] The shift of the absorption maximum to longer wavelength is also a result of this lowering of the energy of the enone LUMO. A potentially attractive photochemical equivalent of the above would be a general Lewis acid catalysis of [2+2] photocycloadditions to enones. The double bond being added to the enone could either be conjugated to it, as in the photoreaction of neutral eucarvone, or in an isolated position, such as in the well known conversion of carvone into carvone camphor.[22] The final and perhaps synthetically most useful possibility would be intermolecular addition.



Although there is still no direct theory or method of quantifying the strength of Lewis acids, a rough ordering has been made on the basis of several different methods, including ^1H NMR,[23] UV,[24] infrared spectroscopy,[25] polarography,[26] nuclear quadrupole resonance,[27] conductance,[28] and calorimetry,[29] as well as several semi-empirical[30] and theoretical treatments.[31]

The NMR method is based on empirical and theoretical evidence suggesting a linear relationship between ^1H and ^{13}C chemical shifts and the electron distribution in the vicinity of those nuclei.[32] It involved tabulating the chemical shift differences ($\Delta\delta$) for the signals of various unsaturated aldehydes, ketones, and esters with the Lewis acids being studied. Values for methyl crotonate are given in Table 2. When these values are plotted against corresponding values with other bases, slopes for $\Delta\delta$H3 and $\Delta\delta$H4 are typically very close to unity with the lines passing through the origin, indicating similar behavior as regards electron depletion at those sites. The $\Delta\delta$H2 plots behave quite differently however, the lines do not pass through the origin, and there is a much greater sensitivity to change of Lewis acid. Since the Lewis acid is much closer spatially to H2 than either H3 or H4, a through space deshielding of H2 might well be anticipated.[33] Shifts of nuclei closer to the site of bonding are influenced by a local anisotropy, whereas signals for more remote atoms such as H3 and H4 are not significantly affected, and are therefore more likely to accurately reflect the change in electron distribution associated with complexation. The linear relationships obtained were used to set up a Lewis acid scale (Table 3.) based on $\Delta\delta H3$, and thus for systems where $K >> 1$, provide an indication of the differences in the electron distribution in the enone complexes.

Table 2. ^{1}H Chemical Shift Differences ($\Delta\delta$) of Methyl-E-Crotonate on Complexation with Various Lewis Acids[a]

Lewis Acid	Proton $\Delta\delta$ (ppm)			
	H2	H3	H4	OCH_3
BBr_3	1.28	.94	.39	.66
BCl_3	1.14	.87	.38	.63
$SbCl_5$	1.02	.77	.34	.60
BF_3	.68	.70	.28	.51
$TiCl_4$	.54	.60	.24	.51
$AlEt_2Cl$	.40	.51	.17	.34
$SnCl_4$	.41	.43	.17	.28
$AlEt_3$	.19	.38	.13	.28

[a] In ppm (±.01) Chemical Shifts for Uncomplexed Base, ref. 23

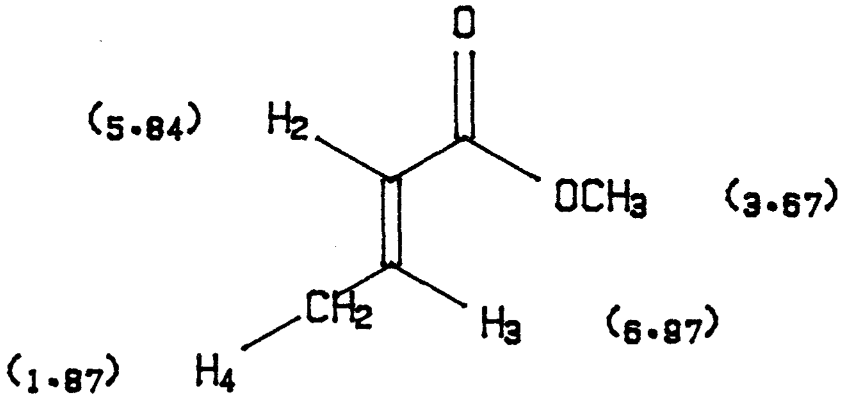
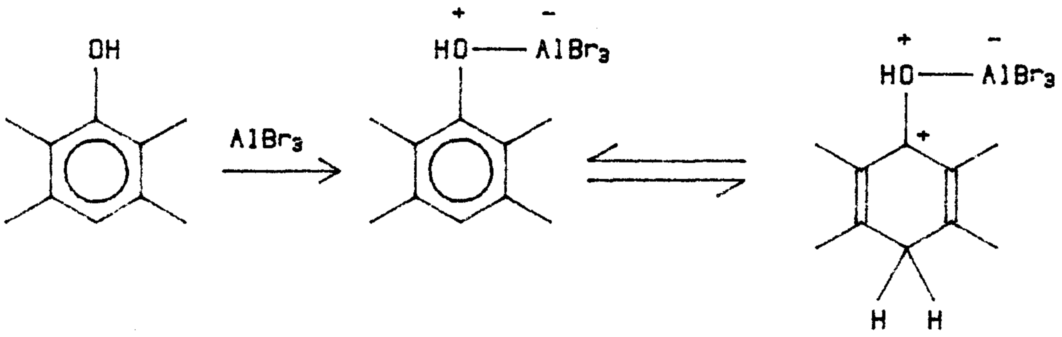


Table 3.[ref. 23] Lewis Acid Scale based on $\Delta\delta$-Values of H3 Resonances of Various Bases

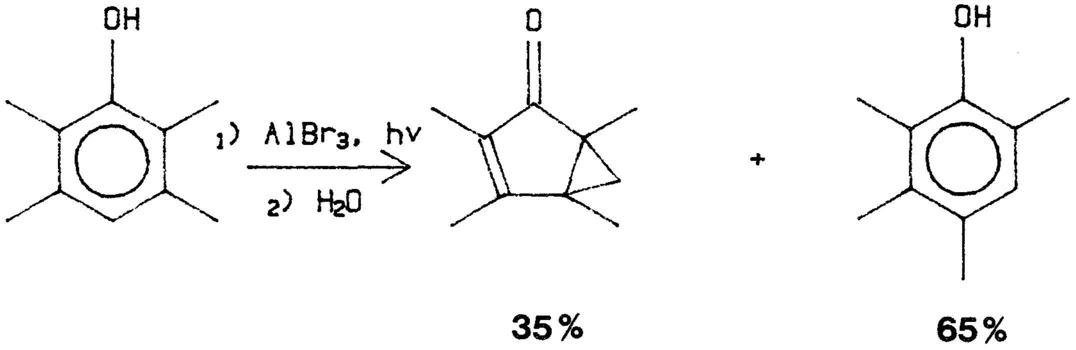
Lewis Acid	Relative Power
BBr_3	1.00 ± .005
BCl_3	.93 ± .02
$SbCl_5$	.85 ± .03
$AlCl_3$	.82
BF_3	.77 ± .02
$AlEtCl_2$	.77
$TiCl_4$	.66 ± .03
$AlEt_2Cl$	.59 ± .03
$SnCl_4$	.52 ± .04
$AlEt_3$	.44 ± .02

3) Photochemistry of Lewis Acid Complexes

It is appropriate at this point to review some of the work being done in Lewis acid catalysed photochemistry. Members of this group have been investigating the Lewis acid catalysed photoisomerizations of various methyl substituted phenols.[34] These are known to react with either $AlCl_3$ and $AlBr_3$ to form two types of complex.[35] The coordination site for the Lewis acid is the oxygen in both cases, however the OH proton can either remain on the oxygen or migrate to the ring as shown below for 2,3,5,6-tetramethylphenol.

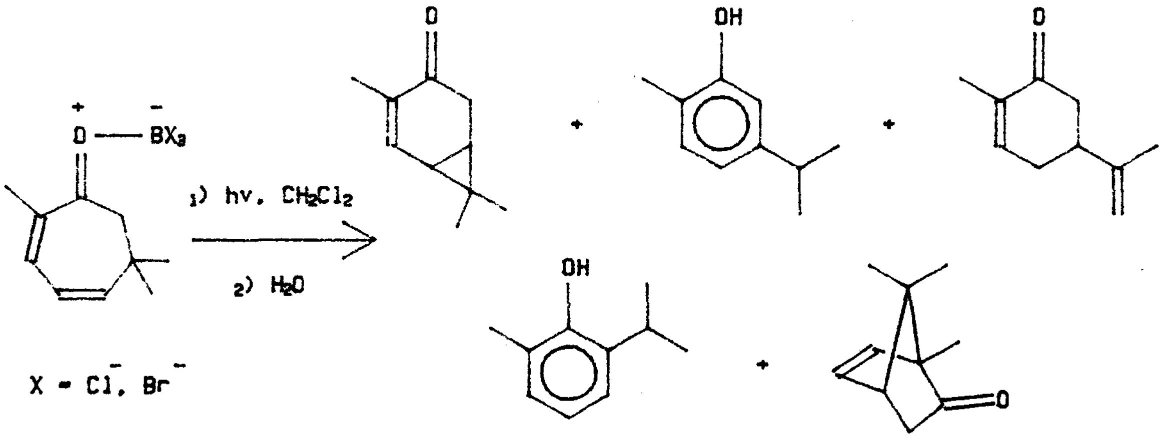


The position of the equilibrium between the two forms was shown to be markedly dependent upon substitution pattern and the Lewis acid / base ratio. When the above complex is irradiated in CH_2Cl_2, a complexed bicyclic ketone is formed in a moderately efficient photoreaction. This in turn reacts photochemically to give an isomeric phenol complex as a secondary photoproduct.[36] It has been established that the photoreactive species is the complexed cross conjugated cyclohexadienone shown above on the extreme right.



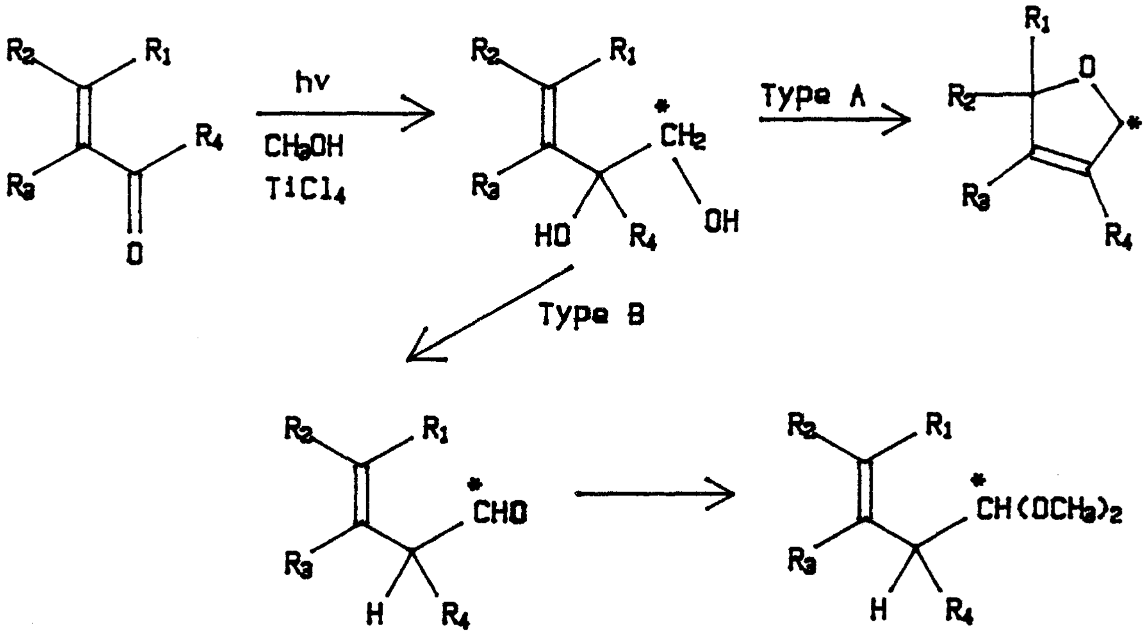
The maximum proportion of the bicyclic ketone complex (expressed as percentage of total products) is about 60%, however upon prolonged irradiation (ca. 24 hrs.) the product ratio reaches that in the equation above. It is clear that the subsequently formed isomeric phenol complex is a secondary photoproduct, obtained by photoisomerization of the bicyclic ketone complex. These photoreactions proceed in an equivalent manner to their protonated analogues.[37] Studies with dimethyl and trimethyl substituted phenols have been interpreted in terms of the photochemistry described above, however only isomeric phenols were isolated and identified as major products.

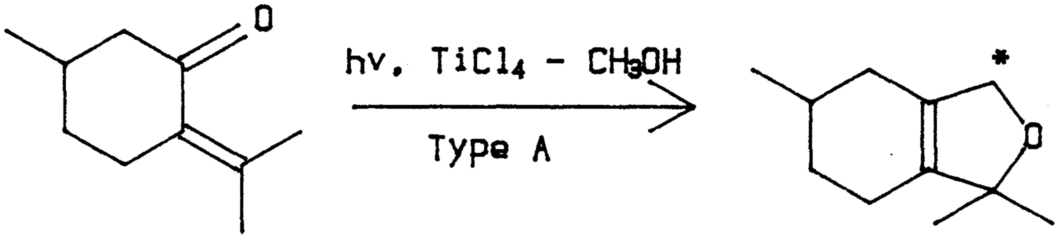
The photochemistry of Lewis acid complexed eucarvone has been investigated,[38] and is very similar to the previously discussed photoreactions of protonated eucarvone.



Studies were done with BCl_3 and BBr_3, and it is quite clear from the investigations that the product ratio is markedly dependent on the Lewis acid being used. What is equally apparent is the absence of an intramolecular [2+2] addition as is observed with neutral eucarvone.

Sato and co-workers have observed a remarkable photoreaction of α,β-unsaturated ketones in methanol in the presence of $TiCl_4$.[39] Two types of reaction were observed: (A) cyclization to form a dihydrofuran, and (B) dimethyl acetal formation. The reactions are notable in that a one carbon fragment (marked with an asterisk) is incorporated into the enone. This addition is accompanied by the loss of the carbonyl funtionality. An example of each of reactions Type A and B is given below.





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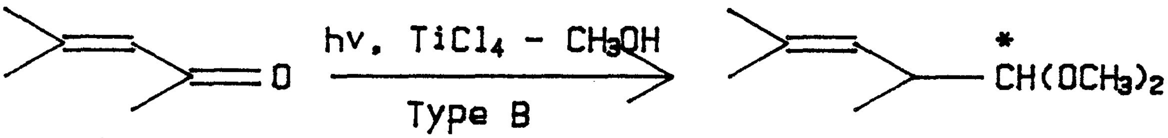
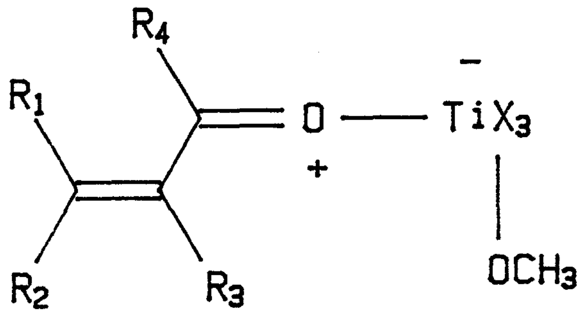


Mesityl Oxide

Titanium tetrachloride is too strong a Lewis acid to exist in methanol, and reacts with that solvent to establish a series of substitution equilibria.

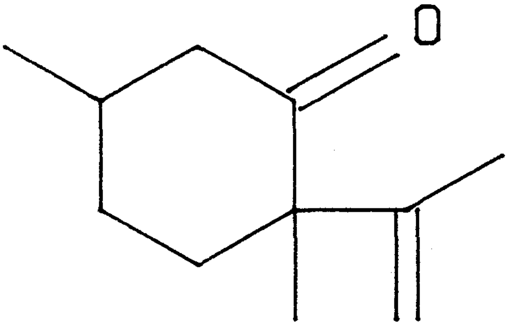
$$[\mathrm{TiCl_4}] \rightleftharpoons \mathrm{TiCl_3(OCH_3)} \rightleftharpoons \mathrm{TiCl_2(OCH_3)_2} \rightleftharpoons \mathrm{TiCl(OCH_3)_3} \rightleftharpoons \mathrm{Ti(OCH_3)_4}$$

Athough Sato does not advance a possible mechanism for these reactions, it seems likely that the carbon being introduced comes from such a titanium bound methoxy group, originating from a chromophore of the type depicted below.



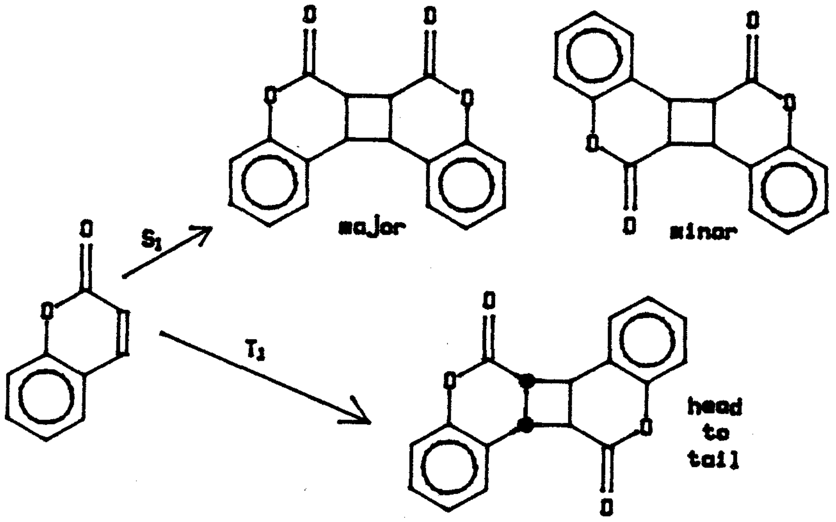
X = Cl, OCH_3

Irradiation of any of Sato's α,β unsaturated ketones in the presence of HCl or $BF_3 \cdot (OEt)_2$, or their standing in the presence of $TiCl_4$ in the dark resulted either in methanol addition to the double bond or isomerization of the double bond (E/Z or positional to β,γ). The photochemical reaction is characteristic of the α,β unsaturated system, the β,γ unsaturated ketone shown below was recovered intact under these conditions.

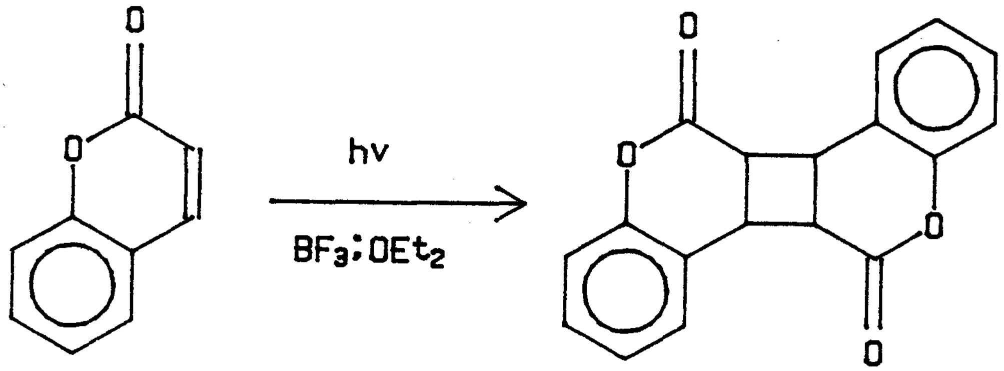


Irradiation of the enones in methanol in the presence of $Ti(OCH_3)_4$ did not lead to the formation of the photoproducts. $Ti(OCH_3)_4$ is a much weaker Lewis acid, and while HCl is not the catalyst, its presence in the reaction mixture is essential, even if only to preserve the strength of the Lewis acid.

Lewis and Oxman recently reported a Lewis acid catalysed photodimerization of the α,β unsaturated ester coumarin.[40] The photodimerization of coumarin in solution has been the subject of numerous mechanistic investigations.[41] The syn head-to-head dimer and the syn head-to-tail dimer are the major and minor products respectively of a relatively inefficient singlet state reaction ($\Phi \sim .001$ for .3M coumarin) and the anti head-to-tail dimer is the major product of triplet state dimerization ($\Phi \sim .1$,benzophenone sensitization).



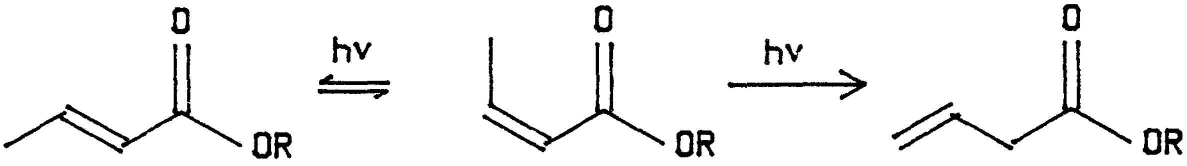
Irradiation of the ester in the presence of $BF_3 \cdot OEt_2$ afforded the syn head to tail dimer exclusively, in >85% yield.



The quantum yield of dimerization is highest with a .13 molar equivalent of the Lewis acid, and drops rapidly when greater amounts are used. This is consistent with an excited state complex reacting with an uncomplexed species in the ground state. That the absorbing species is complexed was ascertained by absorption spectroscopy.

The photochemical E/Z isomerization of alkenes is a well known reaction, presenting the only direct method for the contrathermodynamic conversion of the E to Z isomer,[42] and has played an important role in the development of theoretical and mechanistic photochemistry.[43] One detrimental feature limiting synthetic applications of this reaction is its reversible nature, which in the absence of other reactions reaches a photostationary state frequently containing approximately equal amounts of both isomers, necessitating separation and recycling steps.

The use of various additives,[44] and studies with protic acids,[3,12,45] have failed to yield mixtures rich in the thermodynamically less favoured Z isomer. The photoisomerization may also suffer from competing side reactions, such as in the photochemical deconjugation of crotonate esters.[46]

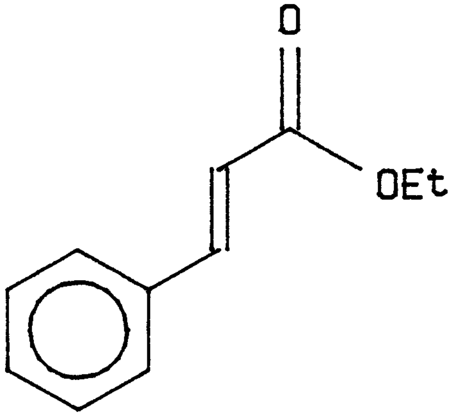


Recently, Lewis and Oxman reported that the position of the photostationary state reached with α,β unsaturated esters and carboxylic acids can be dramatically altered if a strong Lewis acid is present in solution.[47] For example, irradiation of 1 in benzene containing less than a molar equivalent of ethylaluminumdichloride ($AlCl_2Et$) yields a photostationary state consisting of 85% of the Z-isomer, 2. In the absence of the Lewis acid only 42% 2 was present at the photostationary state. Lewis acid complexation of esters is known to occur at the carbonyl oxygen,[48] providing the added advantage of inhibiting γ-hydrogen abstraction involved in photochemical deconjugation.

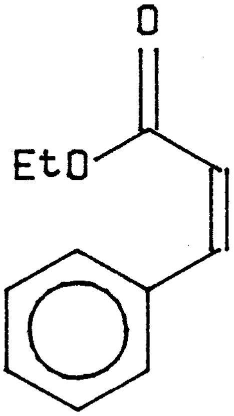
Objectives of this work:

The results described above regarding the effect of a Lewis acid upon the irradiation of α,β-unsaturated esters seemed surprising considering the minimal changes observed in the photostationary states reached with the fully protonated material. Lewis' explanation was based primarily on an apparent Lewis acid enhancement of the quantum yield for the E to Z isomerization relative to that of the reverse process, and of an increase in the extinction coefficient of the E isomer. It seemed likely these observations indicated some mode of interaction between enones and Lewis acids not present in the corresponding protonated systems, and thus a closer examination into the cause of this phenomenon seemed an excellent place to begin examining photochemistry unique to enone-Lewis acid complexes.

In pursuing this, initial efforts were focused on one of Lewis' compounds, ethyl-E/Z-cinnamate (1 and 2 respectively). Not only is 1 readily available, but there are several other easily obtained cinnamate derivatives which would provide a suitable point to examine the possibility of extending this form of catalysis to other functional groups, such as ketones and nitriles.



1

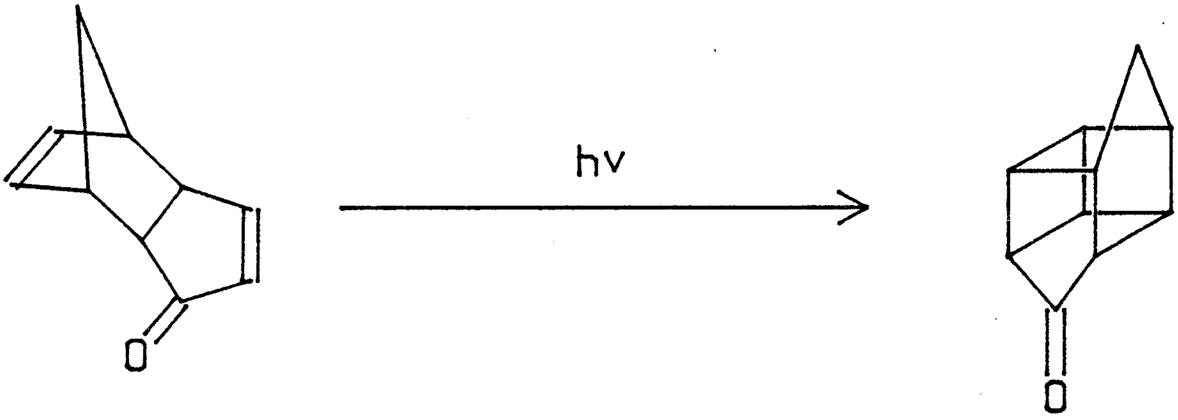


2

The first objective was to devise a series of experiments to test Lewis' explanation, and perhaps to advance a better one if findings indicated it to be incomplete, then to explore the generality of this catalysis.

The interesting question that follows from Lewis' investigation of coumarin dimerization, is whether there is a general photochemical addition reaction of enone complexes in the presence of alkene. Not including a possible enhancement of quantum yields or any interesting stereochemical or regiochemical modifications of the course of the addition in going from a neutral to a complexed species, at the very least, the presence of a Lewis acid would allow the use of much lower concentrations of the alkene, since the intermolecular addition of two enone complexes is likely to be unfavourable.

The final focus of this work deals with an examination of the photochemistry of an enone/Lewis acid complex where E/Z isomerization cannot occur due to the restraint imposed on the enone carbon/carbon double bond when it is in a sufficiently small ring. The system chosen was endo-tricyclo [5.2.1.0^{2,6}] deca-4,8-dien-3-one.



This compound is known to cleanly and efficiently isomerize to the pentacyclic bis-homocubanone upon irradiation at 340 nm,(Φ=.3-.4).[49] If it were complexed to a strong Lewis acid, this would perhaps create an electrostatic attraction between the electron deficient enone moiety and the relatively electron rich isolated double bond. Could this 'internal solvation' be reflected in an increased quantum yield for the intramolecular addition, or would entirely new photochemistry be observed ?

CHAPTER 2

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

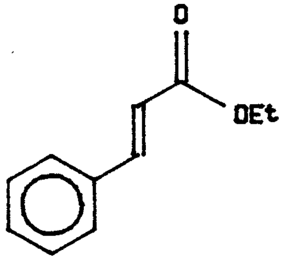
Part I Photoisomerization of Acyclic Enone/Lewis Acid Complexes

Preliminary Characterizations

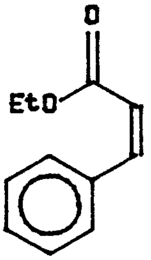
The compounds chosen for this work were the E and Z isomers of ethyl cinnamate, **1** and **2** respectively. The E isomer is available commercially, and the Z isomer was prepared by irradiation of the E isomer in CH_2Cl_2 in the presence of .15 molar equivalents of $AlCl_2Et$, as described by Lewis.[47] Dissolution of **1** and **2** into FSO_3H gave the corresponding protonated materials, **1H** and **2H** respectively. The former cation was stable at 25°C in FSO_3H. UV and ^1H NMR spectra were obtained at this temperature. In the case of **2H**, characterization was performed at −70°C.

For Lewis acid complexes of **1** and **2**, the ester and the Lewis acid were separately dissolved in equal portions of solvent and the two portions mixed together. With the exception of the $SbCl_5$ complex of ethyl-Z-cinnamate, **2-SbCl$_5$**, Lewis acid complexes of **2** were sufficiently stable to permit characterization at ambient temperature. Complexation of $[AlCl_2Et]_2$ with carbonyl compounds is a complex reaction involving disproportionation and reproportionation of the aluminum species.[50] The various complexes which are expected to be formed were not individually detected at ambient temperature, however when characterized by NMR at $-55^{o}C$, the exchange reactions are slow on the NMR time scale, and at least two different complexes for each isomer are observed. The ^{1}H NMR and UV spectral data are given in Tables 4. and 5. respectively.

These studies of the α,β-unsaturated esters suggest that the electronic changes attendant upon complexation to a Lewis acid are qualitatively similar to those observed upon protonation, perhaps most notably the characteristic downfield shifts of the vinyl signals in the ^{1}H NMR spectrum (Figure 1.), and the shift to longer wavelength of the UV absorption maximum.



1



2

Lewis and Oxman proposed that the change in the photostationary state composition attendant upon complexation to a Lewis acid is due mainly to an increase of both the extinction coefficient of the E-isomer and also of its quantum yield of isomerization relative to the less enhanced values for the Z-isomer. The photostationary state compositions could seemingly be accounted for by substituting the appropriate data into equation 1.

Table 4: ^{1}H NMR Data for α, β Unsaturated Compounds

				Chemical Shift[a,b], ppm				Coupling Constant Hz
Compound	Solvent	Temp(°C)	Lewis Acid[c]	H_2	H_3	aryl H	Other	$J_{2,3}$
1	CD_2Cl_2	35		6.45 d	7.63 d	7.3-7.6 m	4.27 q 1.35 t	16.1
1	FSO_3H	35		6.87 d	8.62 d	7.5-8.1 m	5.03 q 1.73 t	16
1	CD_2Cl_2	35	$AlCl_2Et$[d]	6.90 d	8.21 d	7.5-7.7 m	4.7 bq 1.5 bt	15.7
				6.88 d	8.29 d			15.8
1	CD_2Cl	-70	$SbCl_5$		8.15 d	7.37-7.6 m	4.66 q 1.50 t	15.8
1	CD_2Cl_2	35	$SnCl_4$	6.83d	7.94 d	7.3-7.6 m	4.66 q 1.50 t	15.9
2	CD_2Cl_2	35		5.90 d	6.95 d	7.3-7.6 m	4.14 q 1.23 t	12.6
2	FSO_2H	-70		6.40 d		7.5-8.1 m	4.9 bq 1.5 bt	12
2	CD_2Cl_2	35	$AlCl_2Et$	6.41 d	7.70 d	7.5-7.7 m	4.54 q 1.24 t	12.2
2	CD_2Cl_2	-70	$SbCl_5$	6.77 d	7.69 d	7.3-7.6 m	4.52 q 1.34 t	12.2
2	CD_2Cl_2	35	$SnCl_4$	6.15 d	7.19 d	7.3-7.6 m	4.5 q 1.20 t	12.4
3	CD_2Cl_2	35		6.75 d	7.58 d	7.3-7.6 m	2.40 s	16.2
3	CD_2Cl_2	35	$SnCl_4$	7.10 d	8.01 d	7.4-7.8 m	2.77 s	16.0
4	CD_2Cl_2	35		6.19 d	6.93 d	7.3-7.6 m	2.19 s	12.7
4	CD_2Cl_2	35	$SnCl_4$	6.46 d		7.4-7.8 m	2.56 s	12.1
5	CD_2Cl_2	35		5.92 d	7.43 d	7.3-7.5 m		16.7
5	CD_2Cl_2	35	$SnCl_4$	6.02 d	7.65 d	7.4-7.5 m		16.7
6	CD_2Cl_2	35		5.48 d	7.17 d	7.3-7.5 m		12.2
6	CD_2Cl_2	35	$SnCl_4$	5.59 d		7.4-7.5 m		12.2

[a] In ppm from CH_2Cl_2 (5.421, -70°C; 5.336, +35°C).

[b] d = doublet, m = multiplet, q = quartet, bp = broad quartet, t = triplet, bt = broad triplet.

[c] 1.1-1.2 molar equivalents of acid were used, conc. = .2-.3 M.

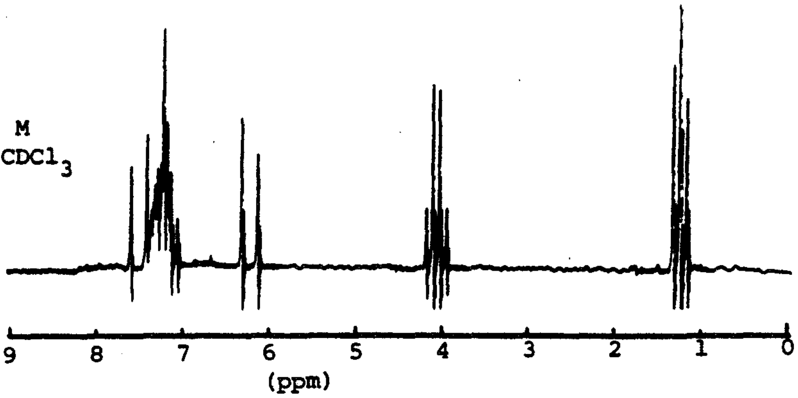
[d] In the case of 1 with 1.2 mol. eq. $AlCl_2Et$, two sets of signals for the ester were observed, indicating the occurrence of disproportionation.

Table 5. UV Data

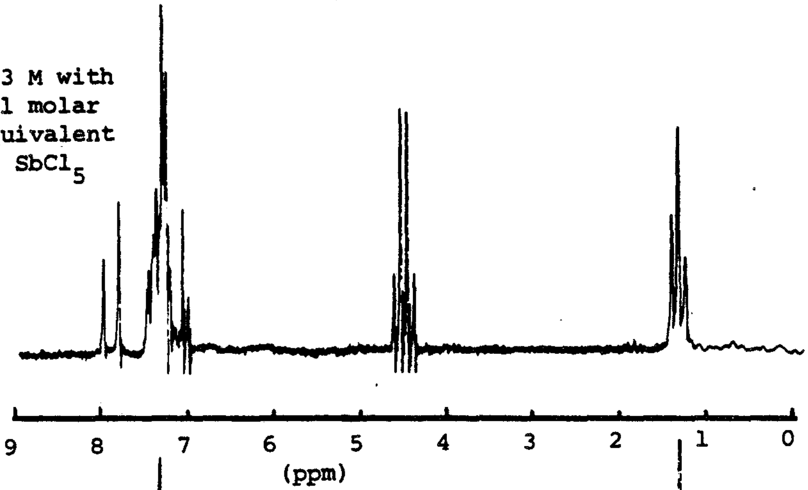
Compound	Solvent	Acid	λ_{max}	log ϵ
1	CH_2Cl_2		277	4.35
	CH_2Cl_2	$AlEtCl_2$	328	4.46
	C_6H_6	$Al_2O_3{\bullet}SiO_2$	320	
		FSO_3H	328	4.30
2	CH_2Cl_2		269	4.03
	CH_2Cl_2	$AlEtCl_2$	328	4.05
3	CH_2Cl_2		268	4.51
	CH_2Cl_2	$AlEtCl_2$	372	4.69
	C_6H_6	$Al_2O_3{\bullet}SiO_2$	330	
		FSO_3H	370	4.76
4	CH_2Cl_2		281	4.18
	CH_2Cl_2	$AlEtCl_2$	372	4.57
5	CH_2Cl_2		275	4.41
	CH_2Cl_2	$AlEtCl_2$	315	4.47
	C_6H_6	$Al_2O_3{\bullet}SiO_2$	310	
		FSO_3H	317	4.48
6	CH_2Cl_2		275	4.25
	CH_2Cl_2	$AlEtCl_2$	322	4.08

Figure 1. ^{1}H NMR (90 MHz) Spectra of ethyl-E-Cinnamate (1)

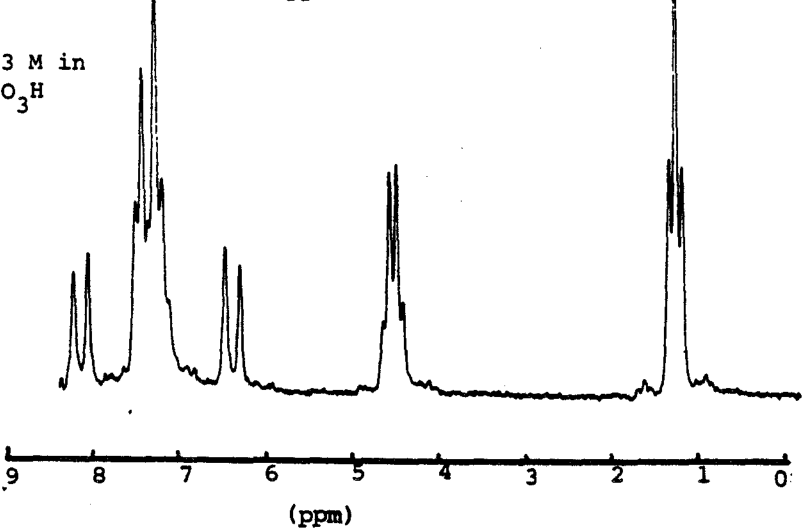
a) 0.3 M in $CDCl_3$



b) 0.3 M with 1.1 molar equivalent of $SbCl_5$



c) 0.3 M in FSO_3H



$$\frac{[Z]}{[E]} = \frac{[\Phi_{E \rightarrow Z}]\ \varepsilon_E}{[\Phi_{Z \rightarrow E}]\ \varepsilon_Z} \qquad \text{eq. 1}$$

This method predicts 83% of 2 at the photostationary state, which compares favourably with the experimentally obtained value of 86%. The quantum yield and extinction coefficient data reported by Lewis are for fully complexed esters however, and the enriched photostationary state was obtained with less than a molar equivalent of Lewis acid.

A simple and direct method of testing the validity of Lewis' explanation would be to compare the photostationary state compositions obtained with a molar equivalence of acid, to that obtained with a molar deficiency. The photostationary states measured for the various systems (Table 6.) were determined with separate samples, one initially pure E, the other pure Z; (0.3 M in CH_2Cl_2). These were monitored by NMR until the two samples appeared to have reached the same composition and remain unchanged upon further irradiation. The mixtures were

Table 6. Summary of Photostationary State Compositions

System	Total Conc. (M)	Solvent	Catalyst	Catalyst[a] Conc. (mol.eq.)	Composition %E	%Z
1/2	.3±.05	CH_2Cl_2			58	42
	.3±.05	FSO_3H			61	39
	.1±.05	C_6H_6	$AlCl_3$	.25±.05	15	85
	.3±.05	CH_2Cl_2	$AlEtCl_2$	.15±.05	14	86
	.3±.05	CH_2Cl_2	$AlEtCl_2$	1.1±.1	42	58
	$1x10^{-2}$	CH_2Cl_2	$Al_2O_3 \bullet SiO_2$		14	86
	$1x10^{-2}$	CH_2Cl_2	Nafion H		29	71
3/4		CH_2Cl_2			48	52
		CH_2Cl_2	$Al_2O_3 \bullet SiO_2$		17	83
5/6		CH_2Cl_2			34	66
		CH_2Cl_2	$Al_2O_3 \bullet SiO_2$		34	66

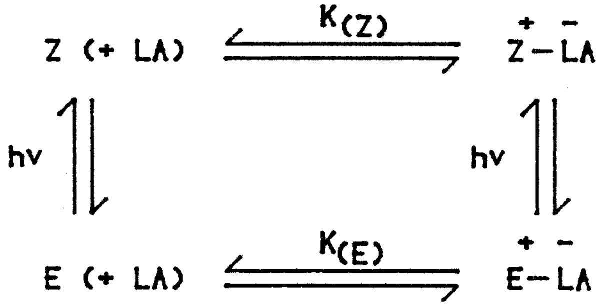
[a] In molar equivalents based on total concentration of Lewis base.

neutralized and the compositions determined by gas chromatography (GC). When 1 or 2 is irradiated in CH_2Cl_2 in the absence of a Lewis acid, the photostationary state composition reached is 42% of 2. In the presence of .15 molar equivalent of $AlCl_2Et$, the photostationary state composition reached is 86% of 2. Upon full complexation of the starting material with an equimolar amount of $AlCl_2Et$, this value decreases to 58% of 2. The results show that Lewis' explanation is incomplete. The measurements of the fully complexed systems clearly show that the enhanced extinction coefficients and quantum efficiencies account for roughly only a third of the increase observed when a molar deficiency of the Lewis acid is present.

Equilibrium Studies

In considering the case where a molar deficiency of the acid is present, there are four possible light absorbing species. Since both isomers are in equilibrium with the Lewis acid, a simple application of eq.1 would be unsuitable. An illustration of the reactions taking place is given below in Scheme 1.

Scheme 1



The values $K_{(E)}$ and $K_{(Z)}$ are the equilibrium constants for Lewis acid complexation of both the E and Z isomers respectively. Although they will both undoubtedly be very large with the strong Lewis acids being used, they need not be the same. Indeed, the pK_{BH^+} values of the analogous protonated cinnamic acids are known to be different, the protonated Z isomer being the stronger acid,[51] suggesting that $K_{(E)}$ might be greater than $K_{(Z)}$. Assuming this to be the case, the presence of a molar deficiency of a suitable Lewis acid would effect the course of the irradiation by establishing a photostationary state between the complexed esters, consequently modifying the composition of the free esters by exchange, as outlined in the equations below.

$$K_{(E)} = \frac{[\overset{+}{E}\text{—}\overset{-}{LA}]}{[E]\,[LA]} \qquad K_{(Z)} = \frac{[\overset{+}{Z}\text{—}\overset{-}{LA}]}{[Z]\,[LA]} \qquad \text{eq. 2}$$

$$\frac{K_{(E)}}{K_{(Z)}} = \frac{[\overset{+}{E}\text{—}\overset{-}{LA}]\,[Z]}{[\overset{+}{Z}\text{—}\overset{-}{LA}]\,[E]} \qquad \text{eq. 3}$$

$$\frac{[Z]}{[E]} = \frac{\left[\dfrac{K_{(E)}}{K_{(Z)}}\right]\,[\overset{+}{Z}\text{—}\overset{-}{LA}]}{[\overset{+}{E}\text{—}\overset{-}{LA}]} \qquad \text{eq. 4}$$

The major pathway for the conversion of the E isomer to the Z isomer would involve three steps: complexation of the E isomer with the Lewis acid, photoisomerization to the Z isomer complex, followed by decomplexation (Scheme 1., counterclockwise from E to Z). This requires that $K_{(E)}/K_{(Z)}$ significantly exceed unity in order to minimize the rate at which the Z isomer is reconverted to the E isomer by the pathway of each of the above three steps in reverse (Scheme 1., clockwise from Z to E). This would also require that as little as possible of the incident radiation be absorbed by the uncomplexed species, more specifically the uncomplexed Z isomer, in order to minimize its direct photochemical reversion. This latter requirement is quite consistent with the fact that the complexed species absorb more heavily at longer wavelength as a result of the π,π^* red shift. The appropriate choice of irradiation wavelength (and filters if desired) could optimize the necessary preferential excitation of the complexed species.

Although there are spectroscopic methods to evaluate $K_{(E)}$ and $K_{(Z)}$ separately,[52] these are usually more accurate when applied to weaker interactions where K is small (weak acid-weak base), such as the formation of the $SnCl_4$ complex of crotonitrile in CH_2Cl_2; K=5.3 L/mol.[24] In the present case, what is needed is the ratio of $K_{(E)}/K_{(Z)}$. This ratio was evaluated directly from competitive complexation experiments, with the concentrations of the various species being determined by ^{1}H NMR. There were two techniques used in these determinations of $K_{(E)}/K_{(Z)}$ with the various Lewis acids. The non-exchanging spectrum method involved determinations of the concentrations of the various species present under conditions where exchange reactions were slow on the NMR time scale, and the data thus obtained (by signal integration, Table 7.) substituted into equation 3. The slightly less direct fast exchange / averaged spectrum method involved similar determinations where exchange reactions were fast on

Table 7. 250 MHz ^{1}H NMR Determination of K_E/K_Z for Ethyl Cinnamate[a] (1/2) with $SbCl_5$

%1 (%E)	%2 (%Z)	conc. $SbCl_5$[b]	Signal	rel. integration[c] 1	 1*	 2	 2*	K_E/K_Z[d]
25	75	.20	vinyl H	.119	.118	.702	.061	11.4
25	75	.20	$-OCH_2-$	.102	.144	.668	.086	11.0
25	75	.25	vinyl H	.109	.171	.628	.092	10.7
25	75	.25	$-OCH_2-$	.099	.182	.612	.107	10.5
30	70	.30	vinyl H	.122	.202	.585	.090	10.8
30	70	.30	$-OCH_2-$	.117	.212	.603	.098	11.1

[a] −70°C, concentration 1 + 2 = 0.3 M.

[b] in molar equivalents based on 1 + 2 (total Lewis base).

[c] * denotes $SbCl_5$ complex.

[d] $K_E/K_Z = (\frac{E*}{E})(\frac{Z}{Z*})$

the NMR time scale (Table 8.). Under such conditions, there would not be separate observable signals for free and complexed species, rather there would be one signal corresponding to each of the various resonances for the E or Z isomer. The relative amounts of free and complexed E and Z isomers were then obtained by recording the positions of the various resonances relative to those previously measured for the free and fully complexed esters. Since the ratio of E and Z isomers is known, enough information is available for substitution into equation 3.

As a rule, systems with relatively strong Lewis acids, such as $SbCl_5$, easily gave the non-exchanging spectra, whereas weaker Lewis acids such as $AlCl_2Et$ or $SnCl_4$ usually resulted in fast exchange and averaged spectra. The corresponding non-exchanging spectra of any system can in theory be obtained by reducing the temperature, using a higher spectrometer frequency, or a combination of the two. In practice, one is limited by the freezing points of suitable solvents, and availability of sufficiently high frequency instruments.

If the Z isomer were less basic, its relative amount should exceed that of the E isomer in order to assure an accurately measurable quantity of the Z isomer complex. Perhaps not too surprisingly, the composition that gives the most easily measured relative amounts of all four species is close to that which is reached upon Lewis acid catalysed irradiation, as the relative proportions of the E and Z isomer complexes are close to being equal.

The non-exchanging spectrum technique requires the use of a high field frequency instrument (250 MHz) to resolve a sufficient number of

Table 8: 80 MHz ^{1}H NMR Determination of K_E/K_Z for α,β unsaturated compounds[a] with $AlCl_2Et$ and $SnCl_4$ at 35°C

System	Lewis Acid (LA)	LA conc.[b] (mol. eq.)	H2	Δδ(ppm)	H3	Δδ(ppm)	relative concentrations[c]				K_E/K_Z[d]
			E	Z	E	Z	E	E*	Z	Z*	
100% 1	$AlCl_2Et$	1.0	.45		.58						
100% 2	$AlCl_2Et$	1.0		.51		.75					
40% 1,60% 2	$AlCl_2Et$	0.15	.12	.02	.16	.03	.30	.11	.57	.024	7.9
40% 1,60% 2	$AlCl_2Et$	0.3	.23	.07	.30	.10	.19	.21	.52	.08	7.2
40% 1,60% 2	$AlCl_2Et$	0.4	.30	.11	.38	.16	.14	.27	.47	.13	7.0
100% 1	$SnCl_4$	1.0	.38		.31						
100% 2	$SnCl_4$	1.0		.25		.24					
15% 1,85% 2	$SnCl_4$	.35	.23	.08	.19	.08	.06	.09	.58	.27	3.2
15% 1,85% 2	$SnCl_4$	.60	.30	.14	.25	.14	.03	.12	.36	.49	2.9
15% 1,85% 2	$SnCl_4$	.75	.33	.17	.27	.16	.02	.13	.27	.58	3.0
100% 3	$SnCl_4$	1.0	.35		.43						
100% 4	$SnCl_4$	1.0		.26							
50% 3,50% 4	$SnCl_4$	.65	.29	.13			.09	.41	.25	.25	4.6
45% 3,55% 4	$SnCl_4$	.75					.05	.40	.21	.34	4.9
100% 5	$SnCl_4$	1.0	.10		.22						
100% 6	$SnCl_4$	1.0		.11							
65% 5,35% 6	$SnCl_4$	.50	.05	.06			.32	.33	.17	.18	.97
65% 5,35% 6	$SnCl_4$	.75	.08	.08			.15	.50	.08	.27	.99

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[a] total conc. E + Z = .3M

[b] based on total Lewis Base concentration

[c] based on Δδ values, *denotes Lewis acid complex

[d] $= \left(\frac{E*}{E}\right)\left(\frac{Z}{Z*}\right)$

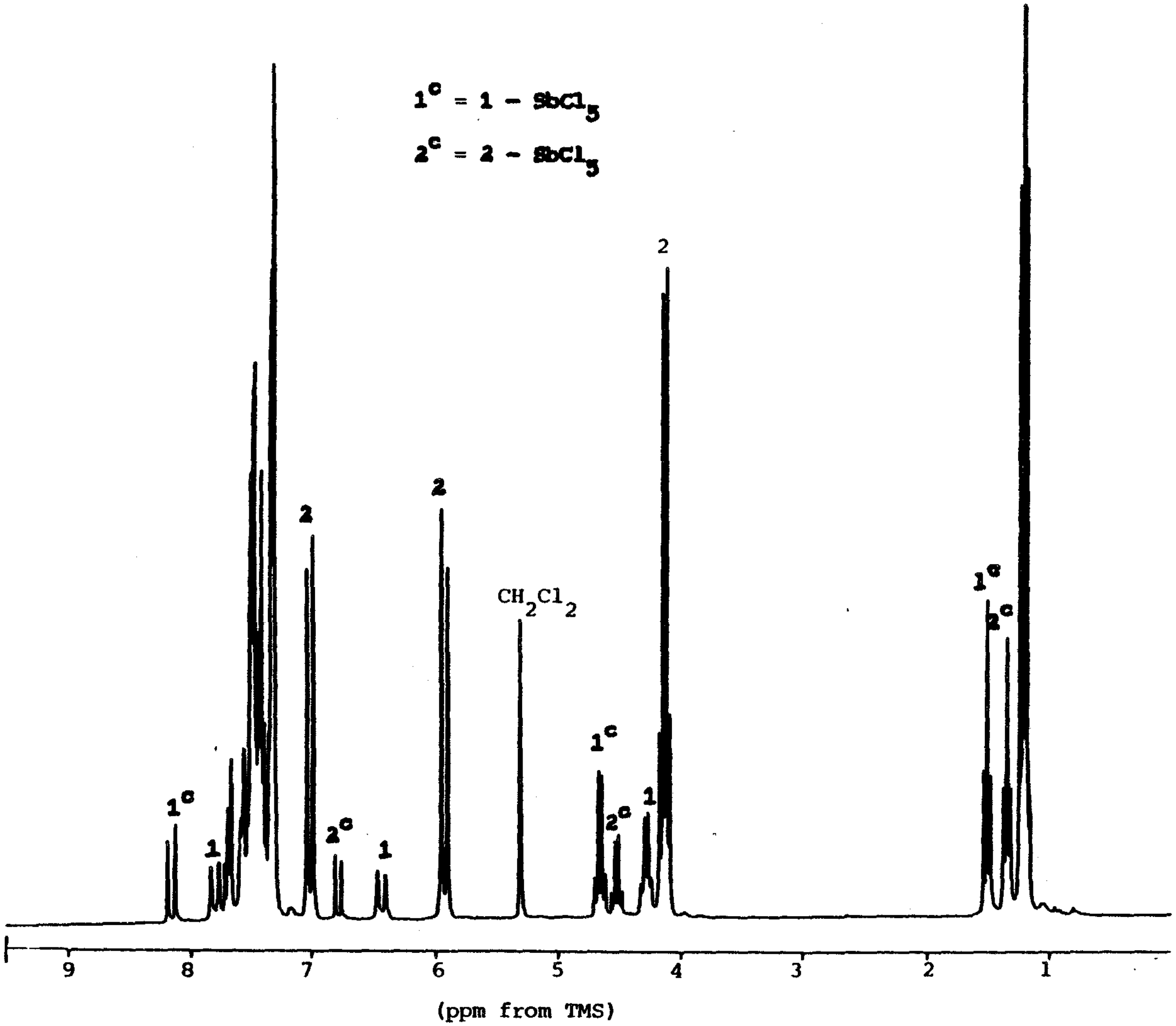
signals for integration. Non-exchanging spectra of ethyl cinnamate with $SbCl_5$ were obtainable at room temperature, however since this Lewis acid dramatically lowers the energy barrier to thermal reversion of 2 to 1, the use of low temperatures became necessary in order to prevent this isomerization. A 250 MHz spectrum recorded at $-55^\circ C$ in CD_2Cl_2 is presented in Figure 2. From the relative concentrations determined for the various species present, the value thus obtained for the 1/2-$SbCl_5$ system; $K_{(E)}/K_{(Z)} = 11 \pm 1$, supports the proposed complexation selectivity mechanism.

Since irradiations using $SbCl_5$ were unsuccessful owing to a slow thermal decomposition of the complexed starting material at low temperatures, as well as the presence of a strong absorption band due to the antimony atom,[53] it was desirable to demonstrate complexation selectivity under conditions known to lead to augmented concentrations of 2 upon irradiation. Samples of 1 and 2 in the presence of a molar deficiency of $AlCl_2Et$ in CD_2Cl_2 were analyzed at room temperature using the fast exchange / averaged spectrum method. The data obtained from this experiment give $K_{(E)}/K_{(Z)} = 7 \pm 1$. Based on this value, the free energy of complexation for 2 is expected to be about 5 kJ/mol less exothermic than for 1, as might be anticipated based on its expected greater Lewis basicity. The $K_{(E)}/K_{(Z)}$ results are summarized in Table 9.

As can be seen from the $K_{(E)}/K_{(Z)}$ data in Table 9 for the various 1/2 systems examined, this quantity appears to be strongly dependent on the Lewis acid being used. It is difficult to explain the

Figure 2. Competitive complexation study of **1**/**2** with $SbCl_5$ [a]

250 MHz ^1H NMR



[a] 75%**2**, 25%**1** with .2 molar equivalent $SbCl_5$, based on total Lewis base concentration

Table 9. Ratio of Equilibrium Constants for Complex Formation

System	Lewis Acid	Temperature °C	K_E/K_Z
1/2	$AlEtCl_2$	35	7.5±1
	$SbCl_5$	-60	11±1
	$SnCl_4$	35	3.1±.5
3/4	$SnCl_4$	35	4.7±.5
5/6	$SnCl_4$	35	0.95±.05

variation of $K_{(E)}/K_{(Z)}$ with Lewis acid as solubility and stability problems precluded study with a sufficiently large series of acids and bases. One would perhaps expect complexation selectivity to be greater for weaker Lewis acids, since the difference in the free energies of complexation for the two isomers would likely be greater than with a strong Lewis acid, however since the observed trend with ethyl cinnamate appears to be in the opposite direction, steric effects at the Lewis acid site are probably important as well. It must also be noted that some Lewis acids behave differently, such as the disproportionation reactions observed with $AlCl_2Et$, and the fact that acids such as $SnCl_4$ and $TiCl_4$ can bind to more than one Lewis base.[54] $SnCl_4$ appears to be the least selective acid of those studied, and indeed Lewis noted it to be a much less effective catalyst for the E/Z isomerization of enones.

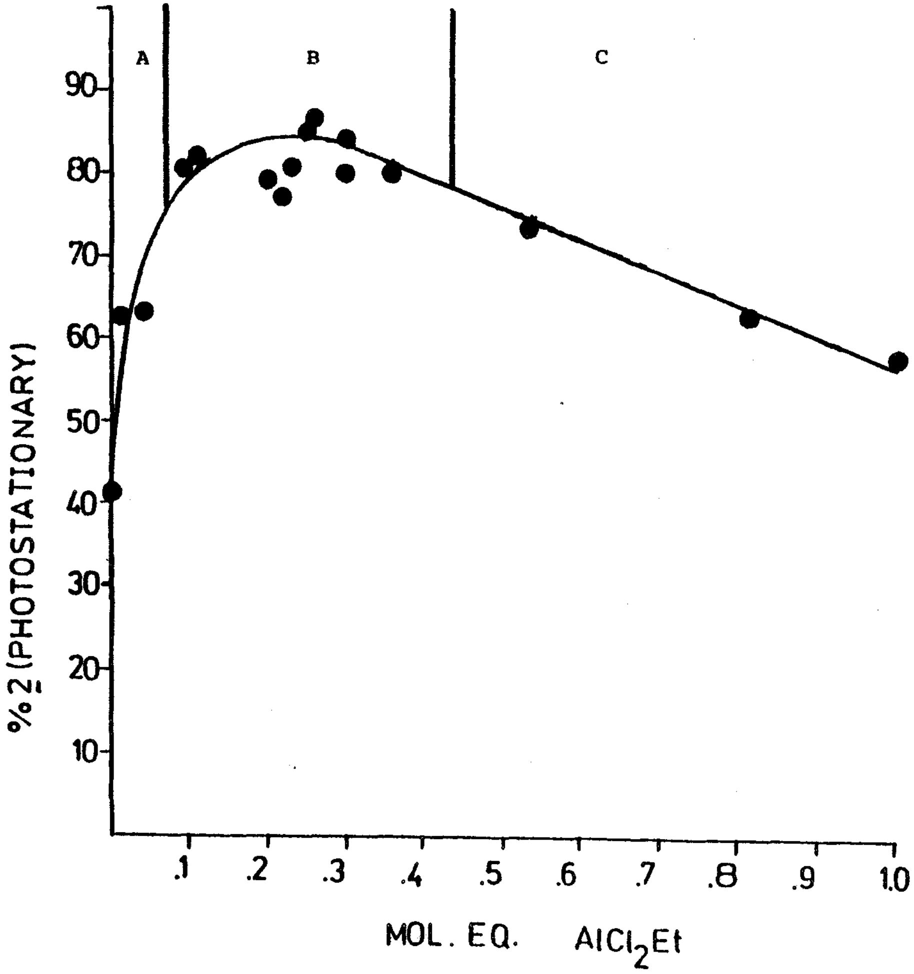
Variation of Photostationary State with Lewis Acid Concentration

Substitution of the value $K_{(E)}/K_{(Z)} = 7 \pm 1$ for **1/2**-**$AlCl_2Et$** into equation 4, along with the value of the photostationary state for fully complexed esters (Table 6.) predicts the composition of the uncomplexed esters to be 90% ethyl-Z-cinnamate, 10% ethyl-E-cinnamate. The overall yield of **2** would be less, since the composition of the complexed esters is expected to be very close to the 57% 2 observed in the presence of an equivalence of acid.

It now remains to show how the percent Z isomer obtained at the photostationary state varies with the amount of Lewis acid present. Photostationary state measurements were performed as previously described using varying amounts of $AlCl_2Et$ (Figure 3.)

Although equation 3 is independent of Lewis acid concentration, complexation selectivity will be most effective if there is a molar deficiency of Lewis acid. If the deficiency is too small however, too much of the incident irradiation will be absorbed by uncomplexed species, and the photostationary state % of **2** will be correspondingly reduced. One would therefore expect an initially sharp increase in the amount of Z isomer obtained at the photostationary state with increasing Lewis acid concentration (Figure 3, region A), peaking where complexation selectivity is optimally balanced against neutral ester

Figure 3. Variation of %**2** at the photostationary state with amount of Lewis acid [a]

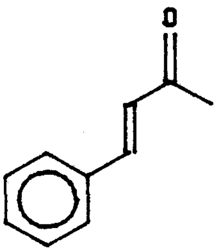


[a] Concentration of **1**+**2**= 0.3 M

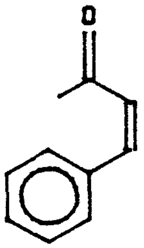
excitation (region B). As the amount of Lewis acid approaches molar equivalence, the effectiveness of complexation selectivity is minimized and the photostationary state would be expected to approach that of the fully complexed esters (region C). The trends evident in the three regions of the graph provide a firm confirmation of the proposed mechanism.

Extension to Other Systems

The obvious elegance of this form of catalysis made it desirable to demonstrate its usefulness beyond the somewhat narrow class of compounds (unsaturated esters) presented up to this point. To this end the focus of investigation was extended to include structurally similar bases with different functional groups. Cinnamic acid was not considered as it would be expected to behave very much like cinnamate esters. The compounds chosen were E- and Z- 4-phenyl-but-3-en-2-one (3 and 4), and E- and Z- cinnamonitrile (5 and 6).



3



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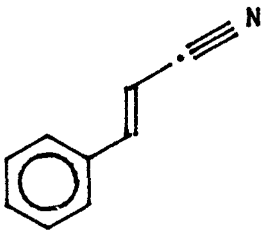

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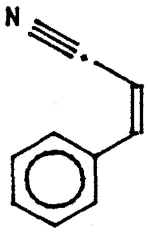


6

The E isomers are commercially available, and the Z isomers were obtained by irradiation of the E isomers in solution, followed by separation using preparative gas chromatography. The protonated forms and various Lewis acid complexes of these compounds were characterized by ^{1}H NMR and UV spectroscopy, Tables 4. and 5.

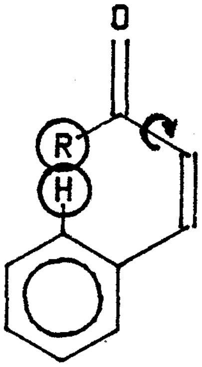
Since the ketones do not have a stabilizing heteroatom adjacent to the carbonyl carbon as do the esters, it was not surprising that the Lewis acid complexes were generally more reactive and not as easily characterized. **4-H** and **4-AlCl$_2$Et** isomerized to **3-H** and **3-AlCl$_2$Et** respectively at 25°C. **3-AlCl$_2$Et** underwent a slow (several hours) thermal decomposition in CH_2Cl_2 and $CHCl_3$ at -55°C, making it unsuitable for photoisomerization. **3-SnCl$_4$** in CH_2Cl_2 or $CHCl_3$ was observed to be a thermally stable complex, but was soluble at 25°C for only short periods of time after which the complexes began to crystallize, possibly due to the slower formation of **(3)$_2$-SnCl$_4$**.

The $SnCl_4$ complexes of 5 and 6 were soluble and thermally stable, however catalysed photoisomerization attempts invariably failed to increase the yield of 6 obtained at the photostationary state. 5 and 6 are much weaker Lewis bases than the corresponding carbonyl systems,[24] raising doubts as to the overall degree of complexation.

$K_{(E)}/K_{(Z)}$ determinations for **3/4-SnCl$_4$** and **5/6-SnCl$_4$**, as well as **1/2-SnCl$_4$** for purposes of comparison, were performed using the fast exchange / averaged spectrum ^{1}H NMR technique previously described (Tables 8. and 9.). These showed that the ketones

3 and 4 behave in a similar fashion to the esters, however no complexation selectivity was observed with **5/6-SnCl$_4$**.

An important question with regard to the cause of complexation selectivity, is why the E isomers of the ester and ketone appear to be more basic, and the ancillary question as to exactly why the E isomer of cinnamonitrile is not. A likely possibility is that these differences arise from steric effects in the Z isomer which make it more difficult for the unsaturated system to be completely planar, thereby reducing their basicity relative to the E isomer. This is consistent with the observed lack of complexation selectivity for cinnamonitrile, where such steric effects are absent.



Since complexation selectivity has been demonstrated with the ketone, it should be possible to produce photostationary states enriched in the Z isomer, if only the difficulties of solubility and stability could be circumvented. A potentially attractive way of doing this would be to use a solid acid catalyst such as an aluminosilicate. In this case, solubility is no longer a consideration, but stability could still pose a problem. There was sufficient precedent to suggest that such an irradiation could be successful, another member of this group observed photostationary states similar to those observed by Lewis when 1 was irradiated in the presence of finely ground, activated aluminosilicate (12% Al_2O_3) powder.[55]

Aluminosilicates contain Al_2O_3 and SiO_2 co-crystallized in a lattice. Activation at elevated temperature and reduced pressure removes surface adsorbed water, leaving Bronsted acid sites derived from chemically bound water, from which a hydroxide is incorporated into the lattice network leaving a proton held to the aluminum atom by electrostatic attraction.[56] More severe conditions remove this water as well, the formally trivalent aluminum atoms now functioning as Lewis acid sites. Aluminosilicate powder was dehydrated at 300 °C, < 0.5 mm Hg for 24 hours, and likely contained both Bronsted and Lewis acid sites.

The adsorption of 1 from anhydrous CH_2Cl_2 onto activated aluminosilcate powder was examined quantitatively, and the results are presented in Figure 4. Surface adsorption is uniform in the range $10^{-3} - 10^{-1}$ M of ester in solution at equilibrium, suggesting monolayer coverage in this range. As is shown in Figure 5., it is only in this concentration range that one observes optimum increases in the amount of Z isomer obtained at the photostationary state.[55]

1 and 3 were adsorbed onto aluminosilicate powder and characterized by UV transmittance spectroscopy. Benzene was chosen as the solvent since aluminosilicate suspensions in this solvent produced the least amount of incident light scattering. Spectra obtained with

Figure 4. Adsorption of **1** onto $Al_2O_3 \cdot SiO_2$ in CH_2Cl_2

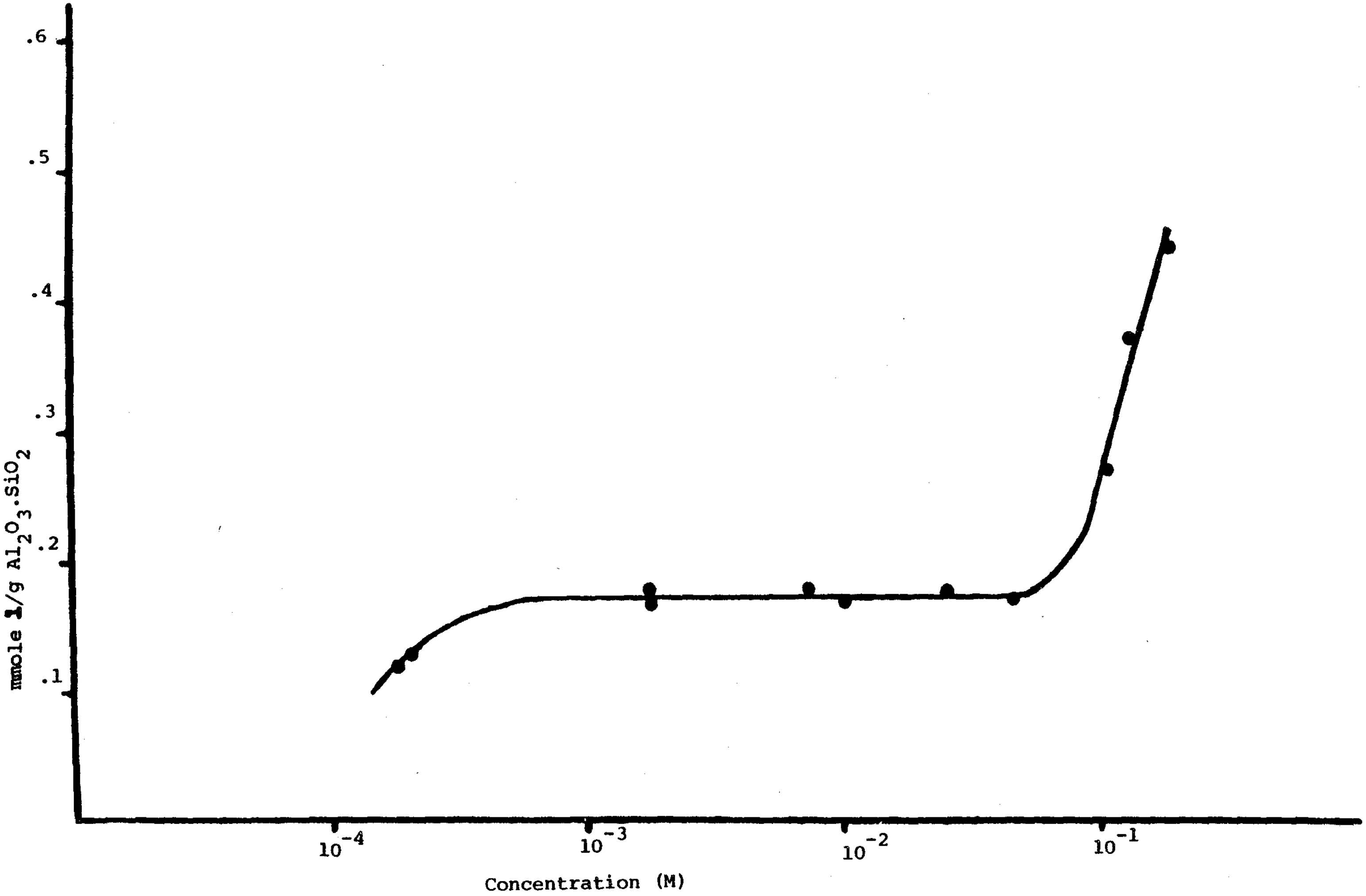
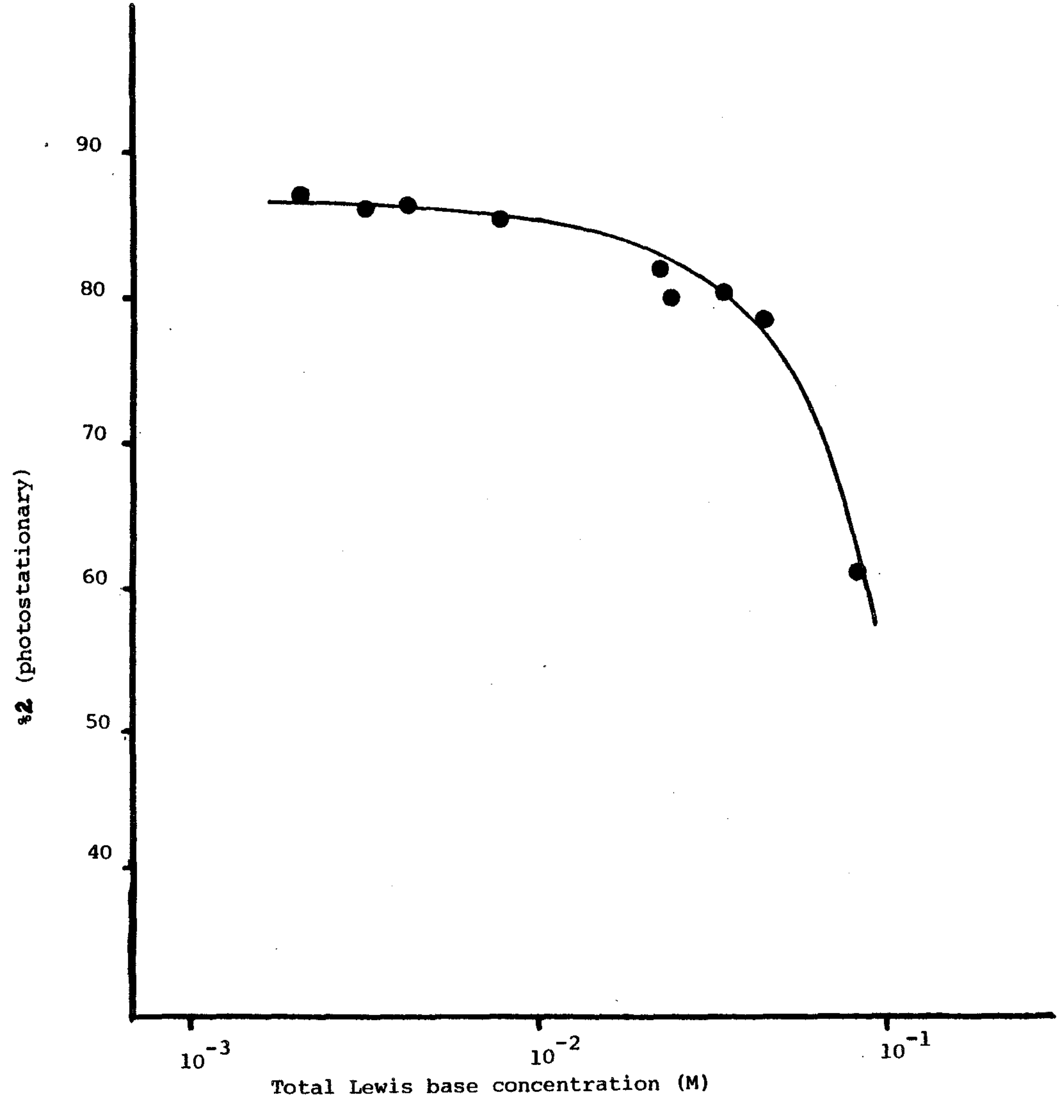


Figure 5. Variation of %**2** at the photostationary state in the presence of $Al_2O_3 \cdot SiO_2$ with solution concentration



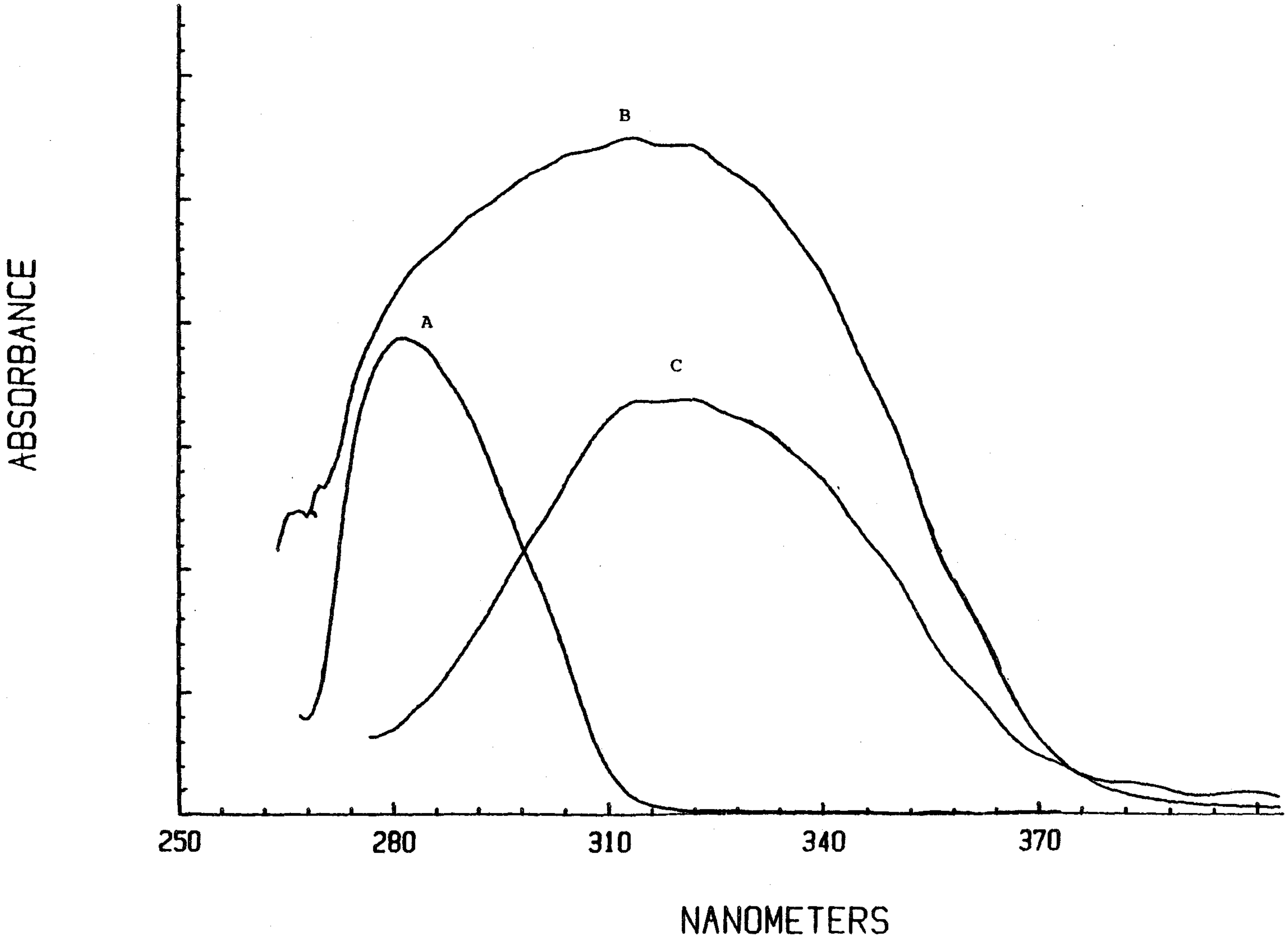
unactivated catalyst showed only negligible changes from the spectra of the free bases in solution. The data presented in Table 4. confirm the similar behaviour of these bases when complexed to either homogeneous or heterogeneous acids. A UV spectrum of $1\text{-}Al_2O_3 \cdot SiO_2$ is presented in Figure 6.

Prolonged exposure (several hours) of **4** in anhydrous CH_2Cl_2 to activated aluminosilicate powder at room temperature resulted in its conversion to **3**, however it was stable at -60 °C for several days.

When a 10^{-2} M solution (50 ml) of **3** containing a rapidly stirred suspension of activated aluminosilicate powder was irradiated at -60 °C, a photostationary state containing 83% **4** was obtained. In the absence of the catalyst, or if unactivated catalyst is used, the amount of **4** obtained at the photostationary state is only 52%. As was expected on the basis of $K_{(E)}/K_{(Z)}$ measurements, the presence of activated aluminosilicate powder did not perturb the photostationary state of cinnamonitrile, but again its lower basicity raises doubts as to the degree of complexation.

These results confirm the potential for use of this type of catalysis where complexation selectivity can be successfully demonstrated. The strategy employed is quite likely to be useful beyond Lewis acids and photochemical reactions, and should be generally applicable to other types of interconverting systems, where such interconversions can be homogeneously or heterogeneously catalysed, and the interconverting components possess different degrees of affinity for the catalyst.

Figure 6. UV Spectra of **1** in C_6H_6 (A), in C_6H_6 in the presence of $Al_2O_3.SiO_2$ (B), and of **1** adsorbed onto $Al_2O_3.SiO_2$, obtained by subtraction of A from B (C)



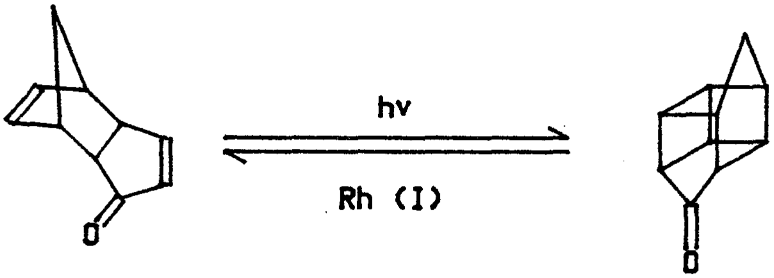
Part II Photoisomerization of Cyclic Enone/Lewis Acid Complexes

Having investigated Lewis acid catalysed photochemistry for enones capable of E/Z isomerism, there remains the question as to the effects of complexation on the photochemistry of systems where the rigidity imposed by cyclization prevents the reaction from occurring. Would complexation serve to only modify the efficiency of existing photoreactions as was observed with acyclic chromophores, or would it more likely give rise to new photoreactions for these systems ?

There are many reported examples of enones which undergo [2+2] additions with a double bond elsewhere in the molecule to give various substituted cyclobutyl systems.[57] The other double bond can be conjugated to the enone system, as with some of the various cycloheptadienones discussed earlier, or it can also be in an isolated position, such as in the conversion of carvone into carvone camphor.

The quantum yield for the formation of carvone camphor has been measured in a variety of solvents, and has been shown to increase markedly with increasing solvent polarity.[58] Since Lewis acid complexation induces charge into the chromophore, it is reasonable to suppose that such complexation could serve to increase the quantum efficiency of the photo-process in a given solvent. In fact, studies of Lewis acid catalysed irradiations of carvone show the complexes to be photochemically inert.[59]

The quantum yield of isomerization of endo-tricyclo $[5.2.1.0^{2,6}]$ deca-4,8-dien-3-one 7 to the bishomocubanone 8 has been shown to be .35-.40 in a variety of solvents.[49] The reaction can be reversed in high yield upon treatment with catalytic amounts of Rh(I) complexes at 140 - 180 °C.[60]



7 8

Low temperature studies of 7 in FSO_3H showed the protonated ketone to be unstable. The isolated double bond would likely be protonated, however Brett's Rule and perhaps more importantly, constraints imposed by cyclization, would preclude a thermal acid catalysed rearrangement that would bring it into conjugation with the enone moiety.

The $SnCl_4$ and $SbCl_5$ complexes (**7-$SnCl_4$** and **7-$SbCl_5$**) were prepared by treatment of 7 with the appropriate Lewis acid, however the former complex was found to be insoluble (CH_2Cl_2, $CHCl_3$, C_6H_6) and the latter unstable (-55°C, 1 hr). **7-$AlCl_2Et$** was soluble in $CHCl_3$ and thermally stable at room temperature, facilitating its ^1H NMR and UV characterization (Table 10.).

Table 10. ^{1}H NMR[a] and UV[b] Data for Ketones

		Chemical Shift[c,d], ppm			Coupling Constants, Hz		λ_{max}, nm	ϵ, ℓ mol^{-1} cm^{-1}
Compound[e]	H_4	H_5	Vinyl H	Other	$J_{4,5}$	$J_{5,6}$		
7		7.38dd	5.88m	3.40m 3.14m 2.96m 2.75m 1.67m	6.6	3.1	225	$6.6\text{x}10^3$
7D		7.39s	5.89m	3.15bs 2.90bs 1.63m				
7-AlEtCl$_2$	6.63d	8.30dd	5.91m	3.80m 3.51m 3.19m 1.94m	6.6	3.0	258	$9.0\text{x}10^3$
7D-AlEtCl$_2$		8.26s	5.92m	3.50m 3.16m 1.90m				
8				2.98m 2.40bt 2.02m 2.4-2.7m				
8-AlEtCl$_2$				2.4-3.4m 1.8m				
9	6.29d	7.71dd	5.82m	3.18m 3.12m 2.4-2.7m	5.5	2.9	229	$8.4\text{x}10^3$
9D		7.69s	5.80m	2.5-2.7m				
9-AlEtCl$_2$	7.00d	8.75dd	5.92m	3.55m 3.43m 2.4-2.9m	5.4	2.8	261	$1.2\text{x}10^4$
9D-AlEtCl$_2$		8.71s	5.92m	2.6-2.8m				

[a] In CDCl$_3$, 35°C.

[b] In CHCl$_3$, 25°C.

[c] In ppm from CH$_2$Cl$_2$ (5.336, 35°C) or CHCl$_3$ (7.249, 35°C).

[d] d = doublet, m = multiplet, bt = broad triplet, s = singlet, bs = broad singlet.

[e] 1.1-1.2 mol. eq. AlEtCl$_2$ was used. This gave rise to (an additional) two signals of lesser intensity for H_4, indicating the occurance of disproportionation.

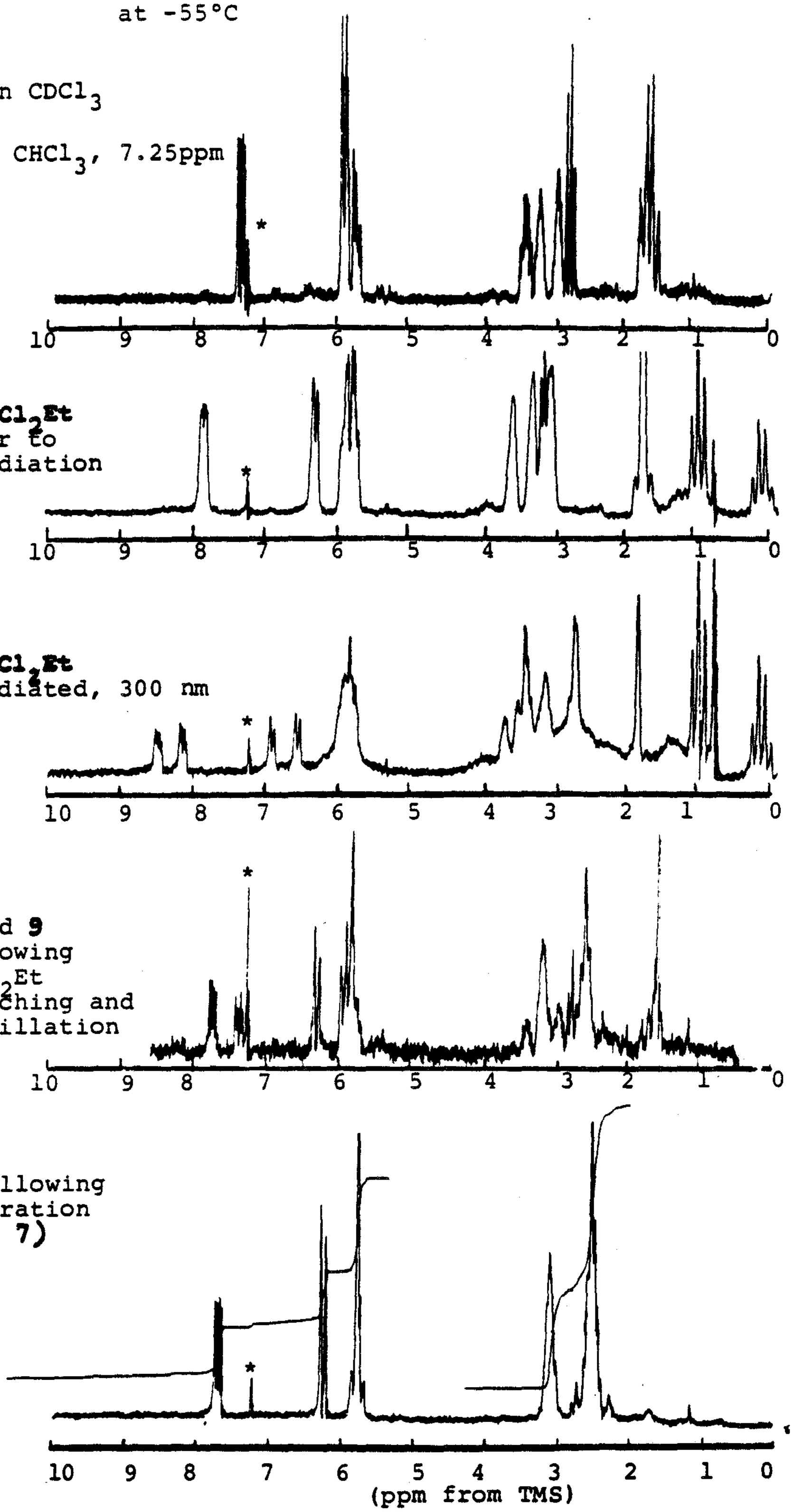
When irradiated with a 300 nm light source the expected intramolecular addition did not take place, rather a photostationary state containing 64% 7-$AlCl_2Et$ and 36% of an unknown $AlCl_2Et$ complex was obtained. The mixture was neutralized, and the product isolated and purified for characterization. The irradiations were much more successful at low temperature (-55°C) as this minimized the formation of insoluble material (Figure 7.). Under such conditions, the recovered yield of the mixture is typically 80-85%.

High resolution mass spectrometry established that the new compound was an isomer, formula $C_{10} H_{10} O$. The coupling patterns and peak positions of the ^1H NMR spectrum showed quite clearly that the integrity of the cyclopentenone fragment had been preserved, and that there was still an isolated double bond present.

Several controls were performed. The $AlCl_2Et$ complexes of both 7 and the new compound were stable at room temperature and did not thermally interconvert. Irradiation of either complex in $CHCl_3$ resulted in formation of a mixture with the same product composition. **8**-$AlCl_2Et$ was shown to be thermally and photochemically inert under the conditions used, thereby ruling out its formation as part of the reaction.

The final control experiment was to investigate whether a 'hidden' 3C + 2C addition might be occurring. This would correspond to a [2 + 2] of an alkene to an allyl cation, a hitherto unobserved photoreaction.

Figure 7. Irradiation of **7** with 1.0 molar equivalent $AlCl_2Et$, in $CDCl_3$ at -55°C



a) **7** in $CDCl_3$

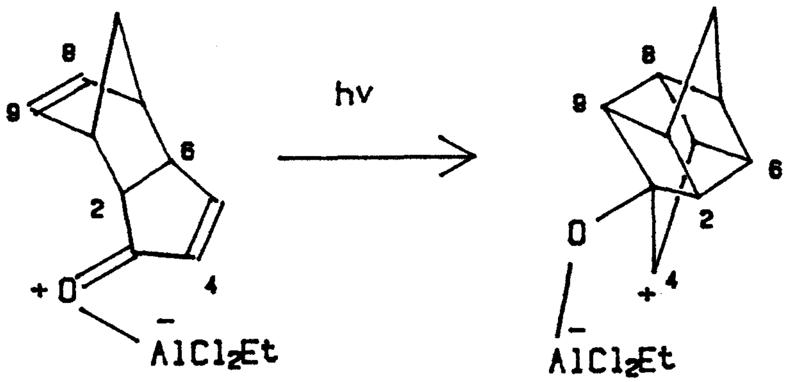
* = $CHCl_3$, 7.25ppm

b) **7-$AlCl_2$Et** prior to irradiation

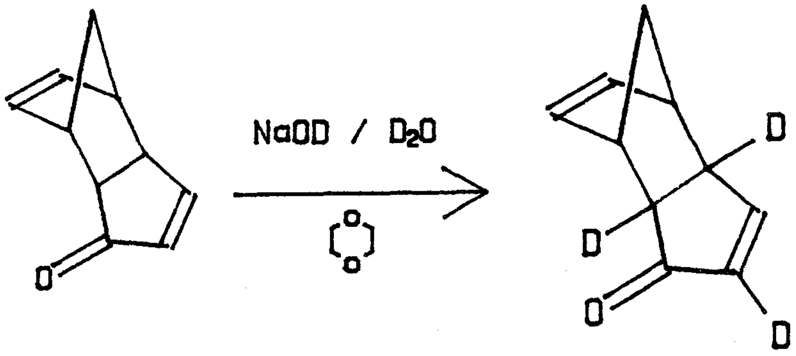
c) **7-$AlCl_2$Et** irradiated, 300 nm

d) **7** and **9** following $AlCl_2$Et quenching and distillation

e) **9** (following separation from **7**)



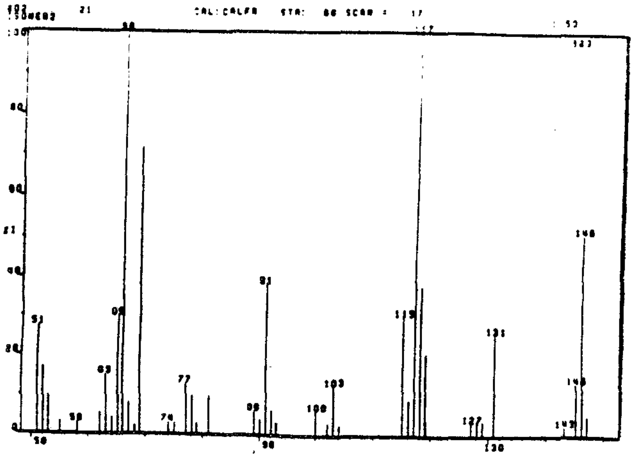
The symmetry of the resulting secondary cation could give rise to two degenerate pathways for decay back to 7-$AlCl_2Et$, which could only be distinguished by substitution or labelling at any of positions 2, 6, 8, or 9. There were several examples of applicable labelling experiments in the literature.[61] 7 was refluxed for several days in a mixture containing OD^-/D_2O and 1,4 dioxane. The isolated product was clearly shown by its ^1H NMR spectrum to be 7D, quantitatively labelled (>97%) at positions 2, 4, and 6 (Figure 8.)

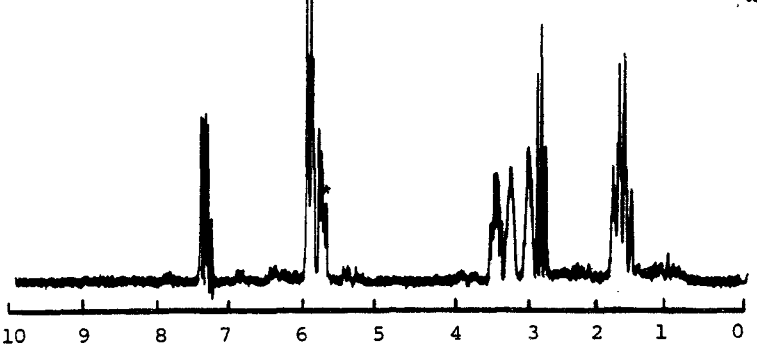


7D

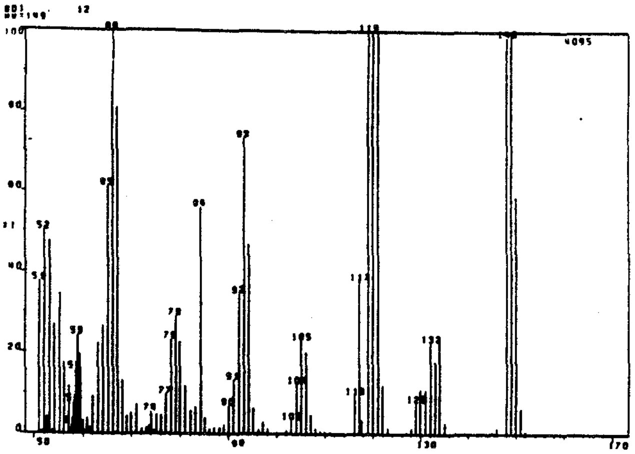
Figure 8. Deuteration of **7**
250 MHz ^{1}H NMR (lower)
Mass Spectrum (right)

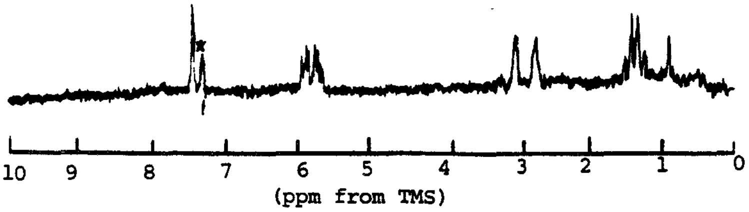
a) **7**, 0.3 M
in $CDCl_3$
* = $CDCl_3$



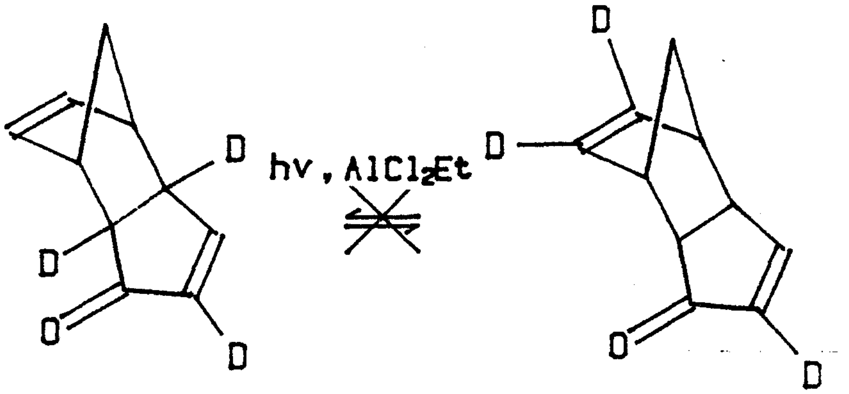


b) **7D**, 0.1 M
in $CDCl_3$



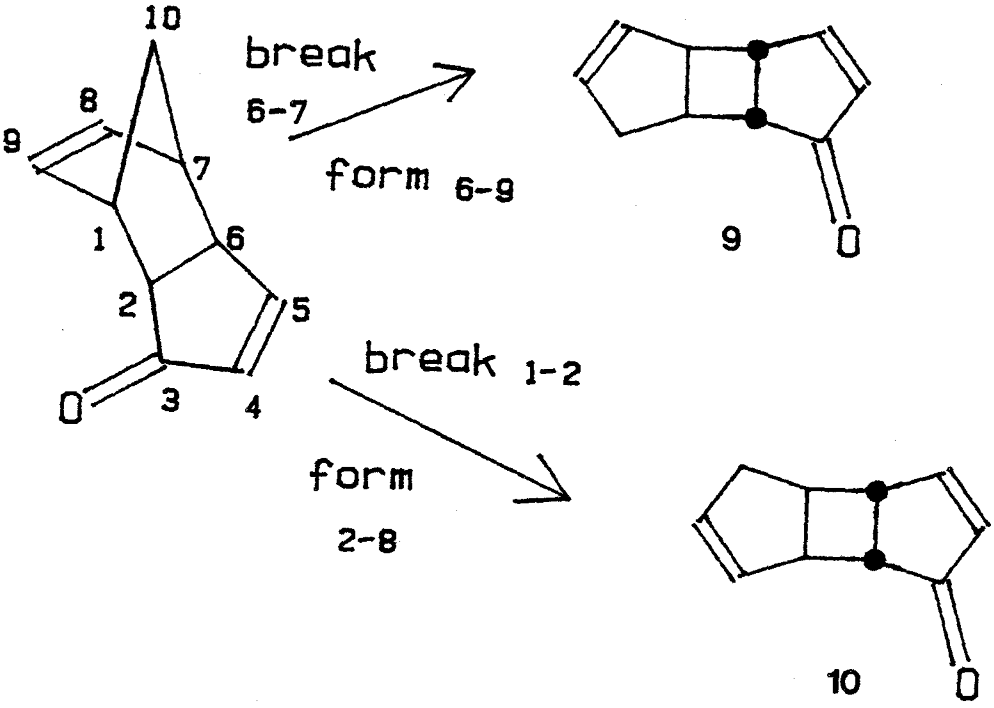


7D-AlCl$_2$Et was irradiated under the same conditions used with its non-labelled counterpart. The reaction was followed by ^{1}H NMR, the irradiation continuing until several hours after the photostationary state had been reached. Characterization of the subsequently isolated and purified starting material showed no evidence of deuterium scrambling, thus ruling out a 3C + 2C addition for 7-AlCl$_2$Et.

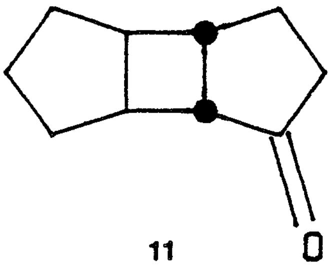


Examination of the ^{1}H NMR spectrum of the unidentified product of the catalysed irradiation of 7-AlCl$_2$Et led to consideration of the structures depicted in Scheme 2. Both pathways can be formally regarded as a [1,3] sigmatropic shift.

Scheme 2

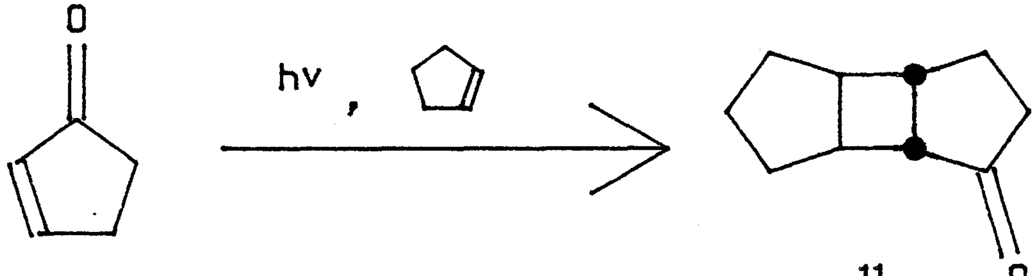


Since both proposed structures possess the same carbon skeleton, the compound was hydrogenated (Pd/$BaSO_4$ in methanol, 2 mol.equiv. H_2) to give a single product whose ^1H NMR and mass spectra suggested the removal of two carbon/carbon double bonds to give **11**.



11

The validity of structure 11 was confirmed by comparison with an authentic sample prepared by a different route,[62] as shown in Figure 9.

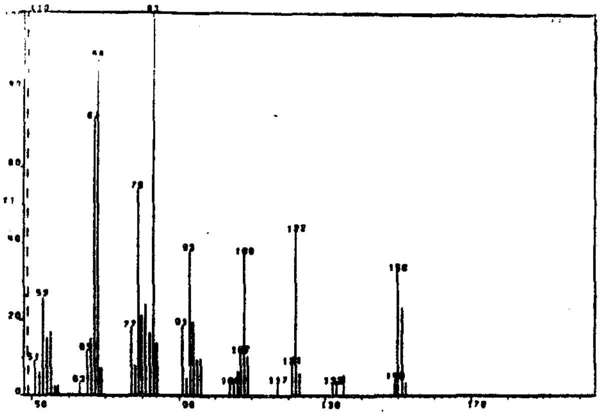


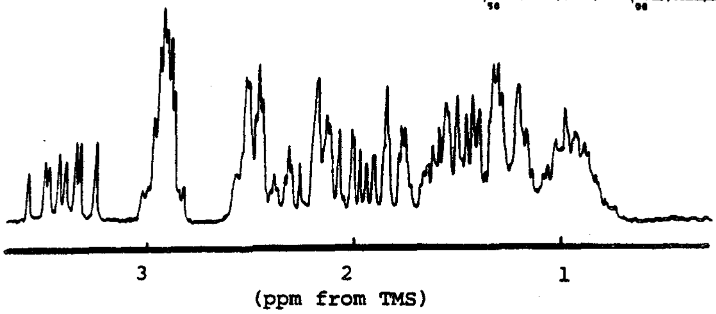
11

With the identification of the carbon skeleton of the photoproduct, the question of the position of the isolated double bond remains to be addressed. This was done by examining the ^1H NMR spectrum of the product in $CDCl_3$ following successive .05 molar equivalent additions of the shift reagent $Eu(TFC)_3$ (Figure 10). Signals for the two methylene protons were clearly shown to be broadened

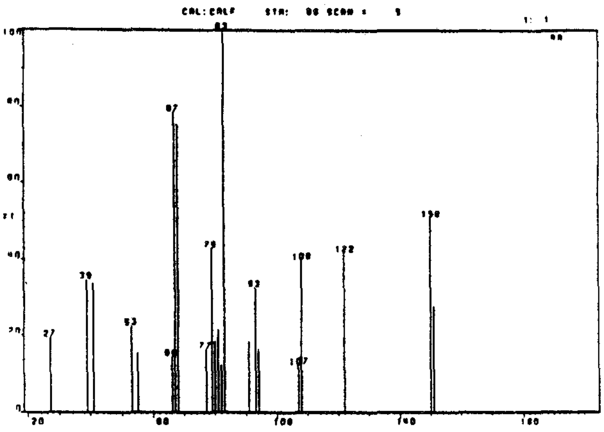
Figure 9. Carbon Skeleton Elucidation of **9**. 250 MHz ^{1}H NMR (lower) Mass Spectrum (right)

a) **11**, from hydrogenation of 9 with 2.0 molar equivalents H_2





b) **11**, from photoaddition of cyclopentene and 2-cyclopentenone



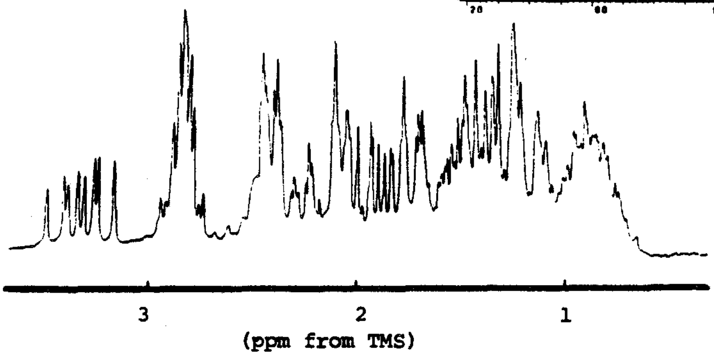
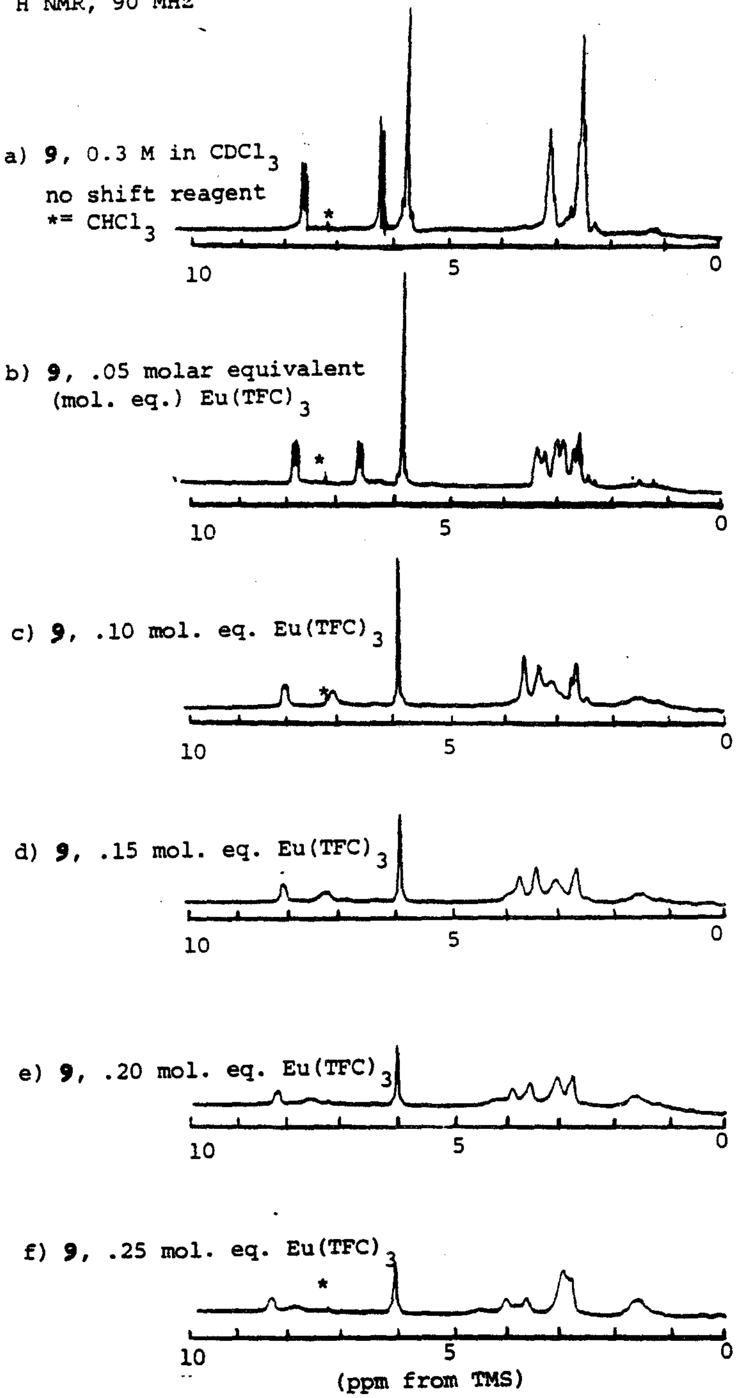


Figure 10. Treatment of **9** with shift reagent Eu(TFC)$_3$

^{1}H NMR, 90 MHz



a) **9**, 0.3 M in CDCl$_3$
no shift reagent
*= CHCl$_3$

b) **9**, .05 molar equivalent
(mol. eq.) Eu(TFC)$_3$

c) **9**, .10 mol. eq. Eu(TFC)$_3$

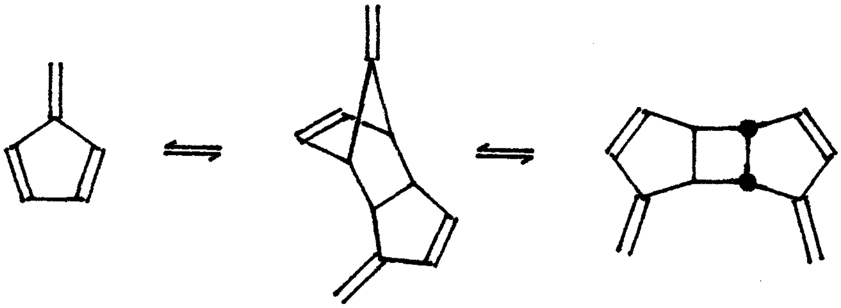
d) **9**, .15 mol. eq. Eu(TFC)$_3$

e) **9**, .20 mol. eq. Eu(TFC)$_3$

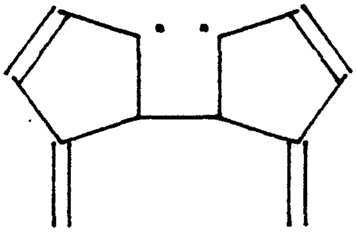
f) **9**, .25 mol. eq. Eu(TFC)$_3$

and shifted downfield, whereas the signals corresponding to the vinyl protons of the isolated double bond were the only resonances in the spectrum not to show any significant line broadening or change in chemical shift, clearly confirming 9 as the correct structure. This position of the double bond was also confirmed by 500 MHz 2D ^{1}H NMR, which unambiguously demonstrated that the two methylene protons (H10) are coupled to H1 and not to H7.[63] The NMR and UV spectra of compounds 7, 8 and 9 are given in Table 10.

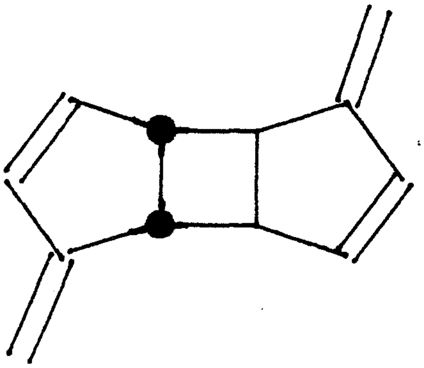
This type of skeletal rearrangement is not without precedent, and has been reported to occur in a thermal transformation of the [4+2] fulvene dimer.[64]



This interconversion is thermally induced, and is believed to result from the homolytic cleavage of the C6–C7 bond to give the following symmetrical diradical intermediate.

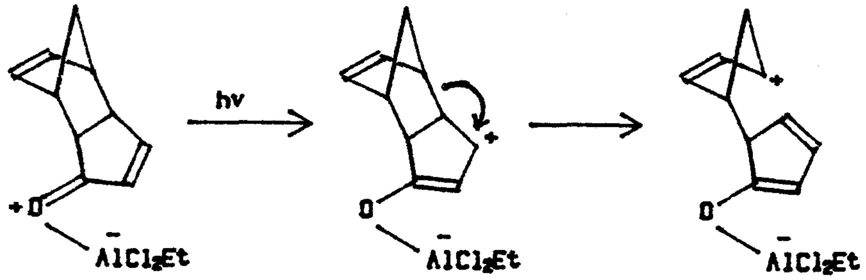


It is worth noting that cleavage of the C1–C2 bond would result in formation of the isomer shown below.



The absence of this isomer is consistent with MINDO/3 calculations done as part of the same study, which show the C1–C2 diradical intermediate to be of higher energy than the C6–C7 diradical.

A concerted [1,3] sigmatropic shift can likely be ruled out as a possible mechanism in the interconversion of 7 and 9, on the basis of the incident radiation being of insufficiently high energy to excite an isolated double bond. A heterolytic bond cleavage similar to that previously described would seem more likely. As was shown in the Introduction, the photoreactions of protonated enones are consistent with the twisting / charge localization model.



Although the rigidity imposed by cyclization would limit the conformational freedom, and hence the degree of charge localization relative to that in 5-methylhex-3-en-2-one, modest amounts of twisting can significantly reduce orbital overlap, and hence some degree of charge localization would be expected to occur. The resulting C5-C6 bond fragmentation would then result in the formation of the allyl cation. Preliminary results by another member of this group indicate the possibility of free carbocation generation by this method.[65]

CHAPTER 3

CONCLUSIONS

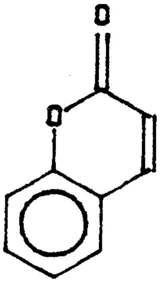
Conclusions

The potential for Lewis acid catalysis in photochemical reactions is enormous. Any compound containing a heteroatom conjugated to an unsaturated system is a potential candidate.

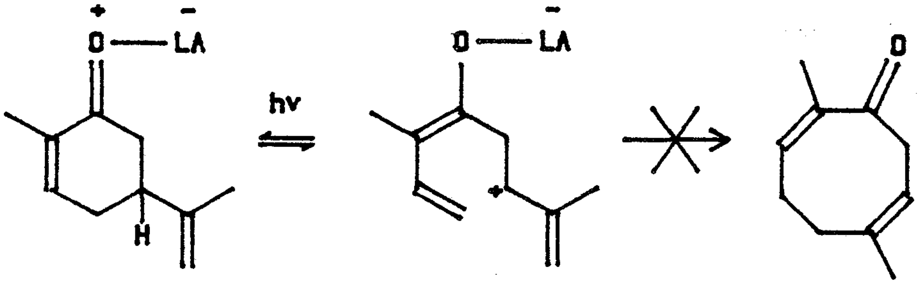
Although the results presented here for acyclic enone complexes deal specifically with E/Z isomerism, the concept of selective complexation may be applied to any system in which photochemically interconverting compounds have varying degrees of affinity for a catalyst. The concept lends itself equally well to both homogeneous and heterogeneous systems.

It seems apparent from the results and reports discussed herein that Lewis acids do not provide a general method for catalysing [2+2] photoadditions to enone carbon / carbon double bonds. This arises partly from the cationic rearrangements that occur as a result of charge localization due to twisting of the double bond upon excitation.

The lack of such rearrangements upon irradiation of the coumarin-$SnCl_4$ complex can be readily understood in terms of its structure.



The site where the photochemically induced twisting of the double bond would localize the positive charge is benzylic, thus the resulting charged intermediate is relatively stable. The lack of photoreactivity observed for carvone-BX_3 complexes could also be interpreted in terms of the mechanistic photochemistry proposed for complexed **7** and **9.**



In this case ring closure reactions of the allyl cation would be expected to favor six membered ring formation over eight. The methyl group in the 2- position would also likely raise the energy barrier to the attainment of the folded configuration of an eight membered ring. An obvious requirement therefore, is that the free energy and / or transition state energy separating a photochemical intermediate from a potential photoproduct not be prohibitively high. Whether a reversible heterolytic cleavage occurs, or whether the complex is truly photochemically inert could easily be determined. If (+)-carvone (essence of caraway) were used, the proposed reversible cleavage would result in a loss of optical activity.

Thus, two requirements necessary for Lewis acid catalysed [2+2] addition are that the enone double bond be in a sufficiently constrained cycle so as to prevent E/Z isomerism, and that the degree of charge localization upon excitation not be so great as to result in cationic rearrangements.

CHAPTER 4

EXPERIMENTAL

EXPERIMENTAL

Instrumentation

NMR spectra were recorded on a Varian EM-390 spectrometer and a Bruker WP-80 or WM-250 Fourier-Transform spectrometers. Chemical shifts of 'neutral' compounds were recorded relative to TMS. Chemical shifts of Lewis acid complexes are in ppm relative to CH_2Cl_2 (5.336, 35°C; 5.421, -70°C) or $CHCl_3$ (7.249, 35°C). All of these instruments were equipped with a variable temperature probe.

UV spectra were measured on a Tracor Northern DARSS system or Pye Unicam instruments.

Mass spectral data were recorded on a V.G. Micromass spectrometer.

Vapour phase chromatography was performed on a Varian Aerograph A90-P3 (preparative) gas chromatograph, and a Hewlett-Packard 5790A (analytical) gas chromatograph. The columns used were:

Preparative Separations:

1) Column A: 5% OV-17 on Chromosorb W 60-80 mesh, 6′ x 1/4" stainless steel
2) Column B: 15% SE-30 on Chromosorb W 60-80 mesh, 6′ x 1/4" stainless steel

Analytical Separations:

3) Column C: 5% OV-17 on Chromsorb W 60-80 mesh, 7′ x 1/8" stainless steel
4) Column D: 2% OV-101 on Chromsorb W 60-80 mesh, 20" x 1/8" stainless steel
5) Column E: 10% Fluorad on Chromsorb W-HP 80-100 mesh, 10′ x 1/8" stainless steel

Materials

Solvents: CH_2Cl_2 and $CHCl_3$ were dried by standard procedures.[66] Benzene, CD_2Cl_2, and $CDCl_3$ were dried for several days over activated (300°C, .3 ± .1 mm Hg, 24 hrs.) Linde 4Å molecular sieves in sealed containers before use.

Lewis Acids: $AlCl_2Et$ (Ethyl Corporation), $SnCl_4$ and $SbCl_5$ (BDH), were distilled and stored in glass ampules. Aluminosilicate pellets (Strem Chemicals, 12% Al_2O_3) were finely ground and activated at 300°C, .3 ± .1 mm Hg, for 24 hrs.

Lewis Bases: Ethyl-E-cinnamate **1**, E-4-phenyl-3-buten-2-one **3** and E-cinnamonitrile **5** (Aldrich Chem. Co.), were distilled and stored in sealed containers over Linde 4Å molecular sieves.

Reactions and Syntheses

Complexations: All manipulations were carried out in a nitrogen glove bag. Glassware to be used with Lewis acids was dried by passing a fast stream of dry nitrogen into the vessel while heating with a torch, allowed to cool (under nitrogen), sealed with a septum cap, weighed, and placed in the glove bag. Where the complexes were unstable at ambient temperatures, manipulations were performed in a glove bag on the bottom of which was a small opening (.5 cm). This was inflated so as to allow a continuous stream of dry nitrogen to escape through the opening, the bottom of the vessel protruding from the hole into a dry ice - acetone bath (-78°C).

Preparative Complexations: Lewis base was added to the irradiation vessel, weighed, and washed down with solvent. The Lewis acid was added to another glass vessel (volumetrically, based on the weight of Lewis base) using an SMI digital pipette, and dissolved in 4 - 5 volumes of solvent. This solution was added slowly to that containing the Lewis base, and washed down with the remaining solvent.

NMR Complexations: The base to be complexed was added to a medium walled glass or quartz NMR tube from a syringe and weighed. Enough solvent was added to wash the substrate into the bottom of the tube. The desired amount of Lewis acid was added volumetrically (based on the weight of Lewis base) onto the side of the tube using an SMI digital pipette, and washed down with solvent. Lewis base concentrations were typically .2 -.3 M.

UV Complexations: Volumetric flasks (needed for the appropriate dilutions) and UV cells were dried by passing dry nitrogen through overnight, but were not heated. A solution of the base (10^{-3} - 10^{-4} M) was added to a UV cell. A large excess of Lewis acid was added using an SMI pipette, the same quantity being added to a reference cell.

The spectra of $Al_2O_3 \cdot SiO_2$ adsorbed species were measured as transmittance spectra of finely powdered aluminosilicate (ca. 0.1g) suspended in a benzene solution of the Lewis base, 5 x 10^{-3} M, cell path length of 0.1 mm. Benzene was chosen because suspensions in this solvent were observed to produce the least amount of light scattering. Spectra of the adsorbed chromophore were obtained by subtraction of the spectrum of the species in solution.

Neutralizations: The reaction mixture was transferred quantitatively into a separatory funnel containing a

1:1 chloroform / water mixture and shaken, the organic layer drained onto anhydrous $MgSO_4$ and filtered. The solvent was removed on a rotoevaporator and the remaining residue distilled.

endo-Tricyclo [5.2.1.$0^{2,6}$] deca-4,8-dien-3-one (7): This was prepared from dicyclopentadiene according to the method of Woodward and Katz,[67] the overall yield being 45%. The product was purified by sublimation (50°C, 10 mm Hg)

^{1}H-NMR: see Table 8.

Mass spectrum (MS): M^+= 146 m/e

G.C.: Column E, 150°C, 25 cc/min., retention time (r.t.)= 30.02 min.

Hydrogenation of exo-tricyclo [5.3.0.$0^{2,6}$] deca-4,8-dien-3-one (9): 10 mg of 9 was dissolved in 3.0 ml of methanol containing 5 mg of catalyst (5% Pd on $BaSO_4$, Koch Light Labs 8877h). The suspension was stirred and 4 ml H_2 (2 mol. eq.) was consumed. The suspension was filtered and the catalyst rinsed with methanol. The combined solvents were removed by gentle heating on a steam bath using a Vigreux column, and the residue distilled (120°C, 1.0 mm Hg)

^{1}H-NMR: 1.4 -2.8 ppm, multiplet, (Figure 9.)

MS: M^+= 150 m/e

GC: Column E, 150°C, 25 cc/min., r.t.=42.74 min.

Deuteration of 7: (at positions 2,4,6): 0.6 g sodium wire was added to 30 ml 1,4 dioxane under nitrogen. 12 ml D_2O was added slowly

from a dropping funnel into the rapidly stirred mixture. After the metal was consumed, 250 mg of 7 dissolved in 5 ml dioxane was added dropwise from the funnel. The mixture was refluxed (100°C) for 5 days, then cooled and neutralized to pH 7 with D_2SO_4 / D_2O (1:4 v/v). The resultant mixture was extracted three times with 25 ml of diethylether, the combined organic layers dried over anhydrous $MgSO_4$, filtered, and the solvent removed on a rotoevaporator at aspirator pressure, 40 - 50°C. The residue was purified by sublimation (50°C, 10 mmHg) to give 150 mg of white waxy crystal. The missing resonances in the NMR spectrum (Table 8.) and resultant loss of coupling suggested quantitatve (> 97%) labelling at positions 2, 4 and 6.
MS: M^+= 149 m/e

Irradiations

These were carried out in a quartz Dewar vessel using a Rayonet Photoreactor (Southern New England Ultra-violet Company) equipped with a variable temperature unit using RPR 3000Å lamps. Pyrex glass containers were used for compounds 1-6, and quartz vessels for compounds 7 and 9.

Preparative Irradiations:

2, 4 and 6: 2 was prepared from 1 according to the procedure of Lewis and Oxman,[47] followed by separation (from 1) on Column A (150°C, 20 cc/min.) and stored in sealed glass ampules. Compounds 4 and 6 were prepared by irradiation of 10 ml of 1M CH_2Cl_2 solutions of 3 and 5 respectively. 4 was purified on Column A (150°C, 20 cc/min.), 6 was purified on Column B (120°C, 20 cc/min.). Both were stored in sealed glass ampules. Injection volumes were 20 ± 5 μl.

9: Two 25 ml $CHCl_3$ solutions, one containing 1.2 g $AlCl_2Et$, the other 1.35 g of 7, were mixed together in a quartz vessel. The solution was stirred and irradiated at -55°C for 24 hours. Following neutralization of the Lewis acid, the solvent was removed on a roto-evaporator and the remaining faintly yellow residue distilled (140°C, 10 mm Hg) to yield 1.04 g of a clear liquid containing 36% 9 and 64% 7 (Column E) The mixture was separated on a 10 cm x 1 cm column containing TLC grade silica (10 g) using 50 ml each of 0, 5, 10, 15, 20 % ether/pet. ether, v/v. 9 eluted first, 300 mg was recovered after solvent removal and distillation (140°C, 10 mm Hg)

^{1}H-NMR: see Table 8.

MS: M^+=146 m/e

High resolution MS: obs. mass = 146.0732

G.C.: Column E, 150°C, 25 cc/min., r.t.= 33.14 min.

Photostationary State Measurements:

These were performed in medium walled Pyrex (**1**-**6**) or quartz (**7** and **9**) NMR tubes with 15-25 mg of base and an appropriate amount of Lewis acid in .2-.3 ml solvent. Samples were prepared in duplicate, one wrapped in foil to serve as a thermal control. These were irradiated and monitored by NMR at regular intervals at the appropriate temperature until no further change was observed. Irradiations were also carried out as above with a similar pair of samples of the 'product' to confirm that both irradiated samples reached the same composition after no further change was observed. Following irradiation, the solutions were quenched and analyzed by GC:

1/**2**: Column D, 120°C, 25 cc/min., r.t.**1**= 2.33 min., **2**= 1.47 min.

3/**4**: Column D, 100°C, 25 cc/min., r.t.**3**= 2.47 min., **4**= 1.52 min.

5/**6**: Column D, 70°C, 25 cc/min., r.t.**5**= 5.74 min., **6**= 4.00 min

7/**9** Column E, 150°C, 25 cc/min., r.t.**7**= 30.02 min., **9**= 33.14 min.

Photostationary State of 3/4 with $Al_2O_3 \cdot SiO_2$:

.15 g of $Al_2O_3 \cdot SiO_2$ (12% Al_2O_3) was ground in a mortar and pestle and activated at 300°C, < 1 mmHg, for 24 hours. The catalyst was transferred (in a dry nitrogen glove box) into a Pyrex tube. To this was added a 5×10^{-3}M solution of **3** in CH_2Cl_2 (25 mg **3** in 30 ml CH_2Cl_2). The tube was sealed, and placed into a quartz Dewar irradiation vessel containing a methanol cooling bath, the temperature of which was maintained at -55°C with a cooling probe placed in the bath. The slurry was stirred, and irradiated with 300 nm lamps. The relative concentrations of **3** and **4** were determined by GC (Column D, as described on the preceding page) at regular intervals until no further change was observed.

CHAPTER 5

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