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Oxygen Abstraction A New Type of Carbene Reactivity and A New Method to Generate Stable Carbenes

presented by

Dalila G. Kovacs

has been accepted towards fulfillment of the requirements for

Ph.D. degree in Chemistry

James E. Jáckson

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Oxygen Abstraction A New Type of Carbene Reactivity and A New Method to Generate Stable Carbenes

by

Dalila G. Kovacs

A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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ABSTRACT

OXYGEN ABSTRACTION A NEW TYPE OF CARBENE REACTIVITY AND A NEW METHOD TO GENERATE STABLE CARBENE

By

Dalila G. Kovacs

A new type of carbene reaction was investigated here, oxygen abstraction by carbenes. Reactions of three different type of carbene, with suitable oxygen donors were studied. For methylene, :CH₂ (triplet ground state), fluorenylidene, Fl: (triplet ground state but rapidly equilibrating to singlet state), and phenylchlorocarbene, PCC: (singlet ground state) experimental and computational tools were employed to demonstrate the carbene ability to abstract oxygen atom and to get some insight into the mechanistic aspects of this new type of reaction.

This new type of carbenes chemistry was experimentally proved, by isotope labeling and products detection and analysis. Rates for some of the investigate reactions of oxygen abstraction reaction were measured. Aspects of the mechanism were revealed by qualitative Laser Flash Photolysis studies and theoretical calculations. A different approach toward synthesis of stable carbene by carbodiimide cyclization reaction proved to be ineffective toward carbene synthesis but a reach subject for mechanistic point of view.

DEDICATION

Părintilor mei, Silvia si Cornel, din adâncul inimii: făra dragostea voastră, constantă si neconditionată, nici unul din succesele mele nu ar fi fost posibil.

Fiicelor mele, Linda si Anca: fãra voi viata mea nu ar avea sens.

AKNOLEDGMENTS

After all this years, finally here!

Dr Jackson, you enriched my professional life by the touch of your mentorship; Evy and you provide me with kind and friendly support through my personal struggle. Thank you!

So many people cross their path with mine during this time and what my life would be without them! I am thankful to all of you for my professional and personal growth; for your warm shoulder when things did not want to go my way and for sharing with me happy moments.

My thoughts go to Linda and Anca who struggled through this Ph. D. with me, taking all the bad moods of an unhappy chemist at work!

And finally, thanks God for give me strength and let me go so far and accomplish my dreams.

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Key to Symbols and Abbreviations:

LFP	laser flash photolysis
PNO	pyridine-N-oxide
DAF	9-diazofluorene
AN	anthronylidene
Fl:	Fluorenylidene
m _{CXY}	carbene philicity parameter
TS	transition state
Fl=O	fluorenone
TMU	tetramethylurea
DMI	1,3-dimethyl-2-imidazolidinone
DMI	1,3-dimethyl-2-imidazolidinone
BDE	bond dissociation energy; note that DH_f for Oxygen is 59.6 kcal/mol at
	298K.
CSE	carbene stabilization energy, defined as the energy change for the
	following reaction: :CH ₂ + CX ₂ H ₂ > CH ₄ + :CX ₂
PCD	phenylchlorodiazirine ()
PCC:	phenylchlorocarbene
k _x	rate constants
PES	potential energy surfaces,
IRC	intrinsic reaction coordinate calculations
NImag	number of imaginary vibrational frequencies
ΔH_{rxn}	heat of reaction 1,
CID	collisional induced dissociation
ΔH^{\ddagger}	activation enthalpy

S–T	Singlet-to-Triplet state energy gap
DMAD	dimethyl-acetylene-dicarboxylate
CDI	carbodiimide
DBCDI	ditertbutyl carbodiimide
THF	tetrahydrofurane
TCNE	tetracyanoethylene
MA	Maleic Anhydride
НОМО	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital

CHAPTER 1

Carbenes and Atom Abstraction Reactions: A Review

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1.1 Introduction

Atom abstraction is one of the typical reactions of carbenes. The most familiar cases involve abstraction of hydrogen or chlorine atoms. In the last decade, a new type of atom transfer has been investigated, mainly as a result of Scaiano's work¹ concerning reactions of triplet diphenylcarbene with nitroxides. More recent work has described oxygen and sulfur atom abstraction from oxiranes and thiiranes.

The idea of generating stable carbenes by oxygen abstraction reactions from carbonyl compounds is the focus of the work presented here. The driving force for such a reaction should be the formation of a thermodynamically stable species as in the abstraction of a divalent heteroatom such as oxygen or sulfur, bonded by two single σ bonds or by a double ($\sigma + \pi$) bond.

1.2 Atom abstraction reactions in carbene chemistry

1.2.1 Monovalent atom abstraction: Hydrogen and Chlorine

Carbenes commonly abstract univalent atoms, such as hydrogen and chlorine, to yield radical pairs.² The spin state of the reacting carbene plays a determinant role. It is commonly accepted that a carbene in its triplet state can abstract hydrogen atoms while the singlet state abstracts chlorine atoms.³ An early noted exception to this rule is methylene. Both singlet and triplet methylene may abstract chlorine from suitable donors. Roth *et al.* studied the chlorine atom abstraction from chloroform, using CIDNP, for several types of carbenes (Figure 1.2)



Figure 1.1 Hydrogen and Chlorine atom abstraction

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The carbene can form either a singlet or a triplet radical pair depending on the its initial spin state.

Laser flash photolysis (LFP) studies⁴ of chlorine atom abstraction by diphenylcarbene, well established triplet ground state, and singlet ground state phenylchlorocarbene, **PCC**:, known to be singlet in its ground state, reveal that both triplet and singlet states may abstract chlorine from a C-Cl bond.⁵ The rate of chlorine abstraction by the triplet state of diphenylcarbene is one order of magnitude faster than the corresponding reaction of singlet **PCC**:. These studies indicate a transition state with a considerable amount of carbene-chlorine bond formation and charge development, and the experimental results⁶ do not support the intervention of a chloronium ylide in the reaction of phenylchlorocarbene with halomethanes.

1.2.2 Oxygen and sulfur: divalent atom abstraction

Transfer of a divalent atom, e.g. oxygen or sulfur, to make a closed-shell π bonded species such as carbonyl compounds, is rare. Only a few donorsdimethylsulfoxide, nitroxides, amine oxides, O₂, oxiranes, and thiiranes-have been mentioned in the literature.

1.2.2.1 Dimethylsulfoxide

In 1967 Hayashi *et al.* reported the oxidation of some carbenes by dimethylsulfoxide.⁷ The authors proposed an ylide intermediate which decomposes to dimethylsulfide and the corresponding carbonyl compound derived from the starting carbene. The yield of the carbonyl compound drops rapidly with time, and the authors suggested further reaction of the produced carbonyl compound with the methylsulfinyl carbanion.

1.2.2.2 Organonitrogen oxides

In 1963 Schweitzer⁸ *et al.* reported the deoxygenation of pyridine-N-oxide (**PNO**) by dichloromethylene. They also investigated the reaction of 9-diazofluorene (**DAF**) with **PNO** in refluxing benzene; 50% of the yield was fluorenone and 35% fluorene-azine.

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Tes n **∏=0**. 19:22 **x**1207 **je**ory s 0*1)* ti ti 013 9.7 T: :0 These results suggested an ylide intermediate which decomposes to give fluorenone,

Fl=O.

In 1984, Scaiano *et al.* investigated the reaction of nitroxides with triplet diphenylcarbene, and found that oxygen atom transfer leads to quantitative yields of benzophenone¹. For 4-hydroxy-2,2,6,6-tetramethylpiperidine-N-oxide the triplet carbene deoxygenates the nitroxide instead of inserting into the O-H bond.



Figure 1.2 Oxygen transfer from nitroxides to diphenyl carbene

Oxygen abstraction is spin allowed, and over 100 kcal/mol exothermic; the attack at the nitroxide center competes successfully with insertion in O-H bond which is usually considered to be a singlet carbene reaction.

In 1988 Schuster *et al.* found that anthronylidene (AN) reacts with PNO to yield 92% anthraquinone.⁹ The reaction is assumed to occur through the singlet ¹AN.



Figure 1.3 Oxygen transfer from nitroxides to anthronylidene

The experiments suggested that in the absence of a good trapping reagent, ³AN converts to ¹AN which can abstract oxygen from PNO.

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1.2.2.3 Oxygen (O₂)

Interest in the reaction of carbenes with molecular oxygen gained popularity due to the general interest in ozone chemistry. Carbenes react with O_2 to form carbonyl oxides, familiar as the Criegee intermediates involved in alkene ozonolysis.

Criegee intermediate Dioxirane

Figure 1.4 Criegee intermediates and dioxiranes

The dioxiranes,¹⁰ isomers of the Criegee intermediates, were studied while mapping out the carbene- O_2 chemistry. The formation of such intermediates, detected by matrix isolation techniques, clearly showed the range of possible carbene reactions with molecular oxygen as well as revealing the novel chemistry of carbonyl oxides and dioxiranes.

In comparison with the previous study⁹ ³AN is oxidized by molecular oxygen at a diffusion controlled rate, two orders of magnitude faster than oxidation of the same carbene by PNO. In general, triplet carbenes react with O₂ at or near diffusion control, whereas carbenes with singlet ground states react much more slowly or not at all. The presence of products from the reaction with molecular oxygen is usually taken as strong evidence for triplet state trapping in a given process.

1.2.2.4 Oxiranes and Thiiranes

Fluorenylidene (**Fl**:) abstracts oxygen from cis- and trans-2-butene oxide,¹¹ to yield the corresponding alkene. The experimental results indicate that singlet state is responsible for this process. The reaction is faster than formation of the known Fl:acetonitrile ylide in acetonitrile solvent, but slower than insertion into the O-H bond of methanol.

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Figure 1.5 Oxygen transfer from oxiranes to carbenes

The yields depend on the nature of the oxirane and, from the above cited work, are: *cis*-epoxybutane 60%, *trans*-epoxybutane 50%, styrene oxide 50% and cyclohexene oxide 30%. An earlier estimate of the rates ¹² was confirmed by recent direct measurements by means of LFP. ¹³ Warkentin *et al.* give rate constants for oxygen abstraction by several carbenes from oxiranes and thiiranes. For the wide range of carbenes studied, rate constants from 10⁴ to 10¹⁰ M⁻¹s⁻¹ were found. Oxygen or sulfur abstraction appears to obey a linear free energy relationship with respect to the carbene philicity parameter m_{CXY}^{14} with higher reactivity for electrophilic carbenes, lower for ambiphilic ones and the lowest reactivity for the nucleophilic carbenes such as dimethoxycarbene. By comparison, the corresponding rate constants for oxygen abstraction from PNO exceed 10⁹ M⁻¹ s⁻¹.

1.3. Oxygen abstraction by atomic Carbon as a model for the reactivity of carbenes.

Atomic carbon is, by itself, one of the most fascinating intermediates encountered in chemistry due to its high energy and its particularly interesting electronic configuration. Of the fifteen possible electronic states, the triplet ground state $C(^{3}P)$ and the two low-lying excited metastable singlet states $C(^{1}D)$ and $C(^{1}S)$ are thought to be involved in most of its reactions. Despite the energy differences among these three states (~30 kcal/mol) all three have to be considered as possible reacting species. Presented in Figure 1.6 is a schematic representation of the electronic structure of these three states, and their heat of formation.



Figure 1.6 The first three electronic states of atomic carbon

As with carbenes, carbon atom chemistry presents chemists with the problem of finding which of the reactive states of the carbon atom is responsible for certain reactions.

Knowledge of the electronic state of the reacting partner and the product(s) are useful for interpreting the results. To probe for the involvement of the triplet ground state $C(^{3}P)$, molecular oxygen is often added to the system and its influence on the overall and particular yields is used as an indication of the participation of the triplet state in the reaction. Molecular O₂ is used as a scavenger for $C(^{3}P)$. The reaction is governed by the spin conservation rule which states the interaction of triplet carbon with triplet oxygen molecule. The same rule applies in carbone reactivity studies, where the reaction with molecular oxygen is a probe for the presence of the triplet state of the carbone in the given reaction under study.

A general trend from the experimental information available to date is that the most reactive species seems to be the singlet ¹D, followed by the triplet ³P and the less reactive singlet ¹S. In this respect the chemistry of atomic carbon parallels the chemistry of carbenes in which the reaction rates of singlet species are generally higher than the corresponding rates of the analogous triplet states of a particular carbene.

Atomic carbon maybe generated from diazotetrazole.¹⁵ The precursor is prepared in tetrahydrofuran (THF) solution and the solvent is evaporated while the walls of the reaction flask are evenly coated with the diazo compound. The substrate may be added in

7

the initial solution of THF or after evaporation of the solvent, UV irradiation or heating to 80° -100° C, decomposes the diazocompound to N₂ and monoatomic carbon in a 3 : 1 ratio (Figure 1.7).



Figure 1.7 Atomic carbon generation

The advantage of this method is that it produces monatomic carbon with low kinetic energy at moderate running temperatures, $\sim 100^{\circ}$ C, for the subsequent reaction of the substrate with carbon.

Due to its unfilled outer electronic shell, atomic carbon acts mainly as an electrophile. This aspect of its reactivity governs the competition between insertion into σ or π bonds and atom abstraction. Monoatomic carbon presents, in several cases, unexpected selectivity. In interactions with organic substrates, atomic carbon follows two possible routes, both typical reactions for carbenes as well: insertion into σ or π bonds and atom abstraction (Figure 1.8).¹⁶

Figure 1.8 Possible reaction routes for atomic carbon

Particularly interesting is the behavior of carbon atoms toward halocarbons.¹⁷ Halogen abstraction is most likely the primary process, generating monovalent CF or CCl intermediates.¹⁸ Preference for insertion into the C-Cl bond but not into the C-F bond may be explained by considering the strength of the C-halogen bond. This side of carbon atom chemistry allows further analogies to the chemistry of carbenes. The reactions with heteroatom–containing moieties are not entirely understood but they do produce highly reactive carbenes. The presence of heteroatoms with their nonbonding electrons (as in the case of ethers, thioethers or aziridines), directs the attack of carbon toward the electron lone pair. The main course of the reaction is atom abstraction with the formation of carbon monoxide CO, CS, or CNH (Figure 1.9).¹⁹ The reaction is thought to follow a mechanism similar to that of carbene reactions with oxiranes and thiiranes (Reference 11 and references therein). A carbon atom in its singlet state is similar to a singlet carbene and the reactions of singlet carbon atoms as an oxygen abstractor have been studied both experimentally and theoretically.



Figure 1.9 Heteroatom abstraction by atomic carbon

However, the most interesting cases are the reactions of carbon atoms with carbonyl or nitroso compounds. In such cases, C atoms abstract a double bonded oxygen atom. In 1983 Shevlin mentioned for the first time the possibility of excited singlet methylene formation in the deoxygenation of formaldehyde by atomic carbon.²⁰ The main products are carbon monoxide and the corresponding carbene or nitrene²¹ and this reaction is used generally to generate these species (Figure 1.10).



Figure 1.10 Double bonded oxygen abstraction by atomic carbon

ju: Pac Ŷæ Hg 231 (es) ùt 1.4 ii. Ylið Wit iler ₽ŀ⊓ . [][Of interest to us is its similarity to the carbene reaction involving abstraction of double bonded oxygen from suitable donors, especially carbonyl compounds.



Figure 1.11 Oxygen transfer between atomic carbon and an aldehyde

Predicted in 1968 by Hoffmann, the formation of ¹:CH₂ was finally completed in 1983 by Shevlin; the stepwise addition to olefins confirms its spin state.

Highly energetic species are generated in the carbon atom case, but by carefully directing a similar reaction from a thermodynamically less stable carbene to a more stable one, the designed procedure may become a new route to generate thermodynamically stable carbenes.

1.4 Ylide formation: first step in a possible heteroatom abstraction

The interaction of a carbene with the lone-pair electrons of heteroatoms, such as nitrogen, oxygen, phosphorus and sulfur, usually leads to zwitterionic species known as ylides (Figure 1.12). They are the result of interaction of a singlet carbene empty p orbital with lone electron pairs of the reaction partner.²² Numerous ylides are mentioned in the literature, involving heteroatoms such as nitrogen (with amines, isoquinoline, 4-picoline, pyridine and nitriles), oxygen, halogens, phosphorus (mainly triphenylphosphine), sulfur (sulfonium, sulfoxonium, and thiocarbonyl), arsenium, antimony, bismuth, selenium, and tellurium.

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Figure 1.12 Ylide resonance structures

Ylide formation is a certainty well established and ylides of sulfur, nitrogen and halogens have been detected, isolated and characterized.²³ As a consequence, the idea of ylides as intermediates in carbene reactions has solid experimental support. Generally, the presence of an ylide as an intermediate in a certain reaction is accepted if characteristic transformations are observed²⁰. Figure 1.13 lists reactions where the intermediacy of an ylide is generally accepted.

a. α',β -elimination

$$\begin{array}{c} \bigoplus_{X \to CR_2} & \bigoplus_{X \to CR_2} & H_2C=CH_2 \\ & H & H \end{array}$$

b. [1,2] sigmatropic rearrangement-Stevens rearrangement

$$\begin{pmatrix} + & \ominus \\ X - CR_2 \\ CH_2R \end{pmatrix} \Delta \qquad X - CR_2 \\ CH_2R \end{pmatrix}$$

c. carbene insertion in X-H bonds where X=O, N, S

d. [2,3] sigmatropic rearrangement-allylic rearrangement

$$\overset{\ominus}{\longleftarrow}_{\mathsf{R}}^{\mathsf{O}} \overset{\Delta}{\longrightarrow} \overset{\mathsf{X}^{\mathsf{C}}\mathsf{R}_2}{\overset{\Lambda}{\longleftarrow}_{\mathsf{R}}}$$

e. fragmentation of three membered rings



Figure 1.13 Ylides reactivity
127 127 15 ŝk 500 ي مر 127 ¥3 che 50 20(ŝ¢'i Ĵ he đa in: ici; <u>Sti</u>] str, ЧĊ We are interested here in ylide formation as a possible first step in oxygen atom transfer. Usually, an ylide may follow several different reaction paths (Figure 1.13), depending on its ability to react with the available partners and on its thermodynamic stability. Commonly mentioned are the paths a and b in Figure 1.13. In the presence of a dipolarophile, [2+3] dipolar cycloadditions (path a) are frequently encountered and specifically used for probing ylide intermediacy in certain processes. In the absence of a suitable partner, ylides may cyclize to the corresponding oxirane (path b) or, in some cases, decompose to more stable species (path c). However, if a previously generated carbonyl ylide has no choice other than to decompose to the carbonyl compound and carbene, the ylide itself becomes a reliable source for carbenes. Indeed, such a procedure was pioneered in J. Warkentin's labs at McMaster University and has made its way in the chemistry world.

Is interesting that it was thought that only carbenes with electron-withdrawing groups attached to the carbenic center or carbene precursor, frequently a diazocompound, could generate stable ylides. However, despite popular belief of their involvement in several processes, carbonyl ylides remained only hypothetical intermediates to the late 70's. In 1978 Bartlett *et al.* published results for carbonyl-ylide intermediates obtained in the decomposition of Δ^3 -1,3,4-oxadiazolines²⁴ formed through the reaction of diazoalkanes with ketones. The presence of products from the reactions of 1, 3 dipolar intermediates was considered strong evidence for the existence of a short lived ylide intermediate. Literature data are available about the solid-state photolysis of *trans*-stilbene oxide which allowed the observation of an intermediate with an ylide-like structure.²⁵

The first stable carbonyl ylide was reported in literature in the late '80s.²⁶ The thermodynamic stability of this designed ylide is the result of its existence mainly in the

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zwitterionic polar form, a fact confirmed by the X-ray crystal structure data which clearly reveals different lengths for the two C–O bonds (Figure 1.14).



Figure 1.14 Ylide of tetramethylurea and tetrakis(trifluoromethyl) cyclopentadienylidene

At the beginning of 90's, Warkentin published a new method to generate asymmetric alkoxy-carbenes via thermolysis of Δ^3 -1,3,4-oxadiazolines substituted with different alkoxy groups. The mechanism proposed by the authors involves ylide formation with N₂ loss by a concerted, irreversible, 1,3-dipolar cycloreversion, followed by the fragmentation of the ylide.²⁷



Figure 1.15 Oxadiazoline synthesis and reactivity

Ylide formation and reactivity is the subject of several theoretical studies. In 1978 a series of results was published by Devaquet *et al.* and described investigations of the overall thermal and photochemical behavior of oxiranes, using ethylene oxide as a prototype. Their results parallel the experimental data.²⁸ For oxiranes bearing substituents which do not stabilize zwitterionic forms, C-O bond rupture is the most effective primary process. For the other oxirane derivatives, C-C bond rupture competes and leads to products less susceptible to reclosure. They can either be trapped by 1,3-dipolar cycloaddition or fragment into a carbenic entity and carbonyl compounds.²⁹



Figure 1.16 Ylide synthesis: theoretical studies results

In 1980 Houk *et al.* published an analysis of the structure and reactivity of substituted carbonyl ylides.³⁰ Ylides containing amino, cyano and phenyl groups were considered using*ab initio* methods (STO-3G, 4-31G basis set with 3 x 3 CI).



Figure 1.17 Ylide cleavage to carbene and carbonyl compound

When X = Y = H the cleavage reaction is calculated to be endothermic by 38 kcal/mol but for X = H, $Y = NH_2$, it becomes exothermic by 17 kcal/mol. Also, the authors concluded that thermal fragmentation of a carbonyl ylide from a coplanar ground state is an orbital forbidden process. The same study concludes that ylides can easily form from excited state oxiranes.

In 1982 Volatron *et al.* published also an *ab initio* study (STO-3G and 4-31G basis sets plus extensive CI) which analyzes the electrocyclic ring opening of oxiranes.³¹ In these calculations, a highly energetic point was considered to correspond to an ylide-like transition state with a significant diradical character. The authors suggest that the best way to consider the mechanism of such reactions is through an ylide intermediate which has a planar structure. The transition state (TS), is an orthogonal ylide-like structure which corresponds to the rotational isomerization of the planar ylide.

Finally, the paper published by Warkentin *et al.* in 1981 presents experimental results that relate to Houk's calculations. It shows the fragmentation of alkoxy substituted

carbonyl ylides as a thermal process which leads to a carbone and a carbonyl compound.³²

1.5 Conclusions

The precedents presented in this overview of carbene reactivity set the stage for an exploration of the possibility of generating thermodynamically stable carbenes by means of oxygen abstraction reactions. We reasoned that by choosing a carbene product such as diaminocarbene, we should endow the reaction with sufficient driving force. The known cases of oxygen abstraction from nitroxides or from oxiranes should represent good reference points in the exploration of this proposed new reaction. The similarity of carbon atom chemistry with that of singlet carbenes leads to the choice of a , highly reactive singlet carbene to perform the abstraction of the double bonded oxygen. However, other species were considered as well. One well known case is the one of phosphorus atom as it behaves in the Corey-Winter reaction.³³ The mechanism of such a reaction is intriguing and constitutes a rich subject to be studied.

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Species	∆H _{Exp}	Species	∆H _{Exp}	Species	∆H _{Exp}
C ₁ (³ P)	171	СН	142.4	iso-C3H7	22.3
$C_{l}(^{l}D)$	201	¹ CH ₂	99.8	H ₂ C=CH	63.4
$C_1(^1S)$	233	³ CH ₂	92.3	H ₂ C=CH ₂ CH ₃	40.0
C2	200.2	CH3	34.8	НО	9.3
C ₃	196	n-C3H7	16.8	H ₂ N	45.1

 Table 1.1 Experimental heats of formation

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CHAPTER 2

Carbene-to-Carbene Oxygen Atom Transfer: A New Type of Carbene Reactivity and a Potential Path to Generate Nucleophilic Carbenes

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Abstract:

Fluorenylidene (Fl:) abstracts oxygen from pyridine-N-oxide (PNO), to give fluorenone (FI=O) in high yield. Other substrates—N-methyl morpholine-N-oxide (MNO), sulfolane, trimethyl phosphate, tetramethylurea (TMU), 1,3-dimethyl-2-imidazolidinone (DMI), and dimethyl carbonate (DMC)—also oxygenate Fl:. The latter three, TMU, **DMI**, and **DMC**, should yield carbenes instead of stable deoxygenated byproducts. This heretofore unexplored carbene-to-carbene exchange has been verified by two observations: the ¹⁸O label is transferred from TMU to FI=O, and tetrakis(dimethylamino)ethylene (the dimer of the product carbene) is detected by its chemiluminescent reaction with atmospheric oxygen. Competition between methanol and oxygen donors along with laser flash photolysis studies in acetonitrile show that Fl: deoxygenates PNO as fast or faster than it inserts into methanol O-H bonds: $k_{PNO}/k_{MeOH} = 1.7 \pm 0.4$; analogous experiments with TMU and DMI give $k_{TMU}/k_{MeOH} = 0.49 \pm 0.02$ and $k_{DMI}/k_{MeOH} = 0.52 \pm 0.02$. These relative rate data translate into absolute rate constants of 2.6 and 2.8 x 10⁸ M⁻¹s⁻¹, respectively, in good agreement with an independently determined LFP value of 3 x 10^8 M⁻ 1 s⁻¹ for quenching of **FI:** by **TMU**. These measurements represent the first absolute rate constants measured for carbene-to-carbene oxygen atom transfer processes.

2.1. Introduction

We report here evidence for carbene-to-carbene oxygen atom transfer, according to the reaction :

$$R_2C: + O=CR'_2 \longrightarrow R_2C=O + :CR'_2$$
 (Reaction 1)

Singlet atomic carbon abstracts oxygen atoms from a wide variety of carbonyl compounds to produce carbon monoxide and carbenes¹; these highly exothermic processes can produce "hot" carbenes with unusual behavior.² We now report that the reactive carbenes fluorenylidene (**Fl**:) and methylene (:**CH**₂) behave analogously if the carbene product is sufficiently stabilized with electron donor groups (see Table 2.1).³ Besides its intrinsic interest as an abstraction of a *doubly bonded* atom,⁴ this type of reaction represents a new photochemical pathway to generate nucleophilic carbenes and study their chemistry.

Carbenes do abstract oxygen atoms from suitable donors such as N-oxides⁵, nitroxides⁶, or epoxides.⁷ Many carbenes react with molecular oxygen to give carbonyl oxides and their isomeric dioxiranes.⁸ With simple carbonyl compounds such as aldehydes,⁹ ketones,¹⁰ esters,¹¹ amides,¹² and ureas,¹³ electrophilic singlet carbenes attack the oxygen lone electron pairs to form carbonyl ylides **1** (Figure 2.1). These intermediates may then cyclize to form epoxides¹⁴ or undergo cycloaddition with a second equivalent of carbonyl compound to give dioxolanes.^{9,10g} A third, almost unexplored pathway, is fragmentation to a new carbene/carbonyl compound pair. Indeed, Warkentin *et al.* have shown¹⁵ that explicit synthesis of ylide **1** (R=CH₃, R'=OCH₃) via oxadiazoline decomposition leads to acetone and dimethoxycarbene products.

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Figure 2.1 Fluorenylidene, methylene, phenylchlorocarbene and carbene-carbonyl ylide

2.2 Carbenes and oxygen donors

In this work, fluorenylidene (Fl:), methylene (:CH₂) and phenylchlorocarbene (PCC:) have been examined as oxygen abstractors. The carbenes were photolytically generated from diazofluorene (DAF), diazomethane (DAM), or phenylchlorodiazirine (PCD), respectively, and their reactions were studied by product analysis and laser flash photolysis (LFP).

DAF is a relatively stable diazo compound, readily available in two steps from fluorenone.¹⁶ Irradiation of DAF with UV-VIS light from a high pressure Hg lamp (500 W) filtered through uranium glass generates **Fl:**. **DAM** is synthesized via established methods and trapped directly in the neat urea used as the oxygen donor, thereby eliminating ether, the standard solvent used for **DAM** solutions. The diazirine **PCD** is synthesized via Graham's method.¹⁷ After purification, it is photolyzed to form **PCC:** in neat urea or solutions containing the oxygen donor.

Despite its triplet ground state, **FI:** generally shows singlet behavior because of the high reactivity of its singlet state and its small singlet-triplet gap (1.1 kcal/mol).¹⁸ LFP studies of **FI:** via the ylide probe method¹⁹ are well described in the literature. In addition, the oxygenation product fluorenone (**FI=O**) is easily detected. Similarly, singlet reactivity dominates the chemistry of :**CH**₂ in condensed phases due to the singlet's high reactivity and relatively slow rate of intersystem crossing to the triplet ground state.²⁰ The singlet carbene **PCC:** has also been extensively studied by LFP both direct and via the ylide probe method.

By adding the PCC: to our study we were able to cover the entire spectrum of carbene reactivity, from a carbene with typical triplet ground state (:CH₂) to one with a small S-T gap and rapid equilibration (Fl:) to one with a known singlet ground state (PCC:). Also, the known behavior of PCC: and Fl: in LFP studies offer the solid foundation needed in exploring a new reaction type such as oxygen atom transfer reaction.

The oxygen donors used here may be classified as: (i) familiar oxygen donors such as pyridine-N-oxide (**PNO**), 4-picoline-N-oxide, N-methyl morpholine-N-oxide (**MNO**) and *cis*- and *trans*-2-butene oxides,⁷ all expected to follow the previously described chemistry in the literature; (ii)'poorer' donors, such as dimethyl carbonate, sulfolane, and trimethyl phosphate, which may undergo the same types of reaction but with slower rates; and (iii) urea-type donors which are expected to generate stable carbenes substituted by amino substituents at the carbenic center.²¹

The idea of generating stable nucleophilic carbenes is the core of our study. Such species are expected to be more thermodynamically stable compared with the starting carbenes that we plan to use, such as :CH₂. We also expect the carbene–to–carbene oxygen atom transfer to be driven by the favorable thermodynamic outcome of the overall process.

2.3. Product Detection

2.3.1 Identification

In dry degassed acetonitrile or benzene, **FI:** is oxygenated by pyridine-N-oxide (**PNO**), 4-picoline-N-oxide, N-methyl morpholine-N-oxide and *cis*- and *trans*-2-butene oxides⁷ to give **FI=O.** Minor byproducts are bifluorenyl, bifluorenylidene, and in some cases, products of reaction with solvent.



Figure 2.2 Fl: reactions with various oxygen donors used

Given the checkered history of the ylide formed from **Fl**: and acetonitrile (see Platz, M. S., ref. 4d, pp. 285-287 and references therein) we explicitly generated this species by photolysis of the corresponding azirine precursor in the presence of **PNO** to verify that **PNO** oxygenation of this ylide could not make the **Fl=O** observed. In any case, subsequent rate studies showed that, in the concentration ranges studied, the acetonitrile ylide formation could not compete with oxygen atom transfer.²² The poorer oxygen donors—dimethyl carbonate, sulfolane, and trimethyl phosphate—gave similar results when used neat. Yields of **Fl=O** were substantial, ranging from 30-90% based on **DAF**.

In the key reaction of our study we consider the stability (see Table 2.1) of diamino³ and dialkoxy carbenes²³ as the driving force to completion of oxygen transfer. We examined tetramethyl urea (TMU), 1,3-dimethylimidazolidin-2-one (DMI), 1,3-ditert-buthylimidazolidin-2-one (DTBI), imidazolidin-2-one (IM) and dimethyl carbonate (DMC) as substrates. Like the more traditional oxidants, they reacted with Fl: to give Fl=O.



Figure 2.3 Fl: reaction with TMU

X:	$\Delta H_{f}(X:)^{a}$	ΔH _f (XO) ^a	BDE ^b	CSE ^c	k _{XO} /k _{MeOH}	k _{XO} (LFP) x 10 ^{-8 d}
¹ :C:	201	-26	286	51		
Fl:	156 ^e	13 ^f	202	9		
¹ H ₂ C:	102	-26	187	0		
F ₂ C:	-45	-153	168	57		
(MeO) ₂ C:	-35 ^g	-139	163	92	1.2±0.2 x 10 ⁻³	0.01
(H2N)2C:	39 ^h	-59	158	79		
(Me ₂ N) ₂ C:	44 ⁱ	-57	160	72	4.9±0.2 x 10 ⁻¹	2.6 (3)
C ₂ H ₄ (NMe) ₂ C:	56 ⁱ	-41	156		5.2±0.2 x 10 ⁻¹	2.8
:CO	-26	-94	127	120		
(MeO)3P:	-167	-265	158		1.4±0.2 x 10 ⁻²	0.8
C4H8SO	-35	-88	113			
Z-2-butene	-2	-30	88			3
E-2-butene	-3	-31	88			9
C5H5N:	33	14	79		1.7±0.4	9 (4.8)
4-MeC5H4N:	25	6	79		1.7±0.4	9

Table 2.1 Thermochemistry of oxygen donors and selected rate constants for their reactions with **Fl**:.

^a Unless otherwise noted, these are ΔHf values at 298 K, from Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G.; "Gas Phase Ion and Neutral Thermochemistry" J. Phys. Chem. Ref. Data, 1988, 17, Suppl. 1.

^b **BDE** = bond dissociation energy; note that ΔH_f for Oxygen is 59.6 kcal/mol at 298K.

^c CSE = carbone stabilization energy, defined as the energy change for the following reaction: :CH₂ + CY₂H₂ ---> CH₄ + :CY₂

^d Griller, D.; Nazran, A. S.; Scaiano, J. C. J. Am. Chem. Soc, 1984, 106, 2128-39.

^e Li, Y.; Schuster, G. B. J. Org. Chem. 1988, 53, 1273; based on a computational estimate, this can not be considered an independent value.

^f Sabbah, R.; Watik, L. E.; Minadakis, C. Comptes Rendus de l'Academie des Sciences de Paris, **1988**, 307, Serie II, 239.

^g Estimated from the PA (234 kcal/mol) calculated at MP3/6-31+G*//HF/6-31G* and the known ΔH_f (97 kcal/mol) of (MeO)₂CH⁺. The MP2/6-31G*//HF/6-31G* + scaled ZPE reaction energies for F₂C: + (MeO)₂C=O --> F₂C=O + (MeO)₂C: and (H₂N)₂C: + (MeO)₂C=O --> (H₂N)₂C=O + (MeO)₂C: give similar results, -31 and -35 kcal/mol respectively. Overall, the agreement between these three independent calculations leads us to discount the -61 kcal/mol value reported in an earlier experimental study (see ref 21).

^h McGibbon, G. A.; Kingsmill, C. A.; Terlouw, J. K. Chem. Phys. Letter , 1994, 22, 129-34.

ⁱ Substituted diaminocarbene ΔH_f values were estimated via experimental values and the MP2/6-31G*//HF/6-31G* + scaled ZPE reaction energies for the oxygen exchange reactions with urea. In a parallel set of experiments, :CH₂ was examined with TMU, DMI and DTBI. In each case the reaction was run in the neat urea and only products from carbene dimerization were detected

Benzoyl chloride is obtained as major product from the reaction of **PCC**: with **TMU** and **DTBI**, by oxygen atom transfer. Quenching the final reaction mixture with MeOH gave methyl benzoate, which was detected via GC-MS spectrometry. The results listed in Table 2.1 implicate the corresponding stabilized carbenes as byproducts in the urea and carbonate deoxygenations.

In the **TMU** deoxygenation studies we tried to trap the diaminocarbene with alkenes such as cyclohexene, dimethylfumarate, acrylonitrile, norbornadiene or chloroacrilonitrile, as shown in Figure 2.4.



Figure 2.4 Carbene trapping reactions

However, our attempts to trap the bis(dimethylamino)-carbene were unsuccessful and the only products found were those from the reaction with **FI:** and/or **DAF.** Such highly stabilized carbenes may not react significantly with simple olefins, preferring to dimerize instead. In contrast, electron-deficient alkenes, which should be most appropriate for trapping nucleophilic carbenes, readily undergo 1,3 dipolar cycloadditions with **DAF**, destroying the carbene precursor and leading ultimately to fluorene-containing cyclopropane products.

 $FI: + \underbrace{Me_2N}_{Me_2N} O \longrightarrow FI=O + \underbrace{Me_2N}_{Me_2N}: \underbrace{H_2O}_{Me_2N} \underbrace{Me_2N}_{H} OH$

Figure 2.5 Carbene trapping with H₂O and CH₃OH

These compounds were not isolated since they were generated in amounts detectable only by GC-MS, and they are hydrolytically sensitive materials which makes their isolation and characterization challenging.

2.3.2 Chemiluminescence experiments

Like dimethoxycarbene,¹⁵ the bis-(dimethylamino)-carbene generated by TMU deoxygenation dimerizes in the absence of traps. The resulting tetrakis(dimethylamino)-ethylene reacts rapidly with O₂ at room temperature to produce TMU (as in our ¹⁸O-TMU synthesis)²¹ and *visible light*. This characteristic chemiluminescence verified the presence of the carbene dimer when air was bubbled through photolyzed samples of DAF in neat TMU inside a fluorimeter cavity.²⁴ Neither photolyzed samples of TMU without DAF, nor unphotolyzed DAF-containing samples showed chemiluminescence. The same analysis demonstrated that :CH₂, generated by photolysis of diazomethane, also abstracts oxygen from TMU.



Figure 2.6 Chemiluminescence setup scheme

This experiments are correlated with detection of ¹⁸O-Fl=O via GC-MS and FTIR (vide infra).

2.3.3. Oxygen isotope (¹⁸O) labeling experiments

To verify that oxygen transfer occurs as we envisioned, we needed to demonstrate the specific transfer of oxygen from the donor to the **FI**: acceptor to yield **FI=O** as a

product. Thus we required a urea oxygen donor, labeled with ¹⁸O. Tetramethyurea proved the most accessible by far. To build the tetramethyl urea structure with the desired isotopic substitution a rather unconventional synthesis was employed²⁵ involving the reaction of ¹⁸O₂ with tetrakis(dimethylamino)ethylene. After distillation and column chromatography, labeled ¹⁸O-TMU was obtained in near quantitative yield; the content of ¹⁸O-TMU in the final product was 95% (determined by GC-MS).



Figure 2.7¹⁸O-labeling experiment

Reaction of **Fl**: with ¹⁸O-labeled **TMU** was conducted, according to the general procedure described in the experimental part, and the products were analyzed by GC-MS.²⁶ The GC retention times were identical with for the labeled and unlabeled **Fl=O** product while the mass and fragmentation pattern showed that the ¹⁸O was incorporated in the product **Fl=O**, confirming that oxygen transfer occurs from the carbonyl substrate to the carbone **Fl**: (see Appendix).

2.4 Rate Studies

Absolute rate constants for the **Fl**: reaction with oxygen donors were measured by LFP using the ylide probe method.¹⁸ The results are listed in Table 2.1. Competition with insertion into methanol O-H bonds allowed additional rate constants to be calculated via the absolute rate constant for **Fl**: quenching with methanol in acetonitrile.²⁷



Figure 2.8 Competition reaction setup for rate studies

Ratios of **Fl=O** to the 9-methoxyfluorene product were determined either by NMR or GC analysis; the resulting rate constants are included in Table 1. Several absolute concentration ratios of oxygen donor to methanol were examined to ensure that the observed product ratios reflected the direct reaction of **Fl:** with the substrates and not indirect pathways to the same product. Table 2.1 shows that rate constants obtained directly by LFP compare reasonably well with those determined in competition experiments; as expected, the reactivities of oxygen donors with **Fl:** track inversely with C=O bond strengths.

Unpublished data, previously obtained in our labs, prove the singlet nature of the O-transfer reactions from closed-shell donors. Diphenyldiazomethane was photolyzed with **PNO** and methanol. As in the case of **Fl**:, the rate constant for oxygen transfer from **PNO** to diphenylcarbene (**DPC**:) is essentially the same as for O-H insertion. Thus, the reactivity of **PNO** parallels that of methanol for both carbenes, even though **DPC**:, with its larger singlet-triplet gap,²⁸ reacts substantially slower than **Fl**:.²⁹ In contrast, **DPC**: reacts at nearly diffusion–controlled rates with open-shell oxygen donors such as 2,2,6,6-tetramethylmorpholine (**TEMPO**) (see Reference 4b).

In addition to the values obtained for FI: (Table 2.1), our rate studies were extended with an LFP study of PCC: abstracting oxygen from PNO and MNO. Absolute rate constants for the reaction of oxygen transfer to PCC: from the two N-oxides were measured by means of UV-LFP and the pyridine ylide method, using the Stern-Volmer analysis (Reference 31). For more details see Appendix.

Bimolecular rate constants of 2.2 x 10⁹ M⁻¹s⁻¹ and of 2.1 x 10⁹ M⁻¹s⁻¹ were obtained for **PCC**: abstracting oxygen atom from **PNO** and **MNO**, respectively. Oxygen abstraction reactions could not be followed in pentane because of the low solubility of the two N–oxides used here as oxygen donors. Also, the rapid formation of the fluorenyl radical by hydrogen atom abstraction from the solvent would strongly compete with oxygen transfer from N-oxide to **FI**: while the absorption band of FI-H will have a chance to overlap with possible short-lived intermediates.

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Figure 2.9 Stern-Volmer quenching plot for the reaction of PCC: + PNO in CH₃CN



Figure 2.10 Stern-Volmer quenching plot for the reaction of PCC: + MNO in CH₃CN

2.5 Mechanism of oxygen transfer reaction

The mechanism responsible for the oxygen abstraction reaction is intriguing when the transfer of a double bonded atom from a carbonyl compound to a carbene is involved. Such a reaction has no precedent in the literature except for the case of carbon atom chemistry. The pathways we considered in our investigation are depicted in Figure 2.11.



Figure 2.11 Possible pathways for oxygen abstraction by carbene

One attractive pathway is the direct formation of the ylide (Reaction 1), which depending on the specific 1,3 disubstitution pattern, may directly cleave to generate carbene 2 and the carbonyl compound (Reaction 2). Such a two step route for oxygen atom transfer from one carbene (1) to another (2) will be dependent upon the stability of the ylide, the barrier for ylide cleavage in Reaction 2, and competition between the opening of the ylide to the more thermodynamically favored carbene 2 *vs.* ylide closing to the corresponding oxirane (Reaction 3). Another possibility is a single step reaction (Reaction 1 + Reaction 2, where the ylide is not a minimum but a transition state, TS) in which, after reaching the corresponding transition state to the ylide, a direct passage to carbene 2 will be found due to its specific 1,3 disubstitution. If carbene 1 directly adds to the carbonyl C=O bond in a [1+2] cycloaddition the first step will be oxirane formation (Reaction 4) followed by C-C oxirane ring opening (Reaction 5) to the ylide. The ylide will cleave to carbene 2 and the second carbonyl compound.

A solid starting point for our analysis is the available literature concerning the mechanisms considered above. Literature data about ylide or oxirane formation and their fate in the cases of :CH₂, Fl: and (PCC:) are presented and are analyzed in connection with our findings.

:CH₂ is the prototype of triplet ground state carbene. Ylide formation in its case should be the result of fast reaction of the singlet before it can equilibrate to the most stable

triplet state. Methylene was found to form a stable ylide with acetonitrile with an absorption maximum at 280 nm.³⁰ The case of the postulated methylene ylide with water is the matter of long-standing controversy. Most of the theoretical studies propose a barrierless process with the intermediate is too short-lived to be experimentally detected. But mass spectrometric techniques used by Wesdemiotis *et al.* found the existence of an intermediate in the gas phase, with the corresponding mass of an H₂C+ OH₂ ylide.³¹ Recent high level theoretical calculations of Wiberg *et al.* describe the ylide as a stable species.³² By contrast, similar high level calculations for the case of dichloromethylene show no evidence for a stable ylide formed from dichlorocarbene, Cl₂C:, and H₂O.³³

:CH₂ is proved to be more reactive toward the C=O bond than to the C-H (α) or C-H(β) of butanone. The relative reactivity was found to be 1:0.08: 0.05.³⁴ Because of the S-T gap of ~9 kcal/mol, the interception of the singlet methylene by the carbonyl compound to form an ylide or oxirane should be faster than the intersystem crossing to its triplet state. High level theoretical calculations for the reaction of Cl₂C: with formaldehyde reveal the ylide as a stable species (calculated as a minimum) with transient character.³⁵ However, the ylide formation was calculated to be 2.5 times slower than direct addition to the C=O bond, which is the dominant process.

The case of :CH₂ and the acetone ylide was investigated experimentally³⁶ by photoacoustic calorimetry. The heat of formation for the ylide is estimated to be 4.5 ± 9.9 kcal/mol for the gas phase and 12.4 ± 10.9 kcal/mol in solution. The same study found the estimated heat of decomposition for the ylide to methylene and acetone to be -45 kcal/mol exothermic. The methylene ylide with formaldehyde is also controversial. The results mentioned above show the thermal cleavage of methylene–acetone ylide as ~45 kcal/mol exothermic and theoretical calculations on methylene and formaldehyde found the cleavage reaction also exothermic by 38 kcal/mol.³⁷ However, a different communication indicates reversible formation of the same methylene-formaldehyde ylide at -78° C because of H/D exchange observed in a system containing :CH₂ and D₂C=O (ref 8a).

With its much smaller S-T gap, **Fl**: presents a different case than :**CH**₂. The literature on **Fl**: indicates a series of ylides detected as short lived transients by LFP.³⁸ The florenylidene ylide with acetonitrile absorbs at 400 nm while those with carbonyl compounds absorb in the region of 620-680 nm.

The case of a carbene with well known singlet ground state, PCC:, is discussed here because of our interest in using this carbene in experimental work. Preliminary experiments in our lab proved qualitatively the possibility of oxygen transfer from urea– type oxygen donors to PCC:. The well established behavior of PCC: in LFP experiments encouraged us to include it in our studies. The experimental detection of ylides from the PCC: reactions with acetone, acetonitrile or ethyl acetate is controversial. Despite their controversial nature, we present here the available data from the literature (vide infra).

Substitution in the para position of the phenyl ring with nitro, chloro or trifluoromethyl groups allows the formation of detectable carbonyl ylides via LFP. ³⁹ Thus, PCC: forms an acetone ylide with λ_{max} at 450 nm (weak) while the *p*-NO₂-PCC: acetone ylide is seen at 590 nm.⁴⁰ In addition, a transient found at 530 nm was attributed to the ylide of PCC: with benzaldehyde.⁴¹ The cyclization of the *p*-NO₂-PCC:O=C(CH₃)₂ adduct was used to explain the appearance of a new absorption at 365 nm, ⁴² attributed to the corresponding oxirane.

Ylides which may be formed in reversible processes have been reported.⁴³ Also, the ylides from biphenylchlorocarbene and ethers are believed to be responsible for the 1,3 dipolar cycloaddition products experimentally obtained.⁴⁴ However, LFP experiments only reveal a 15 nm bathochromic shift in the carbene absorption maximum. A kinetic study on the same arylcarbene system with various concentrations of the ether and monitoring of the carbene absorption allowed determination of the equilibrium constant (Figure 2.13) for the reversible formation of the ylide.

$$\begin{array}{c} A_{F,\dots}\\ C^{\mu} \end{array} \xrightarrow{} K = 0.5 \text{ M}^{-1}, 293 \text{ K} \end{array} \xrightarrow{} \begin{array}{c} A_{F,
} \bigoplus \\ C^{\mu} \bigoplus \end{array}$$

Figure 2.12 Reversible formation of an ylide

Cases in which the carbonyl partner in the formation of an ylide is of urea type are scarcely mentioned in the literature. Of specific interest in our case is an electronically stabilized carbonyl ylide (Figure 2.2.2) formed from tetramethyl urea and tetrakis-(trifluoromethyl)cyclopentadienylidene¹³. This ylide was generated from the corresponding diazocompound of the carbene with TMU in THF and recrystallized from CHCl₃/*n*-pentane as a yellow solid with mp = 190-193 °C.



Figure 2.13 A stable carbonyl ylide

However, this encouraging idea of **TMU**'s capability to form stable ylides with carbenes should be reconsidered with respect to the nature of the carbene. If such stable ylides were formed in our experimental cases with **TMU** and :**CH₂**, **Fl**: or **PCC**:, then the decomposition of the ylide to the diaminocarbene would likely not occur at room temperature. In this respect, a comment by Platz *et al.* ⁴⁵ seems especially important. These authors note that the ylide of cyclopentadienylidene and **TMU** was never detected in their LFP experiments, although several other ylides were generated and observed from cyclopentadieneylidene.

The direct formation of oxiranes from carbenes and carbonyl compounds has been mentioned in literature, ⁴⁶ but it was generally connected with fluorinated or perfluorinated carbenes. Also, the pyrolysis of several perfluoropropylene epoxides around 165° C was found to form exclusively difluorocarbene.⁴⁷

Considering the range of reactivities observed and the uncertainty surrounding processes involving carbenes and their capacity to form ylides, one should not expect the

investigation of a new type of carbene reaction to be an easy task. We have limited our study here to only two modest investigations of the oxygen transfer mechanism. One is the use of theoretical calculations, performed on model systems in order to compare the carbenes' abilities to form ylides *vs.* their known tendency to cycloadd to double bonds and form oxiranes. The other includes experimental investigation by qualitative detection/no detection of transient species, observable by nanosecond LFP. Both sets of results are presented in the following sections.

2.5.1 Theoretical calculations

The interaction of carbenes with carbonyl oxygen atoms was confirmed by our experimental results. The products are a new carbonyl compound and a new carbene. **DAM, DAF** and **DPC** were used as sources for :**CH**₂, **Fl**:, and **PCC**:, respectively, while ureas were the oxygen donors.

Semi empirical and *ab initio* computational methods were used to calculate the results for comparison to the relevant experimental data available. A primary focus of this effort was to understand the thermodynamics involved in the oxygen transfer reaction as a function of carbene stabilization. Exploration of the two possible reaction paths, via oxirane (Reaction 4 in Figure 2.15) or via an ylide intermediate or ylide-like transition state (Reaction 1 and 2 in Figure 2.15) were also key goals. In the case where both paths are available, we looked for the energetically favored path for oxygen atom transfer. It is also possible that both types of intermediates are present on the path that connects them, as shown in Figure 2.15.

In our analysis, we looked at two different types of reactions (Figure 2.15): exchange reactions, where X=Y and cross reactions where X \neq Y. The cases of :CX₂ with X=H, F, NH₂, :C(N(CH₃)₂)₂, FI:, and X₂=CO were studied at the semi-empirical level while the expense of *ab initio* methods limited us to X = H and Y = F, two exchange reactions, :CH₂ + H₂C=O and F₂C: + F₂C=O, and one single cross reaction between

:CH₂ + F₂C=O. An extensive study was carried out on the model reaction CO_2 + :CH₂, and is the subject of Chapter 3.

By following these cases, we hope that our data analysis would allow comparisons among the different carbenes' behaviors and insight into "the" mechanism of oxygen transfer from carbene to carbene. More accurately, each case must be carefully considered with regard to both the nature of the carbene and the oxygen donor.



Figure 2.14 Reaction paths considered by theoretical calculations

2.5.1.1 General considerations

The attack of an electrophilic carbene on a carbonyl-containing partner may occur either at the π bond of the carbonyl moiety or at the lone pair electrons of the oxygen atom. The π (direct) attack leads to formation of an oxirane. The side attack at the lone pair leads to formation of an ylide (Figure 2.15)

If the oxirane is formed initially, its chemistry may involve subsequent C-O or C-C bond cleavage. The C-C bond cleavage leads to an ylide-like configuration, possible an intermediate or only a transition state. Cleavage of the ylide releases a new carbene and the corresponding carbonyl compound. Direct decomposition of oxiranes to ylides and eventually to carbenes and carbonyl compounds was claimed to occur in the case of tetrafluoro ethylene oxide.⁴⁸ There are numerous theoretical studies of oxirane ring opening. ⁴⁹ The existence of the ylide formed in such a way was proved by absorption and emission detection and LPF. ⁵⁰ Detailed, high level calculations for the C-C ring opening of ethylene oxide have also been published.⁵¹ The process is generally described as opening of the oxirane ring to the ylide followed by isomerization of the ylide and its reclosure to the oxirane ring. The isomerization of the ylide was found to be the step with the highest barrier.

Ylide formation is the result of an initial attack on the lone pair of electrons from the oxygen atom. The ylide is usually trapped by 1,3-dipolar cycloaddition reactions. In the absence of a suitable partner for cycloaddition, the ylide itself has two paths for generating a carbene and a carbonyl product: direct decomposition into the new products, and cyclization to the corresponding oxirane.

Special consideration should be given to cases where diazocompounds are used as carbene precursors. In such cases, a cycloadduct of the diazocompound with the carbonyl compound may be formed. It has an oxadiazoline–type of structure and it decomposes, photochemically or thermally, generating N₂ and ylides. The ylides formed through this path are able to decompose with generation of a carbene and a carbonyl compound.⁵² Oxadiazolines' formation and ring opening, however, is not the subject of our investigation.

We describe here a range of molecular orbital calculations run at Semi-Empirical AM1, PM3 and *ab initio* RHF/6-31G* and MP2/6-31G*//MP2-6-31G*⁵³ levels, using Spartan, Mopac⁵⁴ and Gaussian 94⁵⁵ programs. Our goal was to find the differences and similarities among the mechanisms of this reaction and define the method and level of calculations which best fit the requirements for describing such mechanisms. The strategy involved finding (i) possible minima, ylides or oxiranes, (ii) transition states related with these minima, and (iii) paths connecting these two classes of stationary points. Only the ground state potential energy surfaces, PES's, were considered.

2.5.1.2 Results and discussion

Semi-Empirical results

Semi-empirical level calculations were used to evaluate the overall thermodynamic outcome of the oxygen transfer reaction (Δ H_{Reaction}) for **FI**: and **TMU** and the results are presented in Table 2.2. Other carbenes were also considered for the exchange reactions defined in Reaction 1 (Figure 2.15) where X = H, F, NH₂ and X₂ = O. The use of **:CH₂** offers a handle for comparisons with the available experimental and theoretical data. The substituents in the case of X = F and NH₂ should provide information about the role of substituents on the carbenic and carbonyl centers along with the stabilization or destabilization of the possible intermediates by electron donating groups. At the same time F may itself constitute an unpredictable exception.⁵⁶ The case of CO abstraction of oxygen atoms from CO₂ may lead to more complete understanding of CO oxidation and the reactivity of CO₂. Meanwhile, it may prove to be a special case of oxygen atom transfer (see Chapter 3).

Х	E _{Fl:+OCX2}	E _{Compl.}	TS _{to ylide}	ylide	TS _{to oxirane}	Eoxirane
Н	76.4	not found	108.6	89.3	120.0	64.3
F	7.4	1.9	not found	not found	4.8	-33.7
NH ₂	108.5	102.5		73.6	86.8	72.6
N(CH ₃) ₂	129.6	not found	102.8	99.1	113.9	92.6
	E _{:CX2+TMU}	E _{Compl.}	TS _{to ylide}	ylide	TS _{to oxiran}	Eoxirane
Н	65.9	not found	-12.4	-17.5	-2.3	-2.2
F	-112.9	-118.1	-81.5	-155.9	-95.2	-104.9
X2=0	-50.6	-53.2	not found	not found	13.7	-64.2

Table 2.2 PM3 Calculated energies for **Fl**: $+ O=CX_2 \rightarrow Fl=O+:CX_2$ and for $X_2C: +TMU \rightarrow X_2C=O +:C[N(CH_3)]_2$ reactions

As expected, in all cases considered, the oxygen transfer reaction is calculated to be exothermic. For the experimental case of **Fl: + TMU** the oxygen transfer is calculated to be 55.4 kcal/mol exothermic. However, barriers were also computed in all the cases.



Figure 2.15 PM3 calculation for TMU and Fl: oxygen transfer reaction

Our semiempirical results describe the reaction of $:CH_2$ with CH₂O (the case of X = H) with no complex formed between the reactants. A direct path leads to a planar ylide. The ylide cyclizes to oxirane. No direct path to oxirane was found. For the case of CF₂O + $:CF_2$, X=F, one possible pathway leads to oxirane via a high TS. Another path was found direct toward the formation of an ylide. The ylide is less stable than the oxirane but its formation requires less energy than the formation of the corresponding oxirane. In Figure 2.16 below, the energies are plotted with respect to the reaction coordinate. X= (NH₂)₂, (NH₂)₂CO + $:C(NH_2)_2$ a similar behavior as in the case of X = F was found. There are two possible pathways for the oxygen transfer reaction, one through an ylide-like structure, the other through an oxirane one, with similar appearance as in the case of X = F. Carbon monoxide (the case of X₂ = O), with its singlet ground state, was included here because of its analogy to a singlet carbene. The :CO+CO₂ reaction only follows the pathway through an oxirane structure via a defined transition state. A special type of intermediate was found with a four-membered cyclic structure. IRC proved that such a pathway is not related with

oxygen transfer. For these reasons, we concluded that the analogy between a singlet carbene and CO will not give useful informations about the mechanism investigated here and no further analysis was performed on this system. Even though the system is of no interest for the cases investigated here. The CO–to–CO₂ reaction remain an unexplored theoretical model and experimental challenge.

Two possible reaction pathways on the , one through an ylide-like intermediate with a slightly lower activation energy (TS), and another one through an oxirane were found. In the case of $:CF_2$ and $:C(NH_2)_2$ the pathway following the ylide-like structure presents a lower barrier than the one via an oxirane intermediate despite the higher energy of an ylide *vs.* an oxirane intermediate. IRC calculations performed at the AM1 and PM3 levels show no relation between the two paths, implying that there is no pathway on the reaction PES from ylide to oxirane or vice versa.



Figure 2.16 PM3 IRC calculation at for degenerate reaction, X=F and $X = NH_2$

Even though the ylide, when found, is less stable than the corresponding oxirane, the activation energy required to generate the ylide is much smaller than is needed for the oxirane to cleave to carbene (see Table 2.3).

X,X	E_a to ylide E_a to oxirane ΔE_a				
Н	no ylide	-33.2			
F,F	16.5	25.8	9.3		
H ₂ N,NH ₂	36.3	47.7	10.5		
=0	no ylide	49.6			

Table 2.3 ΔE_a (kcal/mol) for the exchange reactions

For the cross reaction $F_2C=O + :CH_2$ the ylide path require less energy despite the

fact that the ylide is calculated to be less stable (Figure 2.17).



Figure 2.17 PM3 PES of cross reaction F₂C=O + :CH₂

Ab initio results

MO *ab initio* calculations were performed at the HF/6-31G* level for optimization, vibrational analysis and IRC. Single point calculation and occasionally, geometry optimization and vibrational analysis were run also at MP2/6-31G*. The energy data obtained for the stationary points and the corresponding transition states are presented in Table 2.6 and 2.7 as differences, in kcal/mol.

The case of the methylene and formaldehyde exchange reaction presents the same general patterns here as found at PM3 level.

 $H_2C=O + :CH_2 ---> H_2C: + O=CH_2 \qquad \Delta H_{exp/calc} = 0 \text{ kcal/mol}$

Initial attack at the oxygen lone pair leads, via a complex, directly to a planar ylide intermediate. The ylide evolves into the oxirane via a TS.


Figure 2.18 PES of exchange reaction H₂C=O + :CH₂

Discrepancies between the results at the HF and MP2 levels were not surprising as long as HF level calculations is generally provide poor descriptions of cases like the one under discussion here.⁵⁷ HF/6-31G* IRC calculations confirm the connection of the starting species with the oxirane via $TS_{complex to ylide}$. However, single point calculations at the MP2 or MP4/6-31G* level starting with HF geometries as well as full optimization at the MP2/6-31G* found no barrier on the path from H₂C=O + :CH₂ to ylide. The barrier for C-C cleavage is calculated to be extremely high ~ 82 kcal/mol. A direct one step path through a possible ylide-like TS was found only at HF, over a barrier of 15.5 kcal/mol. A similar structure could not be found at higher level of calculations

Two possible mechanisms were found for the reaction with X = F:

 $F_2C=O + :CF_2 ---> F_2C: + O=CF_2$ $\Delta Hexp/calc = 0 \text{ kcal/mol}$

Initial attack at the oxygen lone pair leads to a complex ~2 kcal/mol lower in energy than the starting species. Two different pathways were found for the attack of **:**CF₂ on the carbonyl compound. One is a two-step pathway through an oxirane intermediate, with Ea = 23 kcal/mol at the HF level (TS _{complex to oxirane}) and 10 kcal/mol at MP2 level. The other pathway, found only at the HF level, is described as an one-step oxygen transfer via an ylide-like TS (TS _{complex to ylide}), with Ea = ~86 kcal/mol. IRC calculations confirm the evolution of the reaction in one step, with an overall transfer of an oxygen atom from one molecule of **:**CF₂ to another. The HF level of calculations does not lead to an ylide as a minimum on the PES. However, while searching for the corresponding TS of the one-step reaction at the MP2 level, a minimum was found (with a geometry close to the ylide-like TS found at HF), 34 kcal/mol higher in energy than the starting F₂C: + O=CF₂ (Figure 2.20).⁵⁸

	HF	MP2
$(H_2N)_2CO + :C(H_2N)_2$	0.0	0.0
Ylide	+26.6	
Oxirane	+5.6	+13.3
vdW complex	-9.5	-11.9
TS through ylide	+33.6	+88.5
TS through oxirane	+29.9	+79.2
CO ₂ +CO	0.0	0.0
vdW complex	-0.4	-0.6
Oxirane	+49.9	+74.8
TS through oxirane	+53.2	+80.2

Table 2.4 Ab initio calculated energy differences for exchange reactions

As for the case of X = F, calculations were run only at the HF/6-31G* and MP2/6-31G*//HF/6-31G* levels for urea-type of oxygen atom donors, where $X = NH_2$. The energy difference values for $X=NH_2$ and $X_2=O$ are summarized in Table 2.4. A full optimization on the structure of TMU-formaldehyde ylide run at MP2/6-31G* found such an ylide a minimum. This result, even though it may not be interpreted in terms of the barriers on the PES, indicates that ylides may be short-lived intermediates in the carbene oxygen atom abstraction reaction.



Figure 2.19 PES of exchange reaction F₂C=O + :CF₂

For the case of cross reaction, $F_2C=O + :CH_2 ---> F_2C: + O=CH_2$ $\Delta H_{exp} = -20$ kcal/mol, $\Delta H_{calc} = -25$ kcal/mol, initial attack at the oxygen lone pair leads to a complex, ~6 kcal/mol lower in energy than the starting species. From the complex the reaction follow the path which leads to an oxirane intermediate through a transition state, TS1 which we were unable to locate. In a following step, oxirane evolves via TS2 to a new complex 6 kcal/mol lower in energy than the products. Finding such a complex indicates a possible significant interaction between the formaldehyde oxygen atom and the empty π orbital of the singlet :CF₂. The transition state for the oxirane ring opening is calculated to be ~ 50 kcal/mol higher in energy than the difluorooxirane but ~26 kcal/mol below the energy of $F_2C=O + :CH_2$.



Figure 2.20 PES of cross reaction F₂C=O + :CH₂

Table 2.5 Calcula	ted ab initio er	nergy diffen	rences for	$X_2CO + C$	X ₂ exchange an	d cross reaction	ons (X=H, F)		
	HF/6-31G*	HF+ZP	MP2/HF	MP4/HF	MP2/6-31G*	MP2+ZPE	MP4/MP2	G2	Exp
		ц							
H ₂ CO + :CH ₂ (reagents)									
complex	-10.7	-3.95	-14.15	-13.44	-20.19	-8.13	-18.4		
ylidē	-11.48	-3.13	-50.40	-44.81	-53.38	-40.80	-48.42		
oxirane	-82.47	-71.27	-102.9	-96.32	-104.02	-88.70	-97.68		
TS one-step	7.94	15.51			-20.18	-8.17			
TS compl-to-vlide	-5.41	2.20	-22.49	-20.62					
TS ylide-to-oxirane	4.09	10.50	-8.29	-7.17	-11.52	-0.30	-10.31		
AH rescents to ovirane	-82.47	-71.27	-102.9	-96.32	-104.02	-88.77	-97.42	-85.1	-88.6
F ₂ CO + :CF ₂ (reagents)									
complex	-1.51		-2.20	-2.18	-2.51	-2.46	-2.7		
vlide					31.06	34.22			
oxirane	-15.76		-27.44	-23.59	-27.11		-22.94		
TS compl-to-vlide	87.47	85.95	32.41	32.46					
TS compl-to-oxirane	21.63	23.09	5.11	4.29	9.41	10.65	9.7		
AH reacgents-to-oxirane									
									i
F2CU + :CH2 (reagents)	7 C C		202						10-
comprexi	(0. 1	00.2-	0.0-	02 21	01 10		LV C0		
	-04.72	5 22	70.10-	10.00-	01.10-		14.70-		
I S ox-to-compl2	0.12	C7.C	00.02-	06.02-					
IS one-step	20.03	31.70	CI.77-	-20.33	-28.21	-21.9/	-21.83		
complexZ	-27.63		-40.02	-41.06	-36.82	-33.68	-40.89		
H ₂ CO + :CF ₂ (products)	-22.98	-22.79	-37.47	-38.90	-35.48	-39.89	-36.78		-71
AH reagents-to-products	-22.98	-22.79	-37.47	-38.90	-35.48	-39.89	-36.78	-30.1	-20

2.5.1.5 Exploring the ability of Marcus Theory to predict the oxygen transfer barrier

Marcus theory was first applied to electron transfer and, later on, to protons or other atom or group transfers. We explore here the possibility of applying Marcus theory to the (gas-phase) carbene–to–carbene oxygen atom transfer reactions.

In the simplest kind of atom transfer, the reaction coordinate involves a concerted motion forming one bond and stretching the other.

 $X-A + X \longrightarrow X - --A - ---X \longrightarrow X + A-X \text{ exchange reaction 11}$ $Y-A + Y \longrightarrow Y - ---A - ---Y \longrightarrow Y + A-Y \text{ exchange reaction 22}$ $X-A + Y \longrightarrow X - ---A - ---Y \longrightarrow X + A-Y \text{ cross reaction 12}$

When the bond breaking-bond forming process is the principal contributor to the reaction coordinate, the equation below can be used to relate the barrier of a cross reaction to those of exchange reactions:

$$E_{12} = E(1 + \Delta E^{0}/4E)$$
 eq 2.5.1

where: E_{12} = the barrier of cross reaction

 $E=(E_{11}+E_{22})/2$ where E_{11} , $E_{22}=$ barriers of exchange reactions

 ΔE^0 = the potential energy change in the cross reaction

Thus, Marcus theory offers a way to predict the activation energy of degenerate exchange reactions. We sought to check the predicted values against those found by exploration of the reaction potential energy surfaces.

A series of oxygen transfer reactions involving carbenes with the general structure X_2C ;, where X=H, F, Cl, Br, and I were investigated. Because of the heavy atoms involved and the computer time required, the calculations were performed only at the PM3 semiempirical level. As detailed above, the two possible paths, through oxirane and ylide-like intermediate were found in all cases.



Figure 2.21 Generic reactions used for Marcus theory applications

Comparison of the computed (Appendix 1) energies with those obtained using Marcus theory are in fairly good agreement. Our results, calculated PM3 semi-empirical level are listed in Table 2.7 as differences in energy, in kcal/mol. For easier interpretation of Table 2.7 the relative energies of carbene involved along with the energies of the corresponding carbonyl compound are included in the last two column of the table. The last column in Table 2.7 contains the difference between the calculated at Semi-Empirical and calculated values using Marcus' theory. The range of differences is very broad, from 23.6 kcal/mol for X = F, Y = Br to only 3.1 kcal/mol for the case of X = H, Y = F. The fact that for X=H and Y=F, the difference is only 3.1 kcal/mol as it is in the case of X = Br, Y = I, may be only the cancellation of error effect rather than a better description of the theory applied.

Only with this data in hand is difficult to predict the capacity of Marcus theory to elucidate the barriers in the oxygen atom transfer. First, the level of calculations used, PM3, may give only a qualitative picture of the ranges of energies involved. more detailed ab initio data will be required to conclude about the possibility of Marcus's theory applicability on the oxygen atom transfer.

Tab	le 2.5	TS analysis by	use of Marcu	is theory for o	xygen transfer	· via ylide path				
X	Y	ΔEpot	TSylid CX	20+ CY2	Exy Calc.	$(E_{xx}+E_{yy})/2$	E _{xy} Marcus	Ecalc-Emarcus	ΔHf ^a	γHfb
									:CX ₂	0=CX ₂
H	Н		46.1	79.4	-33.34				0.0	0.0
ц	ц		-182.4	-208.7	26.26				-178.1	-110
บ	บ		16.4	8.4	8.07				-53.4	-17.6
Br	Br		79.9	79.6	0.27				-6.0	6.1
Ι	I		131.6	120.1	11.49				10.7	30.0
Η	ц	68.1	-82.1	-98.7	16.579	-3.54	13.485	3.094		
Η	Ū	35.9	31.4	25.9	5.4	-12.635	-3.6675	9.0675		
Η	Br	12.1	53.5	73.4	-19.93	-16.535	-13.5025	-6.4275		
Η	Ι	19.4	94.5	90.1	4.38	-10.925	-6.08	10.46		
щ	บ	-32.2	-91.4	-84.1	-7.33	17.165	9.115	-16.445		
ц	Br	-56	-60.9	-36.6	-24.314	13.265	-0.7275	-23.5865		
ц	Ι	-48.7	-25.1	-19.9	-5.204	18.875	6.695	-11.899		
บ	Br	23.8	4	55.7	-6.87	4.17	10.1075	-16.9775		
บ	Π	-16.5	86.4	72.5	13.92	9.78	5.6575	8.2625		
Br	I	7.2	108.8	96.2	12.59	5.88	7.6825	4.9075		
a Re	lative to	o :CH2 heat of for	mation, conside	ered zero. Absolu	ute calculated en	ergies as follows: :(CH2, 0 (79.4); C	F2, -178.1 (-98.7);	CCl ₂ , -53.4	(26.0); CBr2

•

-6.0 (73.4); CI2, 10.7 (90.1).

b Relative to O=CH2 heat of formation, considered zero. Absolute calculated energies as follows: CH2O, 0, (90.1), CF2O, -110 (-19.9); CCl2O, -17, 6 (72.5); CBr2O, 6.1 (96.2); CI2O, 30.0 (20.1).

2.5.1.5 Summary and Conclusions of Theoretical Results

From the calculations presented here it appears that semiempirical results provide a reasonable estimate of the heat of reaction and in many cases a qualitative picture of the overall mechanism of carbene-to-carbene oxygen atom transfer. The findings are similar to the *ab initio* data, but in some of the cases, an ylide described as a minimum at the PM3 level becomes a TS at *ab initio*.

Our calculated data suggest general characteristics for the oxygen transfer reaction mechanism:

(i) on the singlet PES, the attack of the carbene on the lone pair of the carbonyl oxygen predominates (except for the F_2CO case).

(ii) oxirane intermediates are located in deep wells on the PES. However, C-C bond closure requires, in general, traversal of high energy barriers.

(iii) at the level of calculation used here, one-step mechanisms, via ylide-like TSs, present barriers comparable or higher then those via oxirane.

(iv) when the thermodynamics of the reaction is favorable, a direct path for oxygen transfer from carbene-to-carbene via an ylide intermediate or TS, with no oxirane intermediate involved, may be preferred.

As a general conclusion, the oxygen transfer seems as expected to be, heavily dependent upon the substituents present at the carbenic center. High levels of theory will likely be required to fully describe the systems under investigation. Our initial survey results, however, indicate that the oxygen atom transfer from a carbonyl compound to carbene is most likely to occur via a transient ylide intermediate. If such a path is available the intermediacy of an oxirane is unlikely. 15.2. (inc mm (. XIII. 1877 ω. D יה אם stidy धावतं; nie r ino:1 الله (acio SIT: pulse densi of th <u>b</u>ubb . ΣΩΠ£ ^{follo} :01) 1 len . liple Nels

2.5.2. Laser Flash Photolysis results

Carbenes form ylides when interacting with carbonyl compounds⁵⁹ and abstract oxygen from CO₂.⁶⁰ Methylene and fluorenylidene abstract oxygen from ureas leading to formaldehyde or fluorenone, respectively.⁶¹

Carbonyl ylides, generated by decomposition of oxadiazolines⁶² or by photolytic or thermal C-C cleavage of oxiranes⁶³ lead, in some cases, to carbenes and carbonyl compounds. In order to experimentally probe the question of the possible intermediates in the oxygen abstraction reaction by carbene, we undertook a laser flash photolysis (LFP) study . ⁶⁴

LFP studies of **PCD** and diazoflorene **DAF** are reported. These compounds, upon irradiation, afford phenylchlorocarbene **PCC**: and fluorenylidene **Fl**:. In addition to our rate measurements (vide supra) we include here LFP experiments for detection of possible short-lived intermediates in the reaction of **Fl**: or **PCC**: with ureas as oxygen donors. Qualitative data about the presence of transient species in the LFP of **Fl**: and **PCC**: in acetonitrile and pentane in the presence of oxygen donor were obtained. A laser setup similar to the one used for rate studies was used here (Nd-YAG laser, 355 nm, 10 ns pulse, 10 mJ). Stock solutions of precursors in acetonitrile and pentane, with a optical density of 0.3 to 0.7 at the irradiation wavelength (355 nm), were prepared. A large excess of the oxygen donor was added and each sample was homogenized and degassed with bubbling Ar for 10 to 15 min.

Control experiments were conducted by irradiation of **PCD** or **DAF** alone in the same solvents to verify the correlation with the available data from the literature. The following ureas were used as oxygen donors: **TMU**, **DMI**, **IM**, and **DTBI**. These compounds also were irradiated alone under the experimental conditions to confirm that no new absorptions were seen. For **FI**: in acetonitrile, the known transient absorptions of triplet **FI**:, at 470 nm, the FIH radical at 500 nm, and the acetonitrile-**FI**: ylide at 400 nm were identified when no urea was present in the photolyzed mixture. Irradiation of **PCD**

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afforded the known transient absorption of **PCC**: at 318 nm with no interference from any other transient.²⁷

In Figure 2.25 and Figure 2.26 the transient absorptions obtained for both **FI:** and **PCC:** are presented. The experiments shown evidence for an intermediate for both **PCC:** and for **FI:**. None of the known absorptions, usually present in the LFP of these two carbenes, matches the new features. Considering that the control experiments showed no additional absorptions than those characteristic for each carbene in the given solvent, the new absorptions have to be the result of processes involving the carbene, **PCC:** or **FI:**, and the oxygen donor, **TMU**, **DMI**, **IM** or **DTBI**.

Considering the possible mechanisms depicted in Figure 2.14, the new absorptions may be attributed to ylide or oxirane intermediates, to the newly generated carbenes or to a combination of these and the known ylide formed by the carbene and the solvent. Since the available literature data correlates with our calculated pathways for the oxygen atom transfer, we believe that the transient absorption in the LFP of our analyzed systems may belong either to a short-lived ylide intermediate or to the main product of the oxygen transfer reaction, the diaminocarbene.

Even though the literature of the last two years abounds in data about new diaminocarbenes with many crystal structures reported, we found no information about their UV-VIS spectra. Table 2.8 lists the literature for the UV-VIS absorption of some carbenes which may be compared with our case.

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	λ_{max} (nm)	
¹ :CH ₂	550-950	gas phase ^a
:CHF	430-600	gas phase ^b
:CHCl	550-820	gas phase ^c
:CF ₂	220-270	matrix ^d
:CCl ₂	480-560	matrix ^e
:CFCl	360-390	gas phase ^f
Ň	360	MeTHF gass ^g
:CCl(OMe)	318	matrix ^h
:CPh(OMe)	290	hexane, -10 °C ⁱ
:C(OMe) ₂	255	matrix ^j
:CF(OMe)	240-280	matrix ^k

Table 2.7. UV-VIS absorption of carbenes

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wavelenght/nm

Figure 2.22 LPF transient absorptions observed for Fl: + oxygen donors











In the case of **PCC:**, a strong new absorption band is easily noticed in the case of **DTBI** + **PCC:**, with $\lambda_{max} = 380-410$ nm. However, the observation of analogous absorptions for **TMU**, **DMI** and **IM** is hampered by the remnant signal from the 350 nm laser pulse and the residual absorption from the carbene itself. In the **FI:** case, as may be noticed from the transient absorption spectra, the presence of the oxygen donor in a photolyzed sample of **FI:** in acetonitrile gives rise to a previously unnoticed broad absorption, with a maximum at $\lambda = 390-450$ nm. The position and intensity of this new absorption change with the urea donors. However, because of the broadness of the band and its overlap with the absorptions of fluorenyl radical ($\lambda_{max} = 500$ nm) and the **FI:** - acetonitrile ylide ($\lambda_{max} = 400$ nm) it is hard to define quantitatively the amount of changes with respect to the ureas used.

These qualitative results show that a new transient species is formed in the oxygen transfer reaction, detectable on the timescale of our LFP experiments. The existence of such a transient, whether it is intermediate or product, may allow direct measurements of rate constants. We are inclined to attribute these absorptions to the newly formed carbene rather than to the possible ylide. With no available data in the literature, however further investigations and different approaches are necessary in order to confirm our assumption.

2.6 Experimental

<u>General methods</u>. Melting points were determined on a Thomas Hoover capillary apparatus and are uncorrected. Fourier-transform infrared (IR) spectra were recorded on a Mattson-Galaxy FT-IR 3020 or Nicolet IR/42 spectrometers. Samples were measured either as thin layers prepared by evaporating a CH₃CN solution on a NaCl plate (liquids) or as KBr pellets(solids). Electron impact (EI) mass spectra were obtained on a Fission VG trio-1 mass spectrometer which operates in line with a Helwett Packard 5890 gas chromatograph for GC-MS measurements.

Routine ¹H and ¹³C NMR spectra were obtained at 300 and 75.43 MHz respectively using either a Varian VXR-300 Spectrometer or a Varian GEMINI 300 NMR Spectrometer. The ¹H NMR chemical shifts are referenced to the ¹H resonance in CDCl₃ (7.24) and acetonitrile-d3 (1.93). The ¹³C chemical shifts are referenced to CDCl₃ (77.0) or acetonitrile-d3 (broad 118.0 and 1.3 septet).

Solvents were purchased from Aldrich and dried and deoxygenated by standard procedures (see Vogel in Reference 66). Gravity and flash column chromatography were performed on E. Merck silica gel (230–400 mesh). Thin-layer chromatography was done on E. Merck plastic-backed plates silica gel 60, F245, 0.2 mm. High resolution mass spectra analysis were carried out on a JEOL JMS-HX110 high resolution double-focusing mass spectrometer.

General procedure

Literature procedures were followed for DAF⁶⁵, DAM⁶⁶ and PCC:¹⁷ synthesis. DAF was recrystallized from pentane. DAM was collected directly in neat oxygen donor. PCD was purified either by distillation or by column chromatography (Reference 17) The physical and spectroscopic data of the carbenes precursors listed above were in agreement with those reported in literature.

General procedure for irradiation: 1 to 2 mL solution of carbene precursor (3 to 5 x 10^{-3} M) in dry acetonitrile was prepared and placed in a standard NMR tube (1 cm x 10 cm). After being purged with dry nitrogen gas for 15 mins, the solution was irradiated for 1 h with a 500W high pressure mercury lamp shielded with a uranium glass filter. The nitrogen purge was continued throughout the process of irradiation. After removal of solvent, the mixture was separated by flash chromatography over silica gel. Same

procedure was used for the case of neat oxygen donor experiments when samples of 1 to 2 mL solutions of carbene precursors in neat oxygen donor were used. The samples were deoxygenated by purging with nitrogen for 10 to 20 min. before irradiation. The carbenes were generated in the reaction mixture by irradiation with light from a 500 W Oriel high-pressure Hg lamp, through an uranium glass filter. Reagents consumption was followed in all the cases by ¹H and ¹³C NMR. GC-MS spectra were taken for the initial reaction mixture and exactly the same conditions were applied at the end of the reaction time to detect the final mixture composition.

¹⁸O-TMU was prepared from tetrakis(dimethylamino)ethylene (TDMAE) purchased from Aldrich by reaction with molecular ¹⁸O₂. 2.1 mL. (0.0073 mol) TDMAE was placed in a round bottom flask and attached to the vacuum line. 74 mL ¹⁸O₂ was added to the flask via vacuum line by heating-cooling cycles, in three portions. The reaction flask was kept under stirring at the vacuum line for 3 hours, after which time the visible chemiluminiscence vanished. The crude product was separated by column chromatography with a solution of isopropanol : acetone in a 3:2 ratio. ¹⁸O-TMU was obtained with a 93.1 % yield and a content of 98% ¹⁸O by GC-MS. The IR taken on NaCl pellets shows v_{C=O}18 shifted to smaller wavenumbers, at 1626, compared with v_{C=O}16 at 1658.

 $Fl=O^{18}$ was prepared by irradiating a solution of 5.3 mg of DAF and 0.1 mL of TMU in 0.8 mL deuterated acetonitrile degassed by 5 freeze-pump-thaw cycles. After the irradiation, the crude reaction mixture was separated by column chromatography, using a mixture of hexane : methylene chloride, 5:1 and was analyzed by GC-MS.

2.7 Conclusions

Carbene-to-carbene oxygen atom transfer has been demonstrated by isotopic labeling and by observation of products from the newly generated carbene. Dimers of the newly generated carbene byproduct have been detected by chemiluminescence. Rate constants for oxygen abstraction by **FI:** from various donors, including ureas, have been determined. Whether these highly exothermic oxygen transfers occur in a single step or via the intermediacy of ylide or oxirane intermediates are questions that we address by theoretical and experimental (LFP) means. Qualitative LFP transient absorption suggests the presence of new species. We tentatively suggest that the new species is the diaminocarbene formed as a result of the oxygen atom transfer. However, the possibility of an ylide intermediate which may absorb in the same region is not excluded. Our initial studies indicate that LFP will be a valuable tool in rate studies of oxygen transfer reaction. Theoretical calculations describe detailed *ab initio* molecular orbital studies of the remarkably convoluted potential energy surfaces for carbene-to-carbene oxygen transfer reactions. The degenerate and cross reactions present the same pattern: the possibility of two competing paths, through an ylide-like intermediate or transition state and through an oxirane. For the cases of : CF_2 and : $C(NH_2)_2$, *ab initio* calculations find the ylide-type structure to be a TS for oxygen atom transfer, rather than a stable intermediate.

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CHAPTER 3:

A Theoretical Investigation of Double Bonded Oxygen Atom Abstraction on a Model Reaction: CH₂ + CO₂ ---> CH₂O + CO

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Abstract:

Ab initio G2 calculated pathways are presented for the reaction $CH_2 + CO_2 --->$ $CH_2O + CO$, in which net transfer of a double bonded oxygen atom occurs from CO_2 to the carbene. Of particular interest are the electronic state of the attacking methylene, the structure of the possible intermediates and the lowest energy path(s) available for this reaction. As expected, our results support the assignment of α -lactone 1 as the intermediate observed by IR in the matrix isolation experiments of Milligan and Jacox (Reference 4); analogous reactions involving substituted carbenes have more recently been reported by Sander *et al.* We obtain $\Delta H_f(1) = -43.7$ kcal/mol at the G2 level while a variety of isodesmic reactions point to slightly higher values (-40 to -42 kcal/mol). Acyclic •CH₂O(CO)• (methylen-oxycarbonyl) and •CH₂CO₂• (acetoxyl) biradicals 2 and 3, respectively, were also considered on both singlet and triplet potential energy surfaces.

According to the calculations, the singlet reaction proceeds with little or no barrier to form 1; subsequent ring fragmentation ($\Delta H^{\ddagger} = 27.4$ kcal/mol) yields the products,

CH₂O + CO. Collision orientation must play a role, however; Wagner *et al.* have reported that reaction is only half as fast as collisional deactivation of ¹:CH₂ to ³:CH₂ which presumably occurs via nonproductive encounter geometries. An activated channel (Δ H[‡] = 24.5 kcal/mol) was also located in which ¹:CH₂ directly abstracts oxygen from CO₂ via an ylide–like TS, ¹2. The lowest energy ³:CH₂ + CO₂ attack forms the triplet acetoxyl diradical ³3 and a higher energy path leads to methylene–oxycarbonyl diradical ³2; no path for isomerization of ³3 to ³2 was found. Barriers for these two processes are Δ H[‡] = 20.1 kcal/mol and Δ H[‡] = 58.9 kcal/mol.

Attempts to locate regions on the triplet approach surface where the singlet crosses to become the lower energy spin state were complicated by the difficulty of optimizing geometries within the composite G2 model. Preliminary efforts however, indicate that such crossings occur at geometries higher in energy than separated ¹:CH₂ + CO_2 , suggesting that their role should be relatively unimportant in the chemistry of this reaction.
3.1 Introduction

We present here a mechanistic analysis of the gas phase reaction of methylene, :CH₂, with carbon dioxide, CO_2 .¹

 $CO_2 + :CH_2 \longrightarrow CO + O=CH_2$ (Reaction 1)

This reaction represents the first reported abstraction of a double bonded oxygen atom by a carbene. Our own recent studies of oxygen transfer from carbonyl compounds to carbenes² focused our attention on the mechanism of such processes and led us to the present computational effort. Of particular interest is the potential existence and the electronic nature of a single-step "pluck" reaction³ in which pairs of bonds are simultaneously broken and formed. The results also shed light on recent suggestions of ylide formation, H₂C:⁻⁻⁻⁺O=C=O.

3.2 Background

Reaction 1 was first observed in 1958 when Kistiakowsky *et al.*, studying the reaction of methylene generated from ketene, noted excess CO production when CO₂ was used as an "inert" buffer gas. They proposed that the attack of triplet methylene on CO₂ forms an intermediate, α -lactone (1), which decomposes to formaldehyde and CO.



Figure 3.1 Potential intermediates in the : $CH_2 + CO_2$ reaction

A few years later, in 1962, Milligan and Jacox⁴ photolyzed diazomethane in a CO_2 matrix, at *ca*. 50 K. Monitoring the methylene generated in the matrix, the authors observed the appearance of a species whose IR absorption bands grow as those from the initially generated :CH₂ decrease. The new IR spectrum shows a carbonyl stretch shifted toward higher frequencies, over 1900 cm^{-1.5} The species was tentatively assigned as the α -lactone **1** in which the carbonyl stretch is shifted due to the ring strain, but the possibility of acyclic diradical intermediates such as ³2 or ³3 was not ruled out.

In 1977, almost two decades after Kistiakowski's initial experiment, Laufer and Bass⁶ studied the kinetics of reaction 1 by flash photolysis with CH_2N_2 and CH_2CO as methylene precursors. The rate constant obtained for reaction 1 was 3.3 x 10^{-14} cm³molecule⁻¹s⁻¹, based on known values for triplet methylene dimerization (k = 5.3 x 10^{-11} cm³molecule⁻¹s⁻¹) and reaction with acetylene (k = 7.5 x 10^{-12} cm³molecule⁻¹s⁻¹). Although the latter rate constant has since been revised,⁷ Laufer's results correctly describe a slow reaction between methylene and CO₂.

In the same year, Hsu and Lin⁸ determined the vibrational energy of the carbon monoxide released from reaction 1, monitoring its production with a continuous wave CO laser. Methylene was generated by photolysis of CH₂I₂ ($\lambda > 210$ nm). The vibrational state population of CO produced was found to be close to that predicted by statistical calculations, assuming a long lived CH₂CO₂ intermediate,⁹ and a total final vibrational energy of 63 kcal/mol, the exothermicity of the reaction. Such an assumption minimizes contributions from reactions slower than reaction 1. The authors found that CO is vibrationally excited up to v = 4, carrying an average of 1.9 kcal/mol. By extrapolation to earlier reported reaction rates the authors assigned the singlet electronic state to the reacting methylene but cited Laufer's then unpublished work, indicating that triplet methylene might be also responsible for some oxygen abstraction.

Sophisticated new techniques allowed Wagner *et al.*¹⁰ in 1990, to perform detailed kinetic measurements on reaction 1. Methylene, generated by laser photolysis of

ketene, was observed by laser induced fluorescence (${}^{1}CH_{2}$) and laser magnetic resonance (${}^{3}CH_{2}$) allowing quantitative evaluation of intersystem crossing (ISC). The authors found that roughly 2/3 of ${}^{1}:CH_{2} + CO_{2}$ collisions relax ${}^{1}:CH_{2}$ to ${}^{3}:CH_{2}$; for the remaining 1/3, three exothermic reaction channels were considered: formation of OCH-CHO (glyoxal), $H_{2} + 2CO$, or $H_{2}CO + CO$. Preliminary experiments in Wagner's lab showed that ${}^{3}:CH_{2} + CO_{2}$ react very slowly even at higher temperatures¹¹ and the products may be only the result of collisional activation of ${}^{3}:CH_{2}$ to ${}^{1}:CH_{2}$ which then reacts rapidly with CO₂. Wagner concluded that formaldehyde and CO are "the probable chemical products", and that α -lactone is a "plausible intermediate".

Based on DeMore's observation¹² that diphenyldiazomethane photolysis in the presence of O₂ generates benzophenone, Sander¹³ investigated :CPh₂ as an "oxygen abstractor" from CO₂ doped into Ar or Xe matrices. The observed intermediate has a high frequency carbonyl stretch (1890 cm⁻¹) and fragments, on UV irradiation ($\lambda > 220$ nm), to Ph₂CO and CO. The intermediate is assigned as diphenyloxiranone **4**. The spin forbidden reaction of the ground state triplet :CPh₂ with CO₂ to form **4** shows a thermal barrier, occurring only when the matrix is annealed to 35 K.¹⁴ Photoexcited :CPh₂, however, reacts rapidly above 10 K to yield the same products, perhaps due to the availability of a low lying empty p orbital as in the singlet case. No direct evidence was obtained for diradical or zwitterionic intermediates such as **5** or **6**, the diphenyl analogs of **2** or **3**.



Figure 3.2 Potential intermediates in the : $CPh_2 + CO_2$ reaction

To clarify the carbene characteristics responsible for oxygen abstraction, Sander *et al.* used four carbenes, 15 two with triplet and two with singlet ground states. 16 The authors found no indication that the reactivity is influenced by the spin state. Instead, the "philicity" of the carbene appears to control the oxygen abstraction via rate determining nucleophilic attack on the CO₂ carbon. With the data available it was impossible to determine whether the reaction is concerted or not.

Reaction 1 has also been probed by Chateuneuf ¹⁷ in a laser flash photolysis (LFP) study of :CPh₂ in supercritical CO₂. The :CPh₂, generated by photolysis from diphenyldiazomethane forms "most likely" diphenyl α -lactone, though no direct observation of the product was reported. The state selectivity of the carbene was also unclear, no differentiation being made between the "spin allowed" concerted addition of the singlet or the "spin forbidden" formation of the lactone through the triplet manifold, via a diradical intermediate.

In a theoretical study by Davidson *et al.* ¹⁸ exploring gas phase dissociation of chloroacetyl anion, three intermediates were suggested as products of anion departure: α -lactone (1), acetoxyl diradical (³3) and a zwitterionic state of the dioxatrimethylenemethane structure 3. Calculations found the lactone to be the most stable,¹⁹ with the diradical 35 kcal/mol higher in energy; the zwitterion collapses upon optimization to α -lactone or separated :CH₂ and CO₂. Davidson's calculations yield a heat of formation for α -lactone 1 of -51 kcal/mol. This value is in reasonable agreement with the experimental data of Squires *et al.* ²⁰ obtained by collision-induced dissociation measurements on several acetate anions; it differs significantly, however, from a more recent computational estimate (-45.2 ± 2.5 kcal/mol via two different isodesmic reactions)²¹ and from our G2 value (vide infra). In a theoretical study of α -hydroxy-carboxylic acid decarboxylation,²² α -lactone is found to fragment to CH₂O + CO with an E_a and TS structure very similar to our own (vide infra). Squires *et al.* ²³ investigated the

formation of α -lactone by tandem mass spectrometry and energy-resolved collisioninduced dissociation and determined the its heat of formation to be -47 ± 4.7 kcal/mol

To address the question of methylene's spin state in reaction 1, we began our theoretical investigation by looking at several modes of methylene attack on CO₂ on both the singlet ¹:CH₂ and triplet ³:CH₂ potential energy surfaces. We envisioned three possible paths (Figure 3.3):

a. electrophilic attack at the oxygen lone pair of electrons, leading to an ylide-like intermediate ¹2; the possibility of direct oxygen transfer via a ¹2–like TS to yield CO + H_2CO was investigated along with further cyclization of ¹2 to 1;

b. ambiphilic attack at a C=O π bond, leading to the formation of α -lactone 1; fragmentation of 1 generates the final products CO + H₂CO;

c. nucleophilic or radical attack at the C atom, leading to acetoxyl diradical ³3; further transformation of ³3 to 1 was considered, it being difficult to envision a direct path from ³3 to CO + H₂CO.



Figure 3.1 Possible reaction paths

In the course of this work other questions were addressed: is there a direct path, concerted or stepwise, via an open ylide-like structure ¹2 (transition state or intermediate) to CO + H_2CO ? Is α -lactone 1 the observed intermediate in the early matrix studies? If so, is it formed in one step (path b), or via cyclization of other species, such as ¹2 or ³3? If attack

occurs at carbon (path c), are there stable acetoxyl-like intermediates ³3? If so, would they close to α -lactone 1 or rearrange to diradicals ³2? If ³:CH₂ reacts with CO₂ to any significant degree, at what point does intersystem crossing occur en route to closed-shell products 1 or CO + H₂CO?

3.3 Methods and procedures

All calculations were performed using the Gaussian 94 package²⁴ run on a cluster of Silicon Graphics computers. All stationary points (NImag=0), were optimized and characterized by vibrational analysis at the HF/6-31G* and MP2/6-31G* level. Single point calculations were run at MP4/6-31G* using HF/6-31G* and MP2/6-31G* geometries, respectively. Transition structures (TS, NImag=1) were characterized by one single imaginary vibrational frequency.²⁵

The connections on the PES among the stationary points and TSs found were verified by running intrinsic reaction coordinate (IRC) calculations, ²⁶ starting from each TS at the HF/6-31G*//HF/6-31G* and MP2/6-31G*//MP2/6-31G* levels. Selected IRC points were analyzed as single points at MP2/6-31G*//HF/6-31G* and MP4/6-31G*//HF/6-31G* levels. To better understand the presence or absence of stationary points on the reaction path from singlet :CH₂ approaching CO₂, B3LYP/6-31G* and QCISD/6-31G* optimizations were also carried out for this reagion of the singlet PES.

Although well-defined economical methods are available for accurate calculations of carbene S-T gaps,²⁷ their general extrapolation to reaction potential energy surfaces is nontrivial. In an effort to obtain experimentally relevant energetics, we computed G2 energies for all stationary points. The G2²⁸ error between experimental and calculated values²⁹ for the singlet-triplet (S-T) gap in methylene is only 2.4 kcal/mol, much closer than with the other above mentioned methods. Also, because of significant differences in the results obtained at different levels (vide infra), key points on the reaction paths were reevaluated using the G2 method.

3.4 Discussion

3.4.1 Overall thermochemistry

The experimental heat of reaction 1, $\Delta H_r = -61$ kcal/mol, ³⁰ is compared in Table 1 to data from our *ab initio* calculations. The overall energy profiles, as calculated here at the three different levels indicated above, may be followed in Figures 3.4a, 3.4b and, 3.4c. Interestingly, G2 and RHF, the most and least sophisticated of the methods used, approximate the experimental heat of reaction most closely. The overall thermochemistry suggests also that the reaction should end on the singlet PES.





Figure 3.4a Overall energy profiles at G2 (ΔE in kcal/mol)



Figure 3.4b Overall energy profiles at MP2/6-31G*(ΔE in kcal/mol)



Figure 3.4c Overall energy profiles at HF/6-31G* (ΔE in kcal/mol)

Though singlet carbene is generally thought to be the initial product formed from all methylene precursors used,³¹ collision–induced equilibration to the triplet ground state occurs readily, raising the possibility of intersystem crossing (ISC) before the CH_2 - CO_2 collision or somewhere along the reaction path.³²

Table 3.1: Overall Thermochemistry

Method	ΔH_{rxn}	ΔH_{rxn}
	singlet PES	triplet PES
HF/6-31G*	-58.7	15.2
MP2/6-31G*//HF/6-31G*	-69.8	32.7
MP4/6-31G*//HF/6-31G*	-69.3	24.5
MP2/6-31G*//MP2/6-31G*	-64.8 ^a	51.3ª
G2	-60.5	22.5
Experimental	-61	23.8 ^b

^a Corrected with zero point energy, ZPE. ^b Calculated from experimental heat of formation of triplet methylene (ref 30) and triplet formaldehyde (from G. Hertzberg, "Electronic Spectra of Polyatomic Molecules" van Nostrand, Princeton, 1967).

3.4.2 Methylene approach

The possible existence of stable van der Waals complexes was investigated for reactants ${}^{1}C_{1}$ (Figure 3.5b), ${}^{1}C_{2v}$ (Figure 3.9b) and products, ${}^{1}C_{p}$ (Figure 3.75b). In the singlet methylene case, a minimum was found at the HF level, 3.2 kcal/mol lower in energy than separated species. In structure ${}^{1}C_{1}$, (Figure 3.5b) the methylene is complexed through the empty π orbital to a lone pair of one of the CO₂ oxygen atoms. IRC calculations at the HF level find ${}^{1}C_{1}$ to be the starting point for a one-step oxygen atom "pluck" pathway, which occurs via a substantial barrier, TS3. As expected, this finding suggests that direct oxygen transfer should begin via electrophilic attack on an oxygen atom lone pair. Despite extensive searching, no conventional CH₂-CO₂ ylide minimum was located, casting doubt on a recent report from the group of Oku *et al.*³³ This result is unsurprising; CO₂ is a weak Lewis base, as evidenced by its low proton and methyl cation affinities, compared to CH₂O (129.2 and 49.4 *vs.* 170.4 and 78.5 kcal/mol,³⁴ respectively), so its affinity toward methylene would be expected to be substantially lower than formaldehyde affinity toward methylene. A second minimum (NImag=0) also

found only at the HF level corresponds to perpendicular nucleophilic methylene attack on the CO₂ carbon (${}^{1}C_{2v}$ in Figure 3.9, path b). The HF/6-31G* IRC calculations connect this minimum with α -lactone 1 via TS1, over a barrier of 3.5 kcal/mol (i.e. 0.2 kcal/mol above separated ¹:CH₂ + CO₂). The ${}^{1}C_{2v}$ structure orients the methylene hydrogens perpendicular relative to the CO₂ moiety, the C-C distance is 3.131 Å, 0.7 Å longer than in ${}^{1}C_{1}$, and its energy is 3.3 kcal/mol below 1 :CH₂ + CO₂, similar to the 3.2 kcal/mol value for ${}^{1}C_{1}$.

No G2 calculations were carried out for ${}^{1}C_{1}$, TS1, or ${}^{1}C_{2v}$ because no corresponding minima could be located on the MP2/6-31G* PES. In all three cases, reoptimization at the MP2 level simply falls onto the monotonically exothermic trajectory of a concerted barrierless attack by ¹:CH₂ on the π system of CO₂ to form α -lactone 1. Similar behavior was found on the B3LYP/6-31G* PES, but at the QCISD/6-31G* level, true stationary points for ${}^{1}C_{1}$ and TS1 were found, 4.3 and 3.6 kcal/mol below the energy of ¹:CH₂ + CO₂. Interestingly, for the ${}^{1}C_{1}$ geometry, the triplet single point energy is 19 kcal/mol higher than the reactants on the triplet surface. Considering that methylene's QCISD/6-31G* S–T gap (optimized geometries) is 16 kcal/mol and assuming two monotonically parallel channels for singlet and triplet approach toward CO₂, with the triplet complex 19 kcal/mol higher in energy (same geometry) we may consider that even though the reaction starts on the triplet PES it may have crossed to the singlet PES before the methylene gets close enough to the reaction partner, CO₂.

For the triplet case, calculations at HF, MP2, B3LYP and QCISD/6-31G* levels yield structures for complex ${}^{3}C_{1}$ with C-C distances ranging from 3.5 to 3.2 Å, and energies 0.6 to 1.1 kcal/mol below 3 :CH₂ + CO₂. G2 calculations starting from the MP2 optimized geometry find an energy only 0.8 kcal/mol lower than the separated species. IRC data connect this species via **TS4** (Figure 3.4a) over a 40 kcal/mol barrier to diradical ${}^{3}2$.

$\Delta E (kcal/mol)^a$	HF	MP2	QCISD	B3LYP
Singlet ¹ C _{2v}	-3.1	-3.3		
Singlet ¹ C ₁	-3.3		-4.3	
Triplet ³ C ₁	-0.6	-1.1	-1.1	-1.1

Table 3.2: Calculated energies for CO_2 + :CH₂ complexes

^a Calculated at the same level of theory, in respect with $CO_2 + 1:CH_2$ or $3:CH_2$.

According to our calculations, the nature of the attack depends on the electronic state of carbene as expected from the findings of Wagner *et al.* and seemingly at odds with the philicity-dominated suggestion of Sander *et al.* However, since philicity is defined in terms of a carbene's substrate selectivities rather than the absolute reactivity (i.e. rate constants) of the carbene's more reactive singlet state, this may be a less significant discrepancy than it appears at first. The singlet prefers electrophilic attack on the π system of CO₂ with the formation of α -lactone **1** in a barrierless process, whereas the triplet prefers to attack at the carbon atom as a radical and follows the lowest energy path toward the acetoxyl diradical ³**3**.

3.4.3 Possible intermediates

Among potential intermediates in this reaction, we have examined α -lactone 1, ylide ¹2, diradical ³2 and acetoxyl diradical ³3 (Figure 3.1). The singlet zwitterionic state of structure 3 was not considered. Although early experimental studies in solution invoked such a dipolar species formed by ring opening of substituted α -lactones to explain formation of polyester products,³⁵ previous calculations of Davidson *et al.* (see ref 18) found the corresponding structure for the parent α -lactone to be higher in energy than the corresponding diradicals, and to collapse without barrier to 1.³⁶ Table 3.3 lists energies in kcal/mol relative to ³:CH₂ + CO₂ for each intermediate. Vibrational frequency data are presented in Table 3.5 and a complete list of the total energies and cartesian coordinates for each species considered here are available in the Appendix 3.

3.4.3.1 Ylide ¹2 (= TS3)

No minimum was found for singlet ¹2, the hypothetical ylide. Only a TS is found in this region of the PES, at all level of calculations used here. If the attack of singlet methylene is directed toward oxygen, the reaction path goes through this species (named here **TS3** or ¹2) and effects an one step oxygen "pluck". The barrier found in our calculation for direct one-step oxygen abstraction via **TS3** is 62.5 kcal/mol at the HF level but significantly lower at MP2 or G2 (see Figure 4.3) with respect to ¹:CH₂ + CO₂.

The geometry of ¹2 changes dramatically when calcualted at the HF and MP2 levels (Figure 3.7). The geometry at HF/6-31G* looks like a late TS, with the formaldehyde part almost formed, with an HCH angle close to 120° (124°). The MP2/6-31G* structure suggests an early TS with the methylene part almost unmodified from its starting geometry. At the same time, the C2–O3–C4 distances are located in the bonding range, indicating strong interactions. IRC calculations, both at HF and MP2 levels, confirm the connectivity between the reagents and the products in one single step, via **TS3** on the singlet PES of the reaction.

A single point energy calculation for vertical excitation of the ³2 diradical from the triplet to singlet electronic structure finds the singlet with the exact same geometry as ³2, 15.2 kcal/mol higher in energy than ¹2 at the HF level but only 6.6 kcal/mol higher at MP4/6-31G*. Considering that the initial S-T gap in methylene at HF is ~30 kcal/mol, the difference between the two calculated structures, ³2 diradical and ylide-like ¹2 is much smaller.

In our endeavor to find a minimum with an ylide-like structure we calculated the open shell version of an ylide starting from both the singlet transition state ¹2 and the triplet minimum ³2 geometries. In both cases, using UHF/6-31G* and UMP2/6-31G* wavefunctions, the calculations found the same minimum with an open shell singlet structure.³⁷ The minimum is lower in energy than the singlet **TS3** and its geometry is

essentially that of the triplet ${}^{3}2$ geometry. The extent of spin contamination in these calculations supports this idea, being so great that we believe the result simply corresponds to the triplet diradical.

Ab initio method	¹ :CH ₂	1	³ 1	¹ 2	³ 2a	3 2s b	³ 3 p	³ 3 s
	CO ₂							
NImag ^c		0		1	0	0	0	1
HF/6-31G*	30.8	-6.9	53.4	89.8	22.0	19.9	1.2	10.0
HF/6-31G* with zpe corr.	30.5	0.1	58.7	93.0	25.2	24.2	8.1	13.3
MP2/6-31G*//HF/6-31G*	21.0	-40.6	55.4	31.2	5.2	4.7	14.3	22.1
MP4/6-31G*//HF/6-31G*	17.2	-40.0	50.0	27.7	3.6	3.4	8.4	16.5
MP2/6-31G*//MP2/6-31G*	20.9	-40.3		40.1	15.8	15.5	17.0	24.0
MP2/6-31G* with zpe corr.	17.6	-34.1		43.4	19.7	16.6	21.2	27.0
MP4/6-31G*//MP2/6-31G*	17.1	-39.7		36.2	14.2	14.2	11.7	18.8
MP2(full)/6-31G*	19.0	-40.9		39.8	15.8	15.5	16.9	24.1
QCISD(T,4ET)/6-311G(dp)	12.5	-36.7		36.8	13.3	13.3	9.2	18.1
G2 (0 K)	6.6	-39.9		31.1	12.5	13.2	9.15	17.9

Table 3.3 Energy (kcal/mol)^a of stationary points

^a Energies are reported as difference value in respect with ³:CH₂ + CO₂: at each corresponding level of theory, as follows: HF/6-31G*, -226.55568; with zpe correction, -226.52450; MP2/6-31G*//MP2/6-31G*, -227.11114 with zpe correcton -227.08165; MP4/6-31G*//MP2/6-31G* -227.152407; MP2(full)/6-31G*, -227.1258165; QCISD(T, 4ET)/6-311G(d,p), -227.269984; G2, -227.43031. ^b Acetoxyl staggered structure optimized at HF/6-31G* level goes to alpha-lactone (see text). ^c NImag = the number of imaginary frequencies obtained by vibrational analysis at bot HF and MP2 levels; structures with Nimg = 0 represent stationary points on PESs, whereas NImag = 1 indicates a transition state.

3.4.3.2 α -lactone 1

Most often mentioned as a possible intermediate, α -lactone 1 is characterized here by geometry optimization and vibrational analysis (see Tables 3.3 and 3.4 and Figure 3.9).³⁸ The first estimated value available in the literature for the heat of formation of α lactone,³⁹ based on bond additivity, is -31 kcal/mol. Davidson's *ab initio* data¹⁸ suggest ΔH_f (1) = -51 kcal/mol. This value was successfully used by Squires to interpret collisional induced dissociation (CID) measurements on acetyl anion.²⁰ More recently Rodriguez *et al.* combined QCISD(T) calculations with known heats of formation of other species in two different isodesmic reactions and estimated a heat of formation for α -lactone of 45.4 ± 2.4 kcal/mol. Recent measurements of Squires *et al.*²³ found ΔH_f (1) = -47.3 ± 4.7 kcal/mol. Our own estimates, calculated using G2 reaction energies and experimental⁴⁰ heats of formation for known species, are shown in Table 3.4.

The ketene + oxirane isodesmic reaction we used (see the fourth reaction in Table 3.4) suggests, from calculated heats of reaction at the G2 level, combined with the experimental ΔH_f of ethene, oxirane and ketene, ΔH_f (1) = -41.5 kcal/mol. Heats of formation directly calculated for ketene and oxirane from G2 atomization energies yield values higher than those experimentally measured. In contrast, for ethene the calculated value is 0.3 kcal/mol lower. This observation suggests that heat of formation for α -lactone 1 may be slightly higher than the value calculated here, -43.7 kcal/mol, and certainly within the error limits suggested by Rodriquez *et al.* (-45 ± 2.4 kcal/mol).

Reactions used to estimate α-lactone ΔH _f	ΔH _{rxn}	ΔH _{rxn} G2	ΔHf	ΔHf	$\Delta H_{f^a} E_{XD}$
	G2(0)	Enthalpy	G2(0)	G2 Enthalpy	-
$^{1}CH_{2} + CO_{2} \longrightarrow C_{2}H_{2}O_{2} (\alpha$ -lactone)	-46.6	-48.4	39.7	-41.5	101.4;-94.05±0.031
$^{1}CH_{2} + CO_{2} \longrightarrow C_{2}H_{2}O_{2} (\alpha$ -lactone)	-39.9	-41.8	42.8	-44.7	92.3; -94.05±0.031
$CO + H_2CO \longrightarrow C_2H_2O_2 (\alpha$ -lactone)	13.99	12.4	-38.0	-44.0	-26.42±0.04; -26.95±0.11
$ A_2 C = C = 0 \longrightarrow A_0 C = 0 = 0 $	-4.96	-5.02	-41.6	-41.5	-12.58±0.15; 12.54
H_3C H_2 H_2 H_2 H_2 H_2 H_2 H_2 H_2	42.51	60.0	-43.5	-43.2	-86.6±0.2
$H \xrightarrow{0}_{H_3C} = 0 \xrightarrow{H_2}_{H_3C} H_2$	58.6	44.97	-43.6	-41.1	-103.3±0.1
$2C + 2H + 20 \longrightarrow C_2H_2O2$ (α -lactone)				-43.7b	
$2C + 4H \longrightarrow C_2H_4$ (ethylene)				12.8b	12.54
$2C + 4H + O \longrightarrow C_2H_4O$ (oxirane)				-13.8b	-12.58±0.15
$2C + 2H + O \longrightarrow C_2H_2O$ (ketene)				-12.1b	-11.4±0.4c
a) Experimental Δ Hf from Lias et al. "Gas Phase Ion and Net Database Number 69-March 1998 Release. b) Calculated Δ HK.; Trucks, G. W.; Pople, J. A. J. Phys. Chem. 1991 , 94, 722	utral Thermoo If from the co 21 and Nicola	chemistry" J. Phys prresponding heats idis, A.; Raul, A.;	c. Chem Ref. s of atomizat Glukhovtse	Data 1988, 17, Suplion with G2 enthalp; v, M. N.; Radom, L.	 J. 1. and NIST Standard Reference (from Curtis, L. A.; Raghavachari, J. Phys. Chem 1996, 100, 17460)
and experimental ΔH_{atoms} corrected with zero point energy	and heat capa	icity (from CODA	TA, J. Chen	n. Thermodyn, 1978,	10, 903.) of elements, at 298 K as

listed below for each accurate the corresponding G2 energy (hartree), G2 energy corrected at 0K, G2 energy corrected at 298K and the corresponding experimental Δ Hf (kcal/mol), H:-0.5, -0.49764, -0.58067, 52.1; O: -74.98203, -74.97947, -75.07445, 59.6; Cgas: -37.78432, -37.78183, -38.05482, 171.3. c) From the values available in the above cited resources for ketene heat of formation, we choose the one closer to G2 calculated values.

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Of the three intermediates considered here, 1 is the most stable and is formed through attack of singlet methylene on a C=O π bond of CO₂ in a barrierless process. Ring fragmentation, 1 --> CO + H₂CO, is calculated (G2) to occur via TS2 with ΔH^{\ddagger} = 28.4 kcal/mol and ΔH_{rxn} = -14.1 kcal/mol, similar to the 32.2 and -12.2 kcal/mol MP2/6-31G^{**} values obtained by Domingos *et al.*²² in their theoretical study of gas-phase α hydroxyacid decarboxylation. These ΔH_{rxn} values differ from Liebman's -23.4 kcal/mol estimated exothermicity³⁹ as expected, given the above adjustments in the estimated ΔH_f of the α -lactone. Ring-opening (path b) to zwitterionic intermediates has been proposed to explain polyester products in solution studies of α -lactone-forming reactions (ref. 35) and references therein). However, as noted above, all singlet biradical structures we examined fragmented or collapsed to 1 upon optimization. Thus, 1 represents a fairly deep potential energy well, and should be easily observed at sufficiently low temperatures. The IR data attributed by Milligan and Jacox to 1 show ¹²C=O and ¹³C=O carbonyl stretches at 1967 and 1933 cm⁻¹, respectively, and as shown in Table 3.5, scaled HF/6-31G* and MP2/6-31G* IR frequencies match experiment rather well both for 1 and for CH_2O and CO.

The triplet α -lactone excited state, ³1, was examined as part of our exploration of the triplet PES and ISC possibilities. The HF/6-31G* structure lies 60 kcal/mol higher in energy than the corresponding singlet and shows substantial pyramidalization at the carbonyl carbon; the MP4/6-31G*//HF/6-31G* energy difference is even larger, at 90 kcal/mol. Upon reoptimization at MP2/6-31G*, the ring opens via C-C cleavage to form diradical ³2 (anti isomer), 52.4 kcal/mol higher in energy than ¹1 at the G2 level. These results indicate that ³1 is energetically out of reach and therefore unlikely to play any role in the title reaction.

3.4.3.3 Diradical ³2

Infrared studies of the reaction of HO• radicals with CO ⁴¹ indicate the existence of linear H-O-CO in two conformations, syn and anti. As expected, our calculations find two analogous conformations for the triplet •H₂C-O-CO• diradical ³2 (Figure 3.5). The energy differences between the two conformers are small at all levels (from 1.2 kcal/mol at HF/6-31G* to 0.6 kcal/mol at G2). On the conformational potential energy surface; for ³2s, (Figure 3.5), barriers of 7 and 9 kcal/mol were found for anti-->syn conversion and for rotation of the CH₂ group of ³2s, respectively.



Figure 3.5 ${}^{3}2a - {}^{3}2s$ interconversion path

IRC calculations connect ³2a with separate ${}^{3}CH_{2} + CO_{2}$ via TS4. Thus, the 12.5 kcal/mol endothermic addition to form ${}^{3}2a$ would occur with a barrier of 59 kcal/mol; subsequent cleavage to triplet formaldehyde and CO, via **TS5** (Figure 3.7) is again endothermic by 10 kcal/mol, over a 17 kcal/mol barrier (Figure 3.8).

The matrix experiments of Milligan and Jacox located the carbonyl stretches for anti and syn HO–CO• species at 1883 cm⁻¹ and 1793 cm⁻¹ respectively. Our calculations (Table 3.5) found the corresponding vibrations for ³2a at 1811 cm⁻¹ (corrected, MP2 see footnote to Table 3.5) and for ³2s at 1781 cm⁻¹ (corrected, MP2) at the MP2/6-31G* level. These frequencies are substantially lower than those for α -lactone and reflect the acyclic connectivity in ³2. Similarly, our values of 126.3° and 129.9° for the O–C–O angles in ³2a and ³2s compare well with the 126.7° and 130.1° for HOCO• calculated by Rauk *et al.*⁴² As shown in Table 3.6, $\Delta H_{f}(32a)$ was calculated to be 9.6 kcal/mol at the G2 level, 3.8 kcal/mol lower than the value obtained by summing the separate enthalpy changes for loss of hydrogen atoms from methyl formate to make a "noninteracting" diradical. This energy lowering can be understood as the stabilization due to interaction between the two unpaired electrons in ³2a.

	ΔH_{f} (kcal/mol)	Experimental ^a	Calculated	Calculated ^e
	Н ₃ С–СО–ОН	-103.2	103.2 ^c	
	H ₃ C–CO–O•		-45.4 ^c	
	•H ₂ CCOOH		-58.1 ^c	
3 3	•H ₂ C–CO–O•		-0.3 ^d	5.8
	H-CO-OCH3	-85.0	-88.7 ^b	
	•CO–OCH ₃		-35.3 ^b	
	H-CO-OCH ₂ •		-40.0 ^b	
3 2	•CO_OCH2•		13.4 ^d	9.6

Table 3.6 Estimated heats of formation for the diradical intermediates

^a Δ H_f from Lias *et al.* in Reference a, Table 3.4. ^b Δ H_f of diradicals calculated from their heat of atomization using G2 enthalpy (see same ref as in Table 3.4) and experimental Δ H_f atoms corrected with zpe and heat capacity, CODATA, *J. Chem. Thermodynamics* **1978**, *10*, 903. ^c Δ H_f from Yu, D.; Rauk, A.; Armstrong, D. A. *J. Chem. Soc. Perkin Trans.* 2 **1994**, 2207-2215; the value calculated with our data for acetic acid is 1.6 kcal/mol higher than our value. ^d Δ H_f calculated considering the loss of hydrogen atom enthalpy as an additive property. ^e Δ H_f of diradicals calculated from their heat of atomization (•CH₂-O-CO• --> 2C + 2H + 2O, Δ H_f = **9.6** kcal/mol and •CH₂-CO•O• --> 2C + 2H + 2O, Δ H_f = **5.8** kcal/mol) using G2 enthalpy and experimental Δ H_f atoms corrected with zpe and heat capacity ⁴³of elements, at 298 K. <u>Note</u>: The difference between the Δ H_f of the two radicals, ³2 and ³3 is 3.4 kcal/mol calculated with G2 total energy *vs.* 3.8 kcal/mol with G2 enthalpy.

3.4.3.4 Acetoxyl diradical ³3

Addition of ${}^{3}CH_{2}$ to the carbon of CO₂ leads to ${}^{3}3$, the acetoxyl diradical, which has been computationally analyzed (ref. 18) in a somewhat different context. Using the 6-31G* basis set (compared with 6-31+G* from ref 18), we also found two structures, planar ${}^{3}3p$ and staggered ${}^{3}3s$. At the MP2 and HF levels, only the planar diradical is a minimum (NImag = 0). The planar and staggered structures of ${}^{3}3$ are higher in energy than ${}^{3}:CH_{2} + CO_{2}$, by 9.2 kcal/mol and 17.9 kcal/mol (G2), respectively. Geometrical data compare well with reported MP2/6-31G* structures of monoradicals •CH₂-COOH and CH₃-CO-O•; energies from the same source (see Rauk *et al.* in ref 42) were used in Table 3.6 to calculate the ΔH_{f} of diradical ${}^{3}3$. Unlike the case of ${}^{3}2a$, the value predicted assuming additivity, -0.3 kcal/mol, is substantially lower than the 5.8 kcal/mol calculated from G2 heats of atomization, suggesting that the two unpaired electrons interact to raise the energy of the entire entity.

Of the two possible ${}^{3}CH_{2} + CO_{2}$ adducts, ${}^{3}3p$ and ${}^{3}2a$, the former is both lower in energy (by 3.3 kcal/mol) and accessible via a lower barrier (20.1 vs. 58.9 kcal/mol via TS6 vs. TS4, respectively, Fig 3.4a). However, completion of the oxygen transfer to form ${}^{3}CH_{2}O$ and CO would require isomerization over a high barrier (via TS7 found only at HF level) to ${}^{3}2a$, before the cleavage (via TS5) which itself has a barrier of 17.9 kcal/mol (G2). The above connectivities on the reaction PES were all confirmed through IRC calculations. According to these results, ${}^{3}:CH_{2} + CO_{2}$ could react at thermal energies to form acetoxyl diradical ${}^{3}3$, but this intermediate's principal choice would be to redissociate or undergo ISC to the singlet surface, followed by barrierless closure to 1. As expected, optimization on the singlet surface starting from the geometry of ${}^{3}3s$ (C_s symmetry) led directly to α -lactone 1, as found by Davidson.¹⁸ Singlet optimization (C_s symmetry) from the analogous planar geometry ${}^{3}3p$ leads to a transition structure for •H₂C-CO₂• bond rotation (NImag=1), 17.9 kcal/mol (G2) higher in energy than ³:CH₂ + CO₂.

The acetoxyl diradical was recently studied²³ by tandem mass spectrometry and by energy resolved collisional induced dissociation. From the appearance energy measurements, a gap of 2 kcal/mol was estimated between the triplet and its lowest singlet state. The triplet lowest energy path is decomposition to ³:CH₂ + CO₂ while the open shell singlet is thought to easily evolve to "hot" α -lactone which, in its turn, decomposes to CO + H₂CO, species detected in the NRMS experiments; their presence is explained only by ring opening of α -lactone.

Comparing the available singlet and triplet data, the region of the PES surrounding 3 appears well suited for ISC. Single point energy calculations for possible singlets with 3p and 3s geometries show the singlet ¹3s much lower in energy than the corresponding triplet and even lower than the energy of starting compounds on the singlet PES (Figure 3.6).



Figure 3.6 T–S direct excitation results for ³3p and ³3s

<u>Note</u>: At QCISD/6-31G* the singlet spin calculations indicate ³3s lower in energy than both ³3p and ³3s and even lower than $CO_2 + 1$:CH₂ on the singlet PES.

Rotation from the planar acetoxyl diradical ³3p to the staggered ³3s, described as a TS by the calculation, offers a possible channel for ISC to the singlet ¹3s which may "roll" downhill into α -lactone, on the singlet PES.

3.4.4 Vibrational analysis from IR calculated data

IR vibrational frequency calculations contain known systematic errors, due to the neglect of electron correlation and anharmonicity. The results give, generally, an overestimate of ~10%-12%. The values reported here in Table 3.5 are corrected by a factor of 0.89⁴⁴ and 0.954⁴⁵ for the HF and MP2 values respectively. The most intense vibration of the experimental IR spectrum is the band at ~1967 cm⁻¹ for ¹²C or 1933 cm⁻¹ for ¹³C with the isotopes in CO₂. This band is assigned to the carbonyl stretch in 1 with the abnormally high frequency attributed to the strain in the α -lactone ring. The deviation of our computed values from the experimental detected value. The other candidates, ³2 and ³3, also show carbonyl stretch vibrations, but at lower frequencies (see Table 3.5). The only other available experimental data are for the diphenyl α -lactone. Three vibrations attributed to the C=O stretch were detected¹³, with the strongest located at 1890 cm⁻¹ and shifting to 1837 cm⁻¹ when ¹³C was used. Our SE/PM3 calculations locate the carbonyl vibration for diphenyl α -lactone at 1990 cm⁻¹ (uncorrected) for ¹²C.

These vibrational analyses support the assignment of the observed bands in the matrix experiments to α -lactone 1.

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Compound	$v_{C=O}$ (cm ⁻¹)	v_{C-O} (cm ⁻¹) ^{HF}
di-Methyl α-lactone ^a	1900	
di-(Trifluoro) α -lactone ^a	1975	
di-n-Butyl-a-lactonea	1895	1163
1 (α -lactone) ^b	1974 ^{HF} ; 1967 ^{MP2}	1210
³ 2a ^b	1879 ^{HF} ; 1811 ^{MP2}	1210
³ 3p ^b	1667 HF; MP2	1225
H ₂ CO (experimental)	1746	
H ₂ CO (calculated)	1804 HF	

Table 3.5 Selected calculated IR frequencies

^a From Chapman, O. L.; Wojtkowski, P. W.; Adam, W.; Rodriquez, O.; Rucktaschel, R. J. Am. Chem. Soc. **1972**, 94, 1365-1367. ^b Values corrected with 0.89 and 0.954 for HF and MP2, respectively.

3.4.5 Possible reaction paths

The connectivities among the found intermediates were established through the various transition structures found, and are presented in Schemes 5 to 8 below.⁴⁷ For the geometry data and the active vibrations see Appendix 3. Their energies with respect to the triplet methylene and CO_2 are presented in Table 3.7. The energy profiles reflect the tremendous differences among the calculated paths at HF/6-31G*, MP2/6-31G*//MP2/6-31G*, and G2 levels, and are presented separately in Fig 3.4.

path a, singlet PES: This is the direct one-step path for an oxygen atom "pluck" (Figure 3.7). It takes place via TS3, a structure proposed for ylide ¹2 (for which no minimum was found). The energy barrier is 62.5 kcal/mol at HF/6-31G*//HF/6-31G* but drops dramatically to 24.5 kcal/mol at the G2 level. IRC calculations confirm the connection from TS3 to separated reactants and to products CO + CH₂O on both HF and MP2 PESs.



Figure 3.7a Path a on singlet PES at MP2/6-31G*//MP2/6-31G*



Figure 3.7b Path a on singlet PES at HF/6-31G*

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path a, triplet PES: This is a two-step process via diradical ³2 (Figure 3.8). Attack of triplet methylene on an oxygen atom of CO₂ leads to ³2 via TS4; subsequent cleavage via TS5 leads to CO + 3 CH₂O. The high barrier and substantial endothermicity of the initial attack (58.9 and 12.5 kcal/mol, respectively) are expected, reflecting the difficulty of breaking a C=O double bond. Two rotation isomers (anti and syn) of ³2 were found, which interconvert via TSrot (Figure 3.5) with a lower barrier than either of the fragmentation channels. With high barriers and an excited state product (3 CH₂O), this overall path, as described, is endothermic and unlikely to play any significant role in the CH₂ + CO₂ reaction.



Figure 3.8 Path a on triplet PES

path b, singlet PES: This is the two-step oxygen transfer via α -lactone 1 (Figure 3.9). At the HF/6-31G* level, the computed reaction path begins in the shallow CH₂ + CO₂ van der Waals complex ¹C₁ and surmounts the 3.5 kcal/mol barrier of TS1 to arrive at α -lactone 1, the most stable C₂H₂O₂ intermediate found by our calculations. At the MP2/6-31G*//MP2/6-31G* level, ¹C₁ and TS1 are no longer stationary points, allowing

 separate $CH_2 + CO_2$ to collapse without barrier to α -lactone 1. Fragmentation of 1 via TS2 then yields $CO + CH_2O$ with a G2 barrier of 36.1 kcal/mol (MP2) or 27.3 kcal/mol (G2). Because of the difference in the results at different levels of theory we further examined the two structures, 1C_1 and TS1, using DFT and QCI methods.⁴⁸ At the B3LYP/6-31G* level, both structures collapsed directly to α -lactone 1, but the QCISD/6-31G* model found 1C_1 to be a minimum 4.3 kcal/mol lower in energy than 1CH_2 and CO₂; TS1 was then a transition state only 1.3 kcal higher than 1C_1 but 3 kcal/mol lower than the starting species. The S–T methylene gap at QCISD is 16 kcal/mol. Because of these contradictory results, the region around TS1 on the singlet PES appears to be a possible site for ISC (vide infra).



Figure 3.9a Path b on singlet PES at G2

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Figure 3.9b Path b on singlet PES at HF/6-31G*

path c, triplet PES: This is a three-step process via acetoxyl diradical ³3 (Figure 3.10). We calculate it to be the lowest energy path for ³:CH₂ attack on CO₂. At the G2 level, ³CH₂ attacks CO₂ at carbon via **TS6** with a 20.1 kcal/mol barrier to form planar acetoxyl diradical ³3p. However, ³3p can not complete the oxygen transfer of interest here, unless it isomerizes to ³2 or closes to α -lactone 1. An isomerization path from ³3p to the diradical ³2 was found only at the HF/6-31G* level and involves passage over a barrier, **TS7**, of 86.1 kcal/mol. Despite substantial effort, no TS7-like structure was found at higher levels, suggesting that **TS7** may be an artifact due to the limitations of the HF theory used. Even if such a path could be followed, completion of the oxygen transfer would require passage over the additional barrier, **TS5** already presented in the context of path a on the triplet PES.

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Figure 3.10a Path c on triplet PES at G2



Figure 3.10b Path c on triplet PES at HF/6-31G*

Direct closure of acetoxyl diradical to α -lactone 1 may occur only if ISC connects the triplet ³3p with the corresponding singlet structure. Optimization of a singlet starting at

the geor those of 3.4.6 In direct (MP4 l singlet variati region the er corres the tv proba the geometry of ³**3p** evolves directly into α -lactone **1**. In this respect our results parallel those of Davidson *et al.*¹⁸

3.4.6 Intersystem crossing.

Selected IRC points describing all the above reaction paths were subjected to direct excitation calculations.⁴⁹ Single point energies were calculated at the MP2 and MP4 levels using the HF optimized structures from the IRC calculations both from singlet and triplet PESs. We switched each structure's spin state and looked for energy variations along the paths. No crossing regions were found, with the exception of the region around TS1 on the singlet PES and TS6 on the triplet PES. A plot (Figure 3.11) of the energy differences between selected points from both the singlet and the corresponding triplet IRC trajectories of TS1 and TS6 show possible ISC in the region of the two described transition states. Our way of approaching intersystem crossing is probably verifiable with nontrivial procedures.
	¹ TS1	¹ TS2	ITS3	³ TS4	³ TS5	3TS6	³ TS7	³ TSa	³ TSrot
Connecting	¹ R-1	1 – ¹ P	lR-lP	³ R- ³ 2	³ 2– ³ P	³ R- ³ 3p	3 3 –3 2	³ 2a- ³ 2s	
HF geometry									
HF/6-31G*	34.2	29.8	89.8	84.8	38.6	31.2	84.9	28.9	23.1
HF/6-31G* with zpe corr.	30.8	24.8	86.5	82.5	36.3	30.2	80.3	25.2	19.4
MP2/6-31G*//HF/6-31G*	10.9	-5.9	31.2	68.0	26,8	22.4	86.4	24.0	18.8
MP4/6-31G*//HF/6-31G*	7.9	-7.9	27.7	63.3	20.2	19.2	80.5	22.0	17.9
MP2 geometry									
MP2/6-31G*//MP2/6-31G*		-6.5	40.4	68.6	41,6	29.3		25.7	20.3
MP2/6-31G* with zpe corr.		-10.3	36.9	66.3	39.7	27.5		22.1	17.0
MP4/6-31G*//MP2/6-31G*		-8.6	36.3	65.2		24.3		23.9	
G2 geometry									
MP2(full)/6-31G*		-6.2	39.9	68.5	41.9	26.4			
QCISD(T,4ET)/6-		-5.5	36.8	63.3	29.5	19.3			
311G(dp)									
G2 G2		-12.6	31.1	58.9	30.4	20.1			

Table 3.7 Transition States Energy ^a (kcal/mol)

perscripts ^a Energy difference, in kcal/mol in respect with the ground state energy of $CO_2 + {}^3$:CH₂, see values in the note a for Table 1 and 3 indicated the state of the carbene in the reactants respectively the electronic state of formaldehyde in the products. Figure 3.11 Energy differences on IRC trajectories from TS1 and TS2





* Expanded plot around TS1 and TS6 PES's region (reaction coordinate = 0)

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The direct excitation calculations mentioned above along with the monotonically downhill process on the singlet PES are analogous to the well known case of non-equilibrium intersystem crossing for the : CPh_2 reaction with methanol.⁵⁰ If the singlet PES is described as having a low or no barrier, as in the case of path b, the crossing with the triplet PES which is going monotonically up-hill, as it is in the case of path c, may occur before **TS6** on the triplet path is reached. The reaction starts on the triplet PES and may "roll" down toward the products on the singlet PES (Figure 3.12) in a so called nonequilibrium surface crossing.



A: Traditional surface crossing; B: Non-equilibrium surface crossing in the reaction of diphenyl carbene with methanol, adapted from Platz, M. S. in ref. 48, Fig 21, page 327. C: Possible non-equilibrium surface crossing for the case of methylene reaction with CO₂.

Figure 3.12 Traditional and non-equilibrium surface crossing

We propose here a possible intersystem crossing in the intersection region of path c with path b before the state described as TS1 at HF/6-31G* level, on path b, is reached.

3.5 Conclusions

Abstraction of oxygen by ¹:CH₂ from CO₂ appears to occur via stepwise processes. Singlet methylene attack on the π bond of CO₂ to form α -lactone was found to be the most favorable process on the singlet potential energy surface, much like the familiar barrierless concerted cycloaddition of methylene to alkenes. The net O-transfer is completed by the lactone's fragmentation into CO from CH₂O. A one-step oxygen atom "pluck" pathway was also found, but with its 24 kcal/mol G2 activation barrier, this process is unlikely to play a significant role at common reaction temperatures. The lowest energy triplet attack is directed toward the carbon atom of CO₂ in a nucleophilic manner. If the reaction remains on the triplet PES, the acetoxyl diradical ³3 is formed but there is a substantial barrier for this process and two further steps (via ³2) are required to complete the overall endothermic oxygen transfer on the triplet PES.

Experimental thermochemical data show reaction 1 (Table 1) on the singlet PES to be 60 kcal/mol exothermic. The α -lactone intermediate, with its high frequency (~1900 cm⁻¹) carbonyl stretch, has also been experimentally observed in matrix isolation experiments. These facts are in excellent agreement with our calculations. But the correspondence between experiment and theory is less satisfactory for the available kinetic data. Singlet methylene is the primary photolysis product from all the precursors studied to date, but with CO₂ it is collisionally deactivated to the triplet state twice as fast as it reacts.^{10, 11} The reaction of triplet methylene with CO₂ is slow, in agreement with our calculated path c. Considering these experimental findings together with our calculated results we propose here three possible parallel channels for the reaction of methylene with CO₂, all starting from the initially generated singlet methylene.

On one of the channels, part of the initially generated ¹:CH₂ forms, in a barrierless process, the most stable intermediate, α -lactone 1, with its excess vibrational energy (the reaction is 46.6 kcal/mol exothermic), more than enough to allow fragmentation to products under low pressure conditions. In a parallel channel, part of ¹:CH₂ may be

energetically "hot" enough to overcome the barrier of one-step oxygen "pluck" process.⁵¹ However, most of the ¹:CH₂ will equilibrate by collisional deactivation with CO₂ to ³:CH₂. In the third of channel, the reaction starts from the ³:CH₂ by nucleophilic attack of ³:CH₂ at the carbon atom of CO₂ (path c) to form acetoxyl diradical ³3. On the triplet PES, the lowest energy path available to ³3 is to fragment back to CO₂ and ³:CH₂, but ISC from path c to path b is a reasonable candidate for completion of the oxygen transfer reaction. Once on the singlet PES, barrierless ring closure makes α -lactone 1.

Supporting information available in Appendix. It contains a complete summary with cartesian coordinates, calculated total energies and frequencies for all the species discussed

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CHAPTER 4

An Alternative Approach Toward Nucleophilic Carbenes Synthesis

Abstract	
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1 Introduction

In the early '60s the idea that a carbene substituted with O, N, S or other electrondonor groups would be more stable than the elusive carbene species known at that time gained substantial attention. Wanzlich tried to synthesize such compounds by deprotonation of the corresponding imidazolium ions, but only the formal products from reaction of the desired carbenes with alcohols and aldehydes or the carbene dimers of the carbenes were identified (Figure 1).¹ It was almost thirty years later when a stable carbene itself was first synthesized, isolated ² and structurally characterized by X-ray diffraction (Figure 2).³



Figure 1 First synthesis of nucleophilic carbene dimers.



Figure 2 1, 3-diadamantyl-imidazolin-ylidene.

Since 1991 several different groups around the world⁴ have contributed to the area of stable, isolable carbene chemistry. The successful synthetic routes described so far (Figure 3) for synthesis of stable carbenes involve either deprotonation of imidazolium or thioimidazolium salts by strong bases,⁵ or desulfurization of imidazolthiones with potassium.⁶ The former procedure proved effective even for synthesis of such species as the first acyclic stable carbene derived from the N, N, N', N'-tetra*iso*propyl-formamidinium ion by deprotonation.⁷



Figure 3 General synthetic methods for preparation of nucleophilic carbene

In addition, special procedures were employed (Figure 4.4) for gas-phase and matrix isolation.⁸



Figure 4.4 Special cases for synthesis of nucleophilic carbenes in matrix

Dithiacarbenes, with two sulfur atoms stabilizing the carbenic center, were also thought to be responsible for the formation of tetrathiafulvalenes, the corresponding dimers of the 1,3-dithiacarbenes.⁹ The path to the 1,3-dithiacarbene dimers generally involves the reaction of carbon disulfide with an electron-deficient substituted acetylene (Figure 4.5). Usually, most reactions of CS_2 proceed from an initial nucleophilic attack at the carbon. In contrast, the chemistry leading to 1,3-dithiacarbenes involves either electrophilic attack of an electron deficient species on the sulfur atom of the CS_2 or a concerted cycloaddition.



Figure 4.5 Synthesis of dithiacarbene dimers.

The role of the triple bond may be extended to other highly reactive species. Benzyne reacts in gas phase with CS_2 and the corresponding dimer of 1,3-dithiacarbene, was identified by mass spectrometry.¹⁰ Nakayama generated benzyne from different precursors in the presence of carbon disulfide and methanol.¹¹ The product of the liquid phase reaction, dithiacarbene, inserts into the H-O bond of methanol, leading to 2methoxy-1,3-benzodithiole as the main product. Nakayama's experiments demonstrated the higher reactivity of benzyne toward CS_2 than methanol (Figure 4.6).



Figure 4.6 Benzyne cycloaddition to carbondisulfide.

Similarly, triple bonds from the highly strained tetramethylcycloheptyne and its sulfur derivative, react with CS_2 , at room temperature, to generate dimers of dithiacarbenes (Figure 4.7).¹²



Figure 4.7 Cycloheptyne reaction with CS₂

The behavior of benzyne and cyclic alkynes, which do not possess electron–withdrawing substituents, focuses attention on a possible direct cycloaddition reaction mechanism as an alternative to electrophilic attack at the sulfur atom followed by rearrangement to the carbene.

Hartzler thoroughly investigated the reaction of hexafluoro-2-butyne and dimethylacetylenedicarboxylate (**DMAD**) with CS₂. At 100 °C, CS₂ added to the triple bond to from three products (Figure 4.8). Tetrathiafulvalene, the dimer of the dithiacarbene, is formed quantitatively only in the presence of a strong acid such as trifluoroacetic acid. With no acid present, a 1:3 mixture of acetylene and CS₂ forms only

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2% of the dimer, while the major product is an interesting adduct containing a 3:2 ratio of the initial species obtained in 60% yield. A 1:6 ratio of acetylene to CS_2 yields a different major product, a 4:4 adduct in 60% yield while tetrathiafulvalene is obtained only in 8% yield. In the presence of acid, the initially formed dithiacarbene probably does not react further with the acetylene due to protonation of the dithiolium ion. It appears that it is not the classical reaction between two singlet carbenes, but the reaction between the carbene and its conjugated acid partner that forms the dimer.



Figure 4.8 Harzler general reaction with the three adducts.

The 1,3-dithiacarbenes were also intercepted with alcohols to form 2-alkoxy-1,3dithioles, phenols aldehydes and ketones. The expected product of carbene insertion into the O-H bond of the acid was not observed. Propiolate esters also undergo these reactions, proving that the presence of only one electron withdrawing group is sufficient to activate the acetylene toward reaction with CS₂.

Beside CS_2 , other cumulenes-carbonyl sulfide and diisopropylcarbodiimidewere briefly tested for the ability to undergo the same type of chemistry and generate nucleophilic carbene. No reaction was observed between COS and hexafluoro-2-butyne; when methanol was present in the reaction mixture, a slow reaction indicated the presence of an initially formed zwitterion which is trapped by methanol. The case of diisopropylcarbodiimide presents no evidence for chemistry similar to carbon disulfide (Figure 4.9). Only the product of a [2+2] cycloaddition followed by a tautomerization was observed.



Figure 4.9 Reaction of diisopropylcarbodiimide with hexafluoro-2-butyne.

The brief investigation of carbodiimide by Hartzler has not extended to date. In terms of simple bond energy calculations, the carbodiimide reaction with acetylenes should be less energetically demanding than that of CS₂. Considering the results obtained by Hartzler with CS₂ two decades ago, and in the light of new examples demonstrating the stability and reactivity of 1,3-diaminocarbenes from the last six years, we tried to extend the investigation of carbodiimides as possible 4π donors as a pathway to new stable nucleophilic carbenes. If the reaction proved to be efficient, a completely new route to stable carbenes, involving reactions of carbodiimides with acetylenes might be found.

2 Results and Discussion

To find a new and effective route to the synthesis of nucleophilic carbenes, and to better characterize and probe their physical and chemical properties, we investigated here the reaction of **DMAD** with 1,3-di-*tert*-butylcarbodiimide (**DBCDI**)

2.1. Reagents

As cumulated double bond systems, we used 1,3-diisopropyl- and 1,3-di-tertbutylcarbodiimide. Both appear to be reasonable candidates for generating 1,3diaminocarbenes. Diaminocarbenes with similar structures are already known¹³ as stable species, in the absence of quenchers such as air, water, and alcohols. The only direct precedent is the investigation performed by Harzler involving diisopropylcarbodiimide. The isolated product seems to be the result of a [2+2] cycloaddition followed by tautomerization made possible by the presence of the an α hydrogen atom from the isopropyl group linked to the nitrogen atom (Figure 4.9). The 1,3-di-tertbutylcarbodiimide was chosen for the present investigation because it has no hydrogen atom in an α position. Thus, the possibility of a hydrogen shift or tautomerization, as in the diisopropylcarbodiimide case, is eliminated. For economical reasons as much as for the ease of manipulation, dimethyl-acetylenedicarboxylate, **DMAD**, was used as the acetylene partner. In addition, brief investigations involving benzyne, maleic anhydride (MA) and tetracyanoethylene (TCNE) were performed. However, the double bond proved to be ineffective in the reaction with cumulenes. Neither maleic anhydride or tetracyanoethylene reacts efficiently with carbodiimide in the manner under investigation here. The only products isolated and characterized were obtained from the reaction of carbodiimide with **DMAD**.

2.2. Investigation of reaction conditions

2.2.1. Energy requirements

According to the literature, the reaction of CS_2 with hexafluoro-2-butyne or dimethylacetylenedicarboxylate substituted acetylenes was slow, requiring heating at 100°C for several days to yield the products of the 1,3-dithiacarbene intermediate. In contrast, benzyne reactions were fast at room temperature. In the liquid phase; their dimeric products were formed within 30 minutes of the addition of CS_2 to a solution of

benzyne prepared in situ. In the same manner, cycloheptyne reacts rapidly at room temperature with carbon disulfide affording a 2:2 adduct, the corresponding dimer of the carbene.

We investigated the energy requirements of the reactions involving **CDI** with **DMAD** by using initiation methods such as light, heat, microwave or ultrasound. The evolution of the reaction was followed by ¹H and ¹³C NMR. The photochemical path seems unlikely at best for the expected cycloaddition. Irradiation with UV light from a 500 W high pressure Hg vapor lamp shielded for wavelengths shorter than 350 nm with an uranium filter or even unshielded proved ineffective. The reaction mixture remained unchanged, by NMR and GC analysis, after 2 hours of continuos irradiation. Reactions performed in an ultrasound water bath, were also unchanged after 2 hours. Heating in an oil bath at 80 to 100 °C for several days led to partial consumption of the reagents, and to drive the reaction to completion required heating for as long as 11 days. In contrast, a sample exposed to microwaves in a sealed NMR tube required only half an hour for total consumption of the reagents but afforded a more complicated mixture of products.

2.2.2 Solvents

The reactions were run in solvents, such as tetrahydrofuran, acetonitrile or ethyl acetate, the media used in the initial experiments of Hartzler. Experiments with neat liquid reagents are were also run, but a higher amount of polymeric products were obtained and separation of the products was more laborious. The three solvents proved equally effective in homogenizing the reaction mixture and no differences were noticed in the course of the reaction. The use of deuterated THF or acetonitrile allowed the reaction to be followed by NMR. Most characterized diaminocarbenes had their ¹³C NMR spectra taken in THF, so it should be possible to make reasonable guesses about the expected resonance position of the carbenic carbon of our expected species in the same solvent.

2.2 3 Traps for carbenes

To detect the presence of the carbene as a short lived intermediate, we tried to trap it with some of the commonly known fast reacting species such as water, methanol or benzaldehyde. Products with the appropriate masses were observed via GC-MS but further confirmation of their structure was not possible because of the small amounts of product.

2.3 Products

Reaction of DBCDI with DMAD. 1 to 2 mL of 10^{-3} M solution of DBCDI and DMAD in THF-d8, EtOAc or CD₃CN in NMR tube were degassed by freeze-pump-thaw cycles and sealed. After heating for 4 to 11 days in an oil bath at 80-100°C with the reagent consumption followed by ¹H and ¹³C NMR, the tube was opened. In all cases pressure developed proving the formation of a gaseous product at RT, which was identified as isobutylene.¹⁴ The product mixture was separated by flash column chromatography over silica gel using a set of hexane: CH₂Cl₂ solvent mixtures with 5:1 to 1:3 ratios. Besides unreacted starting materials and some di-*tert*-butylurea byproduct, Et₂O trituration yielded the dimethyl ester of 2-*N*-*tert*-butylamino-3-cyano-2(E)-butenedioic acid and the tetramethyl ester of s-*trans*-1-*N*-*tert*-butylamino-1,3-butadiene-1,2,3,4tetracarboxylic acid (E, E), 1 and 2, respectively, in Figure 10.



Figure 10 General reaction **CDI + DMAD**.

With no traps present product 1 and 2 were obtained from the reaction of 1,3-di-*tert*butylcarbodiimide with DMAD. With the equimolar ratios of the two reagents or with slight excess of **CDI**, 1 is the major one obtained. When an excess of **DMAD** is used, 2 is obtained in higher yield, eventually becoming the major product with a large excess of

DMAD.

When water and D_2O water was added to the reaction mixture, along with 1 and 2, small amounts of 1:1:1adducts of CDI, DMAD and either H₂O or D₂O were detected by GC-MS spectrometry. Methanol adducts of the same type were detected when MeOH or MeOD were added as traps for the potentially formed carbene.

<u>Reaction of DBCDI with Benzyne.</u> Freshly prepared benzyne¹⁵ was heated in neat CDI or in a 10^{-3} M solution of CD₃CN. No [2+3] cycloadition products were identified. Identified in the reaction mixture were of antranilic acid and unreacted CDI.

<u>Reaction of DBCDI with TCNE.</u> Sample (1 mL 10⁻³M) of DBCDI and TCNE in EtOAc and CHCl₃ respectively, were degassed by 4 freeze-pump-thaw cycles and sealed in an NMR tube. Heating for 4 days in an oil bath at 80-100°C gave a viscous mixture. After extraction with ether and column separation of the unreacted reagents, GC-MS allowed identification of traces of a 1:1 adduct (M=282) of CDI and TCNE with a fragmentation pattern attributable to a [2+3] cycloaddition product. The only other compound identified in both cases was 1,3-di-t*ert*-butylurea. Attempts to further optimized the yields and investigate the adduct were unsuccessful.

<u>Reaction of DBCDI with Maleic Anhydride (MA)</u>. A 1 mL sample of 10⁻³M of DBCDI and maleic anhydride in CH₃Cl was degassed by 4 freeze-pump-thaw cycles and sealed in NMR tube. Heating for 4 days in oil bath at 80°C a polymeric reaction mixture was generated. Extraction with ether and column chromatography allowed identification of

the unreacted starting materials and traces of 1:1 adduct of CDI and MA detectable via GC-MS with a fragmentation pattern which may be explained a [2+3] cycloaddition product. The only product separated from the unreacted starting materials cases was ditert-butylurea. Attempts to further optimized the yields and investigate the adduct were unsuccessful.

Reaction of DBCDI with di-phenyl-acetylene. After heating for 4 days a sample of CDI and acetylene in CD₃CN, degassed by 4 successive freeze-thawed-pump cycles and sealed under vacuum, no reaction was noticed. GC-MS analysis of the mixture showed only starting materials and solvent.

Reaction of DPCDI with DMAD. 1 ml solutions of DPCDI and DMAD in EtOAc, THFd8 or CD₃CN were degassed by 4 freeze-pump-thaw cycles and sealed under vacuum. Samples were heated for 4-5 days in oil bath. Only the starting materials along with some di-isopropylurea were separated from the reaction mixture by column chromatography. No 2-azetine-like product from a presumable [2+2] cycloaddition as in the case of hex afluoro-2-butyne was identified. When CF₃COOH was added as catalyst, the main product was the di-isopropylurea and some polymeric mass probably due to the self Condensation of DMAD.

Reaction of DPCDI with TCNE. A 1 mL 10⁻³M sample of DPCDI and TCNE in EtOAc was degassed by 4 successive freeze-pump-thaw cycles, sealed in NMR tube and heated for 4 days in oil bath at 80-100°C. Extraction of the reaction mixture with ether and column separation of the unreacted starting materials, GC-MS allowed identification of traces of 1:1 adduct (M=254) of DPCDI and TCNE with a fragmentation which may explain a [2+3] cycloaddition product. Attempts to further optimize the yields and investigate the adduct were unsuccessful.

2.3. Discussion

2.3.1 Thermodynamic data

S imple bond energy calculations allow us to predict that the reaction of carbodiimide with an acetylene should be energetically favored over reactions involving carbon disulfide. From this starting point, semiempirical and *ab initio* molecular orbital calculations were performed in order to compare the energetics of the reactions of CS_2 and of carbodiimide with acetylene. The computed systems used here are simplified approximations of the real systems used in the lab, since they include unsubstituted acetylene, CS_2 and unsubstituted carbodiimide (Scheme 11). The overall thermodynamics of the two reactions shows that the reaction of acetylene with CDI is more exothermic than the one with CS_2 and, consequently, more thermodynamically favored. These simple estimations of the overall reaction energy pointed to a possible new route to synthesize diaminocarbene.



Figure 11 Processes followed by theoretical means

ΔH_{rxn}	PM3	HFa	MP2 ^b	MP4 ^c	MP2 ^d
1	-48.1	-40.0	-40.0	-38.7	-38.8
2	-18.9	-26.0	-32.3	-29.7	-32.6
1+2	-67.0	-63.8	-72.3	-68.4	-71.4
3	-11.3	-3.0	-0.2	-0.3	-0.6
4	-24.0	-16.6	-19.2	-18.8	-18.4
5	-7.0	-10.6	-7.6	-8.9	-8.2
6a	-20.8	-31.9	-33.4	-31.5	-33.2
6b	-20.9	-30.6	-30.6	-28.3	-31.5
4+5+6a	-51.8	-59.1	-60.1	-59.2	-59.7
4+5+6b	-51.8	-58.9	-57.4	-56.0	-58.3

Table 1: Comparative thermodynamic data computed for overall reactions 1 to 6

^aHF/6-31G*//HF/6-31G*; ^bMP2/6-31G*//HF/6-31G*; ^cMP4/631G*//HF/6-31G*; ^dMP2/6-31G*//MP2/6-31G*.

The overall thermodynamics show the reaction of CS₂ with acetylene, (Reaction 3 in Table 1) is almost thermoneutral (-3.0 kcal/mol at HF and only 0.6 kcal/mol at the MP2/6-31G* level). In contrast, both reactions involving CDI are calculated to be exothermic. The formation of the four-membered ring, (Reaction 4) as in the experiments of Hartzler, is 16.6 or 18.4 kcal/mol exothermic at HF or MP2, respectively. However, the [2+3] cyclization to diaminocarbene, (Reaction 1), is by far the most thermodynamically favored process of the three considered here, with $\Delta H_{rxn} = -37.8$ or -38.8 kcal/mol at HF or MP2 respectively.

To calibrate the reliability of the thermodynamics calculated here, we compare them with the available experimental data. Using the experimental heats of formation of imidazole and acetylene and with our best estimate for the heat of formation of CDI,¹⁶ we calculated an overall $\Delta H_{rxn(1+2)} = -60.8$ kcal/mol which may be compared with the calculated -63.8 or -71.4 at HF or MP2 level, respectively.

We considered subsequent reactions of the carbene, which may account for the cletected products formation. From diaminocarbene, the 1,2-H shift to 1H-imidazole, (Reaction 2) is strongly exothermic, as expected. The 2-azetine may undergo the typical electrocyclic ring opening to the corresponding imino-ketimine (Reaction 5). In order to explain the formation of a product such as 1, one needs an additional step, (Reaction 6a or 6b) a net 1,5 H shift. If this process is intramolecular, it should initially lead to the *cis* product with an overall exothermicity of ~ -60 kcal/mol. Our experimentally obtained product, 1, has a *trans* arrangement which may result from a 1,5 shift followed by i somerization, or an intermolecular process.

The data available indicate the formation of the diaminocarbene as the most thermodynamically favored product. In contrast, the experiments, both in Hartzler's case and in ours, yield different products. The explanation must be sought in the actual mechanism and the heights of the barriers involved in each step of the possible processes.

2.3.2 Mechanisms suggested in literature

The most common type of reaction mentioned in the literature for cumulated double bonded systems are the [2+2] cycloadditions.¹⁷ The reactions involving reagents such as CS₂, COS, ketenimines or carbodiimiides are [2+2] cycloadditions followed, in most cases, by subsequent thermodynamically or kinetically driven chemistry toward the most stable product or products. Various [2+2] cycloadditions between carbodiimides or phenylisocyanate and acetylenes are known. However the reactions require a catalyst such as iron pentacarbonyl¹⁸ or similar complexes with cobalt¹⁹ or nickel.²⁰

The existing experimental literature regarding possible [2+3] cycloadditions involves only the CS₂ cases and there are no previous mentions of **CDI** involvement in a

cycloaddition of this type. The experimental data available to date about cycloadditions of a cumulated system with acetylene offer two different points of views on this type of reaction. On the one side are the fast reactions of benzyne and tetramethylcycloheptyne with CS₂. The assumption of a concerted [2+3] cycloaddition in these cases is supported by the similar behavior of the two acetylenes, benzyne and strained tetramethylcycloheptyne, which are neither strong nucleophiles nor electrophiles. In the benzyne case, CS₂ reacted even faster than MeOH. Only the product of dithiacarbene i nsertion in the O–H bond of MeOH was obtained, which shows that benzyne reacts much faster with CS₂ than with MeOH and only afterward does the 1,3-dithiacarbene i nsert into the O–H bond of MeOH (Figure 4.6).

On the other side, Hartzler's thorough investigation of the reaction of CS₂ with acyclic acetylenes showed that acetylenes need to have at least one electron-withdrawing group next to the triple bond in order to react with CS₂ and generate dithiacarbene. Unsubstituted acetylene, such as 2-butyne, diphenylacetylene or vinylacetylene are completely unreactive toward CS₂ while hexafluoro-2-butyne or **DMAD** proved to be effective and led to the expected products. But the reaction needs long times and high temperatures (at least 100 °C) and goes better if it is acid catalyzed. These facts are consistent with a step-by-step mechanism, as initially suggested by Hartzler. Such a mechanism implies a nucleophilic attack on the acetylene to generate initially a zwitterion. This ionic species has never been trapped and is thought to cyclize to the carbene faster than to accept a proton.

The generally accepted explanation is that the dominance of cyclization vs. proton **abstraction**, in the presence of acid is not the result of kinetic control via faster cyclization **but** due to the thermodynamic drive toward the additional stabilization by the formation **of** an aromatic structure, such as the 1,3 dithiacarbene. In the absence of suitable traps, **Hartzler** identified the corresponding dimer of dithiacarbene.

Knowing that dimerization in solution is less probable than any other mode of carbene reaction, Hartzler explained the dimer formation, rather than through coupling of two singlet carbene molecules, by initial protonation of the carbene to dithiolium ion and subsequent reaction of the ion with another carbene molecule to form the dimer. The formation of the dimer is a consequence of a long-lived carbene. For the case of interest here, Hartzler's investigation showed no similarity in the behavior of CS_2 and carbodiimide (see Figure 4.9 and corresponding references from the text).

2.3.3 Possible mechanisms

Given the previously suggested mechanisms and the results of our investigation we consider here three possible paths for the reaction of the involved species (Figure 11). a. [2+3] cycloaddition

b. [2+2] cycloaddition

c. Stepwise reaction.

a. [2+3] cycloaddition. For a cumulated a-b-c system free of formal charges, an electron pair at a and c will create two allyl anion systems perpendicular to each other. Charge migration during cycloaddition produces a cyclic allyl cation with an additional anionic charge at b. Among the three resonance structures of the cyclic product formed as the result of the [2+3] cycloaddition, one is free of formal charges but possesses an electron sextet on atom b. If the system is CO₂, CDI or CS₂, a carbon atom will play the role of b and the neutral cyclic species is a carbone.



Figure 12: General [2+3] cycloaddition of cumulenes

There is no mention of such a process in the published literature involving CO₂ and only one investigation involving CDI. Bis[bis(diisopropylamino)phosphino]carbodiimide is the one case in the literature in which a CDI is involved in [3+2] cycloaddition. But even in this case, it is postulated that the bisphosphino substitution is responsible for [2+3] cycloadduct formation with DMAD in 92% yield, because the three pieces include only C and one N from the CDI moiety along with one P atom from the phosphino part of the rnolecule.²¹

By contrast, the experiments with CS_2 as cumulene are at the starting point of a vast literature pool about tetrathiafulvalenes, their synthesis, chemical reactivity and practical use. In the CS_2 case, the available data about its reaction with tetramethylcycloheptyne or benzyne support the idea of a concerted cycloaddition given that d-e is a triple bond (Figure 12). The reduced reactivity toward open chained acetylenes, without electron-withdrawing substituents next to the triple bond of the alkynes along with the requirement of an acid catalyst do not allow one to exclude an initial electrophilic attack at the heteroatom, S or N, and a step by step mechanism.²²

Our calculations for a concerted [2+3] cycloaddition Reaction found a barrier of 63 kcal/mol at HF and much lower at MP2, 24.5 kcal/mol. By contrast the CS₂ case shows a barrier of 52.1 kcal/mol at the HF level (Figure 13 and Figure 14).


Figure 13 Calculated path for [2+3] CDI cycloaddition to acetylene

The two values for the concerted addition at HF for CS_2 and CDI, respectively, support the idea that, CS_2 should add more readily to to acetylene because its barrier is 12 kcal/mol lower than that for CDI. However, the height of the barrier is still significant even for CS_2 case.



Figure 14 Calculated path for [2+3] CS₂ cycloaddition to acetylene

The easier cycloaddition of CS_2 may be the result of the difference in the HOMO-LUMO gap between the two cumulenes,²³ as well as the difference in size between N and S atoms. With sulfur bigger than nitrogen, access to the central carbon may be encumbered and interaction with either of the sulfur atoms in a stepwise reaction or with both in a concerted [2+3] cycloaddition would lead to the experimentally obtained dithiacarbene. In addition, the C=S bond, being longer than C=N bond may allow easier bending for CS_2 molecule compared with CDI and as a consequence, better overlap of both S atoms with the acetylene. Also the substituents on N atom will complicate the situation compared with the S atom.

A possible thermal rearrangement of the carbodiimide to the corresponding nitrile irnine followed by a fast reaction of the nitril imine with **DMAD** may be another **explanation** for the main product obtained.²⁴ Theoretical studies of this type of **rear**rangement at different *ab initio* levels were published.²⁵ The G2(MP2) level shows irninonitril only 2 kcal/mol more stable than the carbodiimide. The rearrangements is **postulated** to take place through a 1 H-diazirine intermediate which is calculated to be, when the same level of computational method is used, 59 kcal/mol higher in energy than **the** carbodiimide.²⁶

b. [2+2] cycloaddition is a common reaction among heterocumulenes.²⁷ Since concerted thermal $[2\pi_s + 2\pi_s]$ cycloadditions are not orbital symmetry allowed, the mechanisms involve an allowed concerted $[2\pi_s + 2\pi_a]$ reaction leading to a four membered ring heterocycle.²⁸ Usually, the olefin is the π^2_s component. The reasoning behind the high reactivity of heterocumulenes such as ketene in [2+2] cycloadditions is the favorable secondary interaction between the HOMO of the olefin and the vacant orthogonal C=O π^* antibonding orbital of ketene.

One may imagine that all cumulenic systems should undergo concerted cycloadditions since they all have an orthogonal vacant π^* antibonding orbital. However, this is not true

for all cumulenes. It is the energy difference between the π^* orbital of the cumulene and the HOMO of the olefin which dictates the possibility of a concerted reaction rather than a stepwise reaction. In the ketene case, there is an usually small gap between its HOMO and LUMO orbitals, (Figure 16). The calculated difference in the carbodiimide case is 16.7 (SCF, with 3-21G* basis set) or 10.96 eV (MNDO).²⁹ More theoretical analyses of c arbodiimide structure and stability are available in literature.³⁰



Figure 16 HOMO-LUMO gap in ketene and CDI



Such a mechanism is used to explain the results in the experimentally known CDI cases. The initial product of [2+2] cycloaddition, 2-azetine, lacks the normal stabilization of an amidine because of the unfavorable azabutadiene resonance structure in its dipolar form. It is also known that azetines readily undergo electrocyclic ring opening and subsequent rearrangements.

c. The stepwise reaction would imply a zwitterionic intermediate, in complete disagreement with the previously cited rapid room temperature reactions of benzyne and tetramethylcycloheptyne with CS_2 . The existence of such an intermediate has never been experimentally proven. There is only one case known, that of carbonylsulfide reacting with hexafluoro-2-butyne, in which an initially formed zwitterion was proposed to exist in equilibrium with the separated species (Figure 15). Cyclization of the zwitterion to form the corresponding five membered ring would than occur via nucleophilic attack at the carbonyl moiety. If there is a suitable trap, the equilibrium would be shifted toward the zwitterion which should react further with alcohols, as in the case CS_2 . Only trans addition to the acetylenes was observed.



Scheme 17. Carbonyl sulfide case

Our calculations found no transition state for a concerted [2+2] cycloaddition in the model reaction between CDI and acetylene. At the approach of the acetylene to the CDI moiety two other possible paths were found, besides the [2+3] cycloaddition route described above. One implies the interaction of only one N atom from CDI with the acetylene, in a concerted [1+2] cycloaddition (Figure 17). There are known cases in the **literature** which describe the isonitrile reaction with **DMAD** or hexafluoro-2-butyne to **lead** to products with similar structure to the one calculated here.³¹ The reaction is **thought** to follow a stepwise path, via a zwitterionic intermediate or a very polar TS.



Figure 18 Calculated TS for formal [1+2] cycloaddition of CDI to acetylene

Our calculations found also a polar TS, corresponding to a barrier of 79.8 kcal/mol at the HIF level (Figure 17). From the TS, the system evolves to azirine and isocyanide. The IRC calculations describe the reaction path from the TS to separated molecules as oriented in such a way to form a favorable H bond between the isonitrile and the N in the azirine ring. This path is of no interest for the case discussed here and, with its high barrier, is probably not competitive, at least under the conditions of our experiments.

The other path is described as a step by step interaction via a zwitterionic intermediate. Published theoretical investigations of similar reactions, such as ketene addition to double bonds, reveal the complexity of the problem. Bernardi *et al.* used an MCSCF wavefunction with STO-3G and 4-31G* basis sets for the reaction of ketene with ethylene.³² Both the perpendicular and the parallel approach of the ketene to the ethylene lead to a short lived diradical intermediate. No reaction path for a concerted $[2\pi_s + 2\pi_a]$ was found in contradiction with the assumption of antarafacial addition of ketene to the suprafacial olefin. Houk *et al.* studied the same reaction theoretically, adding MP2 correlation energy.³³ They found the reaction pericyclic with the bond formation asynchronous.

Our calculations found a TS ~57 kcal/mol higher in energy than the starting species. An IRC calculation from this TS leads to a highly unstable zwitterionic intermediate, 55.1 kcal/mol above the acetylene and CDI starting point, at the HF/6-31G* level. The zwitterion easily closes to 2-azetine, the product of a formal [2+2] cycloaddition. The optimization of the same species at the MP2/6-31G*//MP2/6-31G* level starting with the HF geometry, also closes to 2-azetine. The fact that the zwitterion is a minimum only at the HF suggests that there is no barrier for the closing of the zwitterionic transition state into the 2-azetine ring. IRC calculations starting with the same TS show the direct connection between the acetylene and CDI to the four rmembered ring product (Figure 18).



Figure 19 Calculated path for formal [2+2] cycloaddition of CDI to acetylene

The [2+2] concerted cycloaddition is unlikely to compete with a step by step reaction via a zwitterionic transition state and/or intermediate which cyclizes to 2-azetine. The route from 2-azetine to the product analogous to 1 is 10.5 kcal/mol exothermic and should arise via a Woodward-Hoffman allowed³⁴ electrocyclic ring opening to an iminoketimine intermediate in a concerted conrotatory fashion. The torquoselectivity rules³⁵ force the donor substituent to go outward to minimize the interaction of its filled orbitals with the electron pair of the breaking σ bond. Geometry and energy predictions via computational methods for the cyclobutene ring system, less complex than our case here, are contradictory.³⁶ Barriers for the cyclobutene cases were calculated to be in the range of 30 kcal/mol.

In order to reach a product analogous to 3, the *cis* isomer of 1, a 1,5 H shift process was computed. We found a TS for this direct process with a barrier of 64 kcal/mol at HF/6-31G*. However, our calculations are on a system which only approximates the experimental case, as long as the product obtained is mainly *trans*. Its formation via intramolecular rearrangement has no relevance to the experimental findings from substituted CDIs.

In the CDI cases studied here, the reactions were very slow. In most of the cases, after 3-4 days of heating at reflux, more than 50% of the starting materials were found unreacted. The reaction mixtures contained tars, which makes the work-up difficult. Both carbodiimide³⁷ and DMAD self dimerize or even oligomerize to products of higher molecular mass. In the case of DMAD, tetramers are thermally generated in aged samples of DMAD or by simply heating at 100-120°C for several hours.³⁸ The length of the reaction time and the relatively high temperature probably allow subsequent reactions of the CDI or DMAD dimers which are responsible for the polymeric materials formed. In all the cases pressure was developed in the reaction vessel (always noticed while opening the sealed reaction tube). This pressure development was attributed to isobutylene,

obtained as byproduct of 1 formation reaction. Besides 1 and 2 described earlier in this chapter as the two main products present in all the trials, one additional secondary product, 3, was obtained in some runs. Because of its appearance in the GC-MS close to the 1 signal and its fragmentation path showed in the MS spectrum, we conclude that 3 is the cis isomer of 1.

Following the reaction mixture evolution by ¹H and ¹³C NMR³⁹ showed no traces of free carbene at any time.⁴⁰ Products of the carbene's subsequent reactions with solvents or the added traps were also sought. No new products were formed with benzaldehyde but in the case of water and methanol, GC-MS revealed small amounts of products with masses appropriate to the carbene + trap adducts.

Compound 1 was analyzed by IR, GC-MS, ¹H and ¹³C NMR and X-ray Crystallography (see experimental part). One possible explanation for this product formation as the major one in all the cases where the molar ratio of **DBCDI** to **DMAD** is **close** to 1, is the initially preferred formal [2+2] cycloaddition to form an azetine, similar to one case described in the literature (Reference 9). Subsequent ring opening to an imine-ketimine structure followed by H-transfer coupled with isobutylene elimination may afford the final product **3** (Figure 19).



Figure 20 Suggested mechanism for product 3 formation

However, X-ray analysis shows that the two carbomethoxy groups are trans oriented with respect to the double bond (Figure 4.21).

Figure 4.21 Product 1 x-ray crystal structure



Formation of 1 as the major product may be explained only by a different mechanism than the one suggested for the formation of 3.



Figure 22 Suggested mechanism for 1 formation

Formation of 3: The minor product 3 is tentatively assigned as the *cis*-isomer of 1. Its existence was detected only by GC-MS and the small proportion obtained did not allow isolation and purification for complete characterization. The mass spectrum fragmentation pattern is the only indication that it is the cis isomer of 1. If the structure assignment is correct, its existence in the GC-MS analysis, points to a high barrier for C=C bond rotation in 1, and makes the thermal isomerization of 3 to 1 unlikely. **Product 2** formation. This is the second major product in all trials in which the molar ratio of DBCDI and DMAD is close to 1. When the DMAD is in excess, self condensation with of the CDI leads to more 2 formation. We explain the formation of 2 as the result of subsequent reactions of the initially formed dimer of **DMAD** with **DBCDI** or their initially formed 1:1 adduct, which reacts further with a new molecule of **DMAD**. Elimination of an isobutylene molecule from the 2: 1 adducts leads the final 2. Similar 2:1 adducts of **DMAD** ester with isonitriles are reported in literature.⁴¹

3 Conclusions

The reaction of dialkyl-CDIs with acetylenes and electron-withdrawing substituted alkenes were studied. The purpose of the study was to investigate the potential for addition of alkynes or alkenes to the cumulated double bonds in carbodiimides to generate five-membered cyclic structures, a potential new route to nucleophilic carbenes. The results which were consistently obtained under various conditions indicate that carbodiimide is not an effective partner for [2+3] cycloaddition with electron-poor acetylenes to give nucleophilic carbenes. Although traces of compounds were found with masses consistent with carbene formation and trapping, these products could also have arisen in many other ways. Thus, the [2+3] cycloaddition of dialkyl-CDIs and acetylenes does not appear to represent a useful new route to nucleophilic carbenes. Even though some products of carbene trapping were detected, the reaction was not proved a useful **Procedure** for synthesizing and study nucleophilic carbenes.

However, despite its failure to produce detectable carbenes, the [2+2] reaction of **CDIs** with acetylenes has proven interesting and deserves to be further discussed and **investigated**. For instance, the reactions of **CDIs** with strained alkynes, such as benzynes **or cycloheptynes certainly merit further investigation**. Such reactions may follow a **completely different route than the one found here and may yet represent a reasonable path**way to diaminocarbenes. With the availability of powerful theoretical tools, a better **understanding of these systems may be achieved and strategies for control of the reaction may be found**.

Overall, the work here opens a new perspective on the field of carbodiimides as partners in cyclization reactions.

4.4 Experimental methods

<u>General methods</u>. Melting points were determined on a Thomas Hoover capillary apparatus and are uncorrected. All air sensitive reactions were performed in oven-dried glassware using standard syringe/cannula techniques. Solvents were purchased from Aldrich and dried and deoxygenated by standard procedures. Gravity and flash column chromatography were performed on E. Merck silica gel (230–400 mesh). Thin-layer chromatography was done on E. Merck plastic–backed plates (silica gel 60, F245, 0.2 mm).

Routine ¹H and ¹³C NMR spectra were obtained at 300 and 75.43 MHz respectively using either Varian VXR–300 Varian GEMINI 300 NMR Spectrometers. The ¹H NMR chemical shifts are referenced to the residual ¹H resonance in the deuterated solvents used: CDCl₃ (δ 7.24), acetonitrile-*d3* (δ 1.93). The ¹³C chemical shifts are referenced to the one of deuterated solvents: CDCl₃ (δ 77.0) and acetonitrile-*d3* (δ broad118.0 and 1.3 septet).

Fourier-transform infrared (IR) spectra were obtained on a Mattson-Galaxy FT-IR 3020 or Nicolet IR/42 spectrometers. Samples were measured either as thin layers prepared by evaporating a CH₃CN or CHCl₃ solutions on a NaCl plate (liquids) or as KBr pellets (solids).

Electron impact (EI) mass spectra were obtained on a Fison VG trio-1 mass spectrometer which operates in line with a Hewlett Packard 5890 gas chromatograph for GC-MS measurements. High resolution mass spectra were obtained on a JEOL JMS-HX110 high resolution double-focusing mass spectrometer.

Pyrex or uranium glasses were used as filters for photolysing the samples with light from a 500 W Oriel high-pressure Hg lamp.

<u>General procedures</u>. In a standard NMR tube, 1-1.5 mL solution of **DBCDI** and **DMAD** in a 1:1 to 1:3 molar ratio was placed. The sample was degassed using 3 to 5 freezepump-thaw cycles and sealed under vacuum. Alternatively, sparging with dry N_2 or Ar for up to 1/2 hours was used for degassing procedure.

The sample tube was transferred to an oil bath and heated at 60 to 80 °C, from 1 hour to 11 days, with shaking every 1 to 4 hours to homogenize the solution. For ultrasound and microwave experiments, the reaction mixture was prepared as above, in standard NMR tube and was transferred to a standard ultrasound water bath or to a lab microwave oven. After the competition of the reaction, each sample was brought to room temperature and the tube was opened. The samples were extracted twice with ether and separated from the insoluble polymeric mass. The etheral solution was evaporated and the residue was separated by gravity or flash chromatography over silica gel with hexane and CH_2Cl_2 mixture in ratios 5:1 to 1:3 (in volumes).

The main products 1 and 2, the unreacted starting materials and di-*tert*-butylurea were separated from the reaction mixture.

Reagent consumption was followed in all the cases by ¹H and ¹³C NMR. GC-MS data were taken for the initial and final reaction mixture. IR spectra were taken in thin film on NaCl pellets.

Product 1 isolation.

The major product of DBCDI and DMAD reaction was obtained following the general procedure described above. After chromatography, the product was separated as a crystalline solid, and was recrystallized from hexane. mp=82-83° C. ¹H NMR (300 MHz, CDC13) δ 1.36 (9H, s), 3.76 (3H, s), 3.94 (3H, s), 9.8 (1H, broad); ¹³C NMR (75.5 MHz, CDC1₃) δ 30, 52, 53, 56, 100, 117, 160, 162, 168. IR cm⁻¹ 3130, 3206, 2210 (CN), 1729, 1672. MS (EI) m/e 240(M⁺), 241(M⁺+1), 184, 153, 125. High resolution MS Molecular weight 240.1107.

Product 2 isolation.

The product of **DBCDI** and **DMAD** reaction was obtained following the general procedure described above. After one initial chromatography, the product was separated from a later fraction from an oily mixture by trituration with ether.

¹H NMR (300 MHz, CDCl3) δ 1.29 (9H, s), 3.62 (3H, s), 3.63 (3H, s), 3.70 (3H, s), 3.72 (3H, s), 6.72 (1H, s), 9.10 (1H, broad); ¹³C NMR (75.5 MHz, CDCl₃) δ 30.4, 51.1, 51,9, 52.4, 52.7, 56, 129.0, 140.0, 151.9, 150.9, 164.0, 166.0, 168.0, 167.0. IR cm⁻¹ 1741 (C=O vs) 1724 (C=O vs), 1666 (C=C), 1593. MS (EI) m/e 357(M⁺), 301 (C₁₂H₁₅NO₈), 342, 242 (C₁₀H₁₂NO₆), 210, 178, 150.

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APPENDIX

A Chapter 2

A1 PM3 Calculated energies for exchange reactions
A2 Calculated energies for $CH_2O + :CH_2$ exchange reaction
A3 Calculated energies for $CF_2O + :CF_2$ exchange reaction
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Compound	AM1	PM3	HF/6-31G*
	(kcal/mol)	(kcal/mol)	(hartree)
H2CO	-31.5	-34.2	-113.863312
H ₂ C:	110.6	113.3	-28.8723704
Ylide		22.7	-152.7542324
Oxirane	-8.9	-8.1	-152.867356
TS through oxirane	46.1	46.1	-152.7232732
$H_2CO + :CH_2$	79.4	79.1	-152.7387016
F ₂ CO	-146.1	-141.5	-311.6153061
F ₂ C:	-67.9	-67.2	-236.607441
Ylide	-200.3	-184.9	
Oxirane	-203.8	-205.7	-548.3011706
vdW complex	-215.4	-191.8	-548.2784265
TS through oxirane	-184.8	-182.4*	-548.2415770
TS through ylide	-199.0	-172.7	-548.1152010
$F_2CO + :CF_2$	-214.1	-208.3	-548.2760502
(H ₂ N) ₂ CO	-44.9	-47.0	-223.9846922
(H ₂ N) ₂ C:	20.6	32.6	-149.0413289
Ylide	10.8	12.2	-373.0048292
Oxirane	0.4	-9.2	-373.03449209
vdW complex	-32.5	-24.0	-373.03449291
TS through ylide	11.8	19.2	
TS through oxirane	23.6	15.5	-372.8850031
$(H_2N)_2CO + :C(H_2N)_2$	-24.4	-14.4	-373.0260211
CO	-5.7	-19.7	-112.737877
CO ₂	-79.8	-85.0	-187.634176
vdW complex	-84.8	-105.2	-300.3730608
Oxirane	-37.9	-54.9	-300.2529079
TS through oxirane	-36.2	-51.6	-300.244234
^{CO} 2+CO	-85.5	-104.8	-300.372053

A1 PM3 calculated energies for exchange reactions

	G2	-114.33891	-153.39731		-153.46239	.153.53289				
	MP4/MP2	-114.19202	-153.18581	-153,21510	-153.26298	-153.34147			-153.20224	
	MP2+ zpe	-114.15054	-153.10340	-153,11636	-153.16843	-153.24472	-153.11642		-153.10387	
	MP2/6-31G*	-114.16775	-153.13782	-153 17000	-153.22289	-153.30358	-153.16999		-153.15618	
	MP4/HF	-114.19202	-153.18538	-153 20680	-153.25679	-153.33888		-153.21824	-153.19681	
I CUCULI	MP2/HF	-114.16775	-30.90900	-153 16018	-153.21795	-153.30161		-153.17347	-153.15084	
A CAVININES	HF+ zpe	-113.8372	-152.6915	-152,6978	-152.6966	-152.8050	-152.66679	-152.6880	-152.67476	
~· · · · · · · · · · · · · · · · · · ·	HF/6-31G*	-113.86356	-152.73593	-152,75198	-152.75423	-152.86736	-152.72327	-152.74406	-152.72941	
VI 6100 IV	PM3	-34.2	78.8		22.7				46.1	
	Exp	-26	102 76			-12.6				
100m0 717		H ₂ CO	 H2CO +	:CH ₂ complex	vlide	oxirane	TS one	step TS _{compl} -	ylide TSylide-	oxirane

	Exp	PM3	HF/6-31G*	HF+ zpe	MP2/HF	MP4/HF	MP2/6-31G*	MP2+ zpe	MP4/MP2
	-153	-141.5	-311.61531	-311.59952	-312.24781	-312.27399	-312.25271	-312.23857	-312.27979
	-45	-67.2	-236.66074	-236.65296	-237.10966	-237.13733	-237.11157	-237.10447	-237.14017
<u>т</u>		-208.7	-548.27605	-548.25242	-549.35747	-549.41134	-549.36431	-549.34304	-549.41996
×		-191.8 -184.9	-548.27845		-549.36097	-549.41483	-549.368309 -549.314811	-549.28850	-549.42390
		-205.7	-548.30117		-549.40121	-549.44894	-549.407510		-549.45651
цg		-172.7	-548.14143	-548.11544	-549.30583	-549.35959			
-		-182.4	-548.24158	-548.21562	-549.34932	-549.40450	-549.34932	-549.32606	-549.40450
e									

reaction	
+ :CF ₂	
CF_2O	
or the	
energies f	
Calculated	
A3	

A4 Cal	culated	energies	$c for CF_2O + c$	CH ₂ cross rea	iction					
	Exp	PM3	HF/6-31G*	HF+ zpe	MP2/HF	MP4/HF	MP2/6-31G*	MP2+ zpe	MP4/MP2	G2
F ₂ CO :CH ₂	-153 102	-141.5 113.2	-311.61531 -38.87237	-311.59952 -38.85432	-312.24781 -38.96988	-312.27399 -38.99336	-312.25271 -38.970071	-312.23857 -38.952859	-312.27979 -38.99379	-312.69134 -39.058399
F ₂ CO +:CH ₂	-51	-27.8	-350.48768	-350.45384	-351.21769	-351.26735	-351.22278	-351.19143	-351.27358	
compl1 oxirane		-108.8	-350.49509 -350.59115	-350.45782	-530.22861 -351.35765	-351.40012	-351.361598		-351.40500	
TS _{ox to}		-82.1	-350.48748	-350.44551	-351.25813	-351.30872				
Compi z TSone step		-66.5	-350.44524	-350.40322	-351.25395	-351.29976	-351.26783	-351.22645	-351.31697	
compl2		-84.8	-350.53171		-351.28146	-351.33278	-351.28146	-351.24511	-351.33874	
:CF2	-45	-67.2	-236.66074	-236.65296	-237.10966	-237.13733	-237.11157	-237.10447	-237.14017	-237.45882
H ₂ CO	-26	-34.2	-113.86356	-113.8372	-114.16775	-114.19202	-114.16775	-114.15054	-114.19202	-114.33891
H ₂ CO +:CF ₂	-71		-350.5243	-350.49016	-351.27741	-351.32935	-351.27932	-351.25501	-351.33219	-351.79773

reac
cross
:CH ₂
+0
CF ₂ C
for
energies
Calculated 6
40

A5 Rate studies for PCC: + PNO and PCC: + MNO

Upon irradiation of **PCD** in acetonitrile with a N_2 -YAG laser puls (355 nm, 10 ns pulse, 10 mJ) a long-lived absorption was observed, centered at 315 nm and which decays on the μ s timescale. It was previously assigned to **PCC:**.¹ When irradiation of **PCD** in acetonitrile in the presence of pyridine is performed, the PCC:-pyridine ylide long-lived absorption stable on the ms time scale and centered at 475 nm was observed. This on is also a. This one was previously assigned to pyridinium ylide (ref 18). We found that the intensity of this absorption was inversely proportional to the concentration of the oxygen donor, with constant pyridine and diazirine concentration. The rate of oxygen abstraction may be measured either by the decay of the carbene signal or by Stern-Volmer quenching of the pyridinium ylide signals as described below. In our case the latter was found more convenient due to the relative intensity of the signals. Also, an intermediate absorption was noted, centered around 300 nm which may overlap with the carbene signal.

The ratios $k_x/k_{pyr}[pyridine]$ where k_x are the bimolecular rate constants for the reactions of PCC with the oxygen donor, and k_{pyr} is the bimolecular rate constant for the reaction of PCC with pyridine were determined by linear least-squares analysis of the ratio A°_{ylide}/A_{ylide} versus oxygen donor concentration with the y-intercept defined as 1, according to Stern-Volmer relation² in equation 3 derived from eq 1 and 2.

$k_{obs} =$	$k_0 +$	k _{pyr}	[pyrid	line]	+]	k _x	[oxygen c	lonor] e	\mathbf{q} 1	l
-------------	---------	------------------	--------	-------	----	----------------	-----------	-------	-----	----------------	---

$$\Phi = k_{pyr}[pyridine] / (k_{pyr}[pyridine] + k_x[oxygen donor]) \qquad eq 2$$

$$\Phi_0/\Phi = A^{\circ}_{ylide}/A_{ylide} = 1 + k_x[oxygen donor]/k_{pyr}[pyridine]$$
 eq 3

1 PCC absorbtion reference

Platz, M. S.; Modarelli, D.A.; Morgan, S.; Toscano, J. P. Progress in Reation Kinetics;
 Rodgers, M. A., Ed.; Elsevir: Oxford, 1994; Vol. 19, p 93 and reference therein.



Figure 2.10 Rate measurements by ylide probe method for **PCC:** + N-Oxides donors

In eq 2 and 3, Φ is the quantum yield of pyridinium ylide formation in the absence of a second trap and Φ is the quantum yield of the of pyridinium ylide formation in the presence of oxygen donors. A[°]_{ylide} is the intensity of absorption of pyridinium ylide in the absence of the oxygen donor while A_{ylide} is the intensity of absorbance of the same species in the presence of oxygen donors. The plot for the reaction of **PCC**: with pyridine-N-oxide is shown in Figure 2.1.x. The slope of the line is equal to k_x/k_{pyr} [pyridine]. The values for k_x were than calculated by using the known value for $k_{pyr} = 3.5\pm... \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ (from ref 18), and known concentrations of pyridine, following eq 5 and 6 derived from eq 3.

$$k_{x}[\text{oxygen donor}] = [(A^{\circ}_{ylide}/A_{ylide}) - 1]k_{pyr}[pyridine] \qquad eq 4$$

$$k_x = [(A^{\circ}_{ylide}/A_{ylide}) - 1] k_{pyr}[pyridine]/[oxygen donor]$$
 eq 5

Bimolecular rate constants of $2.2\pm$.. x 10^9 M⁻¹s⁻¹ and of 2.1×10^9 M⁻¹s⁻¹ were obtained for **PCC**: abstracting oxygen atom from **PNO** and **MNO**, respectively.

Alternatively, k_x can be obtained as the slope of the plot of observed rate constant of either the decay of the carbene using the kinetic expression in eq 4 or the growth of

pyridine ylide versus oxygen atom donor concentration using the kinetic expression in eq 1.

$$k_{obs} = k_0 + k_x[oxygen donor]$$
 eq 6

Such a plot constructed from the pseudo-first order rate constants for the decay of the PCC versus [oxygen donor] in acetonitrile yielded a value of $k_x = 2.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ for N-Me-morpholine N-oxide which is exactly teh same with the one obtained by Stern-Volmer quenching of the yield of ylide.

Fl: rate constants for the oxygen atom transfer from N-oxides to spin-equilibrated fluorenylidene Fl: have been measured by Stern-Volmer quenching of the acetonitrile ylide of **Fl:** in acetonitrile solution. After irradiation of **DAF** in Ar saturated acetonitrile solution three transients are observable, centered at 400, 470, and 500 nm.³



Figure 2.11 Rate measurements by ylide probe method for Fl: + N-Oxides donors

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R. L.; Wright, B. B.; Leyva, E.; Platz, M. S. J. Phys. Chem. 1987, 91, 6677.

b).Senthilnathan, V. P.; Platz, NM. S.; J. Am. Chem. Soc. 1980, 102, 7637.

c) Wong, P. C.; Griller, D.; Scaiano, J. C. J. Am. Chem. Soc. 1981, 103, 5934.

The half life time of spin equilibrated **FI:** in acetonitrile is ~17 ns which corresponds to a rate constant of 2.1 x 10^6 M⁻¹s⁻¹, ⁴ which is assumed to be the rate constant for the formation of the **FI:** acetonitrile ylide. Using Stern -Volmer methods similar to that described above for pyridine, we measured the rate constant of oxygen abstraction from pyridine N-oxide and N-Methylmorpholine N-oxide. Fresh prepared deoxygenated solution of **DAF** were used for each concentration of oxygen donor. The rate constant for oxygen abstraction was determined to be $k_x = 2.2 \times 10^9$ M⁻¹s⁻¹ for N-Me-morpholine N-oxide.

⁴ Jackson, J. E.; Soundararajan, N.; Platz, M. S.; Doyle, M. P.; Liu, M. T. H. 1989, 30, 1335.

	ff(Ecalc ⁻ 1arcus)							49.195	7.4725	1.3275	1.58	-7.3025	-11.6275	-5.705	-5.865	9.7375	2.3525
	cus Dil EN							-59.275	-52.4425	-65.8675	-50.72	-24.2175	-37.6525	-22.505	-48.755	-44.8575	-35.1725
	/2 EMan							2.25	1.41	8.91	575	5.16	3.66	325	2.82	485	985
	(E _{xx} +E _{yy})							4	-9	-9	-55.	-10	-7	-10.	4	-29.	-36.
	rgyxy calc. (-87.5	ŝ	-35.32	-50.32	-23.65	0	-10.08	-44.97	-64.54	-49.14	-31.52	-49.28	-28.21	-54.62	-35.12	-32.82
	Y2 Ener	-8.1	-205.7	-26.95	29.29	96.47		108.78	-19.02	8.9	40.93	115.57	-85.84	-48.14	1.24	37.37	63.42
	Oxirane CX2OC								57	L	12		L1	12	14	61	5
	Energypot							-68	35.8	12.1	19.4	-32.2	-55.9	-48.7	-23.7	-61.4	7.2
	CX20+CY	79.4	-208.7	8.37	79.61	120.12		-98.7	25.95	73.44	90.07	-84.05	-36.56	-19.93	55.86	72.49	96.24
	CY2 (111	-67	57.5	105	122		-67	57.5	105	122	57.5	105	122	105	122	122
	CX20	-31.5	-142	-49.1	-25.3	-1.45		-31.5	-31.5	-31.5	-31.5	-142	-142	-142	-49.1	-49.1	-25.3
	Y	Н	ц	บ	Br	I		ц	บี	Br	I	บ	Br	Π	Br	Π	Ι
į	×	H	щ	บ	Br	Ι		Η	H	Η	Η	щ	ц	щ	บ	บ	Br

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	us DEcalc-	DEMarcus						75 14.213	47 7.518	18 7.1945	75 3.022	22 -9.852	93 -11.067	75 -9.15	27 -14.641	57 -4.103	75 8.1155
	DE _{12Marc}							3 0.5	7 -23.4	8 -37.9	8 -19.4	2 -0.2	8 -14.6	3.	5 -10.7	8 -4.1	8 -6.76
	4E							.45 -65.8	415 -129.	.95 -163.	.32 -97.2	355 31.34	0.7 -2.8	.93 63.7	565 -66.6	345 -0.13	.57 -34.2
	: 0.5*	(E ₁₁ +E ₂₂	2	· 00	6	2	6	8 -16	9 -32.4	3 -40	3 -24	4 7.83	- 9	4 15	8 -16.0	6 -0.0	80 80 80
	DE ₁₂ calc		-26.	23.	-8.12	-25.	8.0	14.78	-15.92	-30.72	-16.45	-10.07	-25.7		-25.36	-8.2	1.34
	DEpot		4	2 C	C 0	1 0	2 0	.6 68.1	35.87	57 12.13	19.38	8 -32.2	3 -56	5 -48.7	61 23.75	56 -16.5	15 7.21
	CY ₂ +	CX2	62 (2 -208	5 8.3	9.67 (5 120.1	-30	61.8	9 85.5	9 109.4	2 -116.2	2 -92.5	2 -68.6	9.67 6		9 103.4
	CX_2		5 110.6	2 -67.	1 57.4	3 104.9	5 121.0	2 110.9	1 110.9	3 110.9	5 110.9	1 -67.2	3 -67.2	5 -67.2	3 104.9	5 57.4	5 104.9
theory	CY_2O		7 -31	9 -14	1 -49.	1 -25.	8 -1.4	2 -14	1 -49.	7 -25.	7 -1.4	4 -49.	2 -25.	3 -1.4	2 -25.	3 -1.4	8 -1.4
of Marcus	ylide		4 22	7 -184.	7 0.24	1 54.4	2 128.1	7 -83.91	5 10.02	4 42.71	7 73.61	5 -94.12	6 -62.3	3 -25.3	6 30.49	9 64.2	4 97.58
s by use c	CX ₂ 0+	CY2	62 6	2 -208.	5 8.3	9.67 6	5 120.1	2 -98.	5 25.9	9 73.4	5 90.0	5 -84.0	9 -36.5	6 -19.9	9 55.8	5 72.4	6 96.2
th analysi	CY2		5 110.0	42 -67.2	.1 57.45	.3 104.9	45 121.6	.5 -67.2	.5 57.45	.5 104.9	.5 121.6	42 57.45	42 104.9	42 121.6	.1 104.9	.1 121.6	.3 121.6
Ylide pai	$Y CX_2($		H -31	н Н	CI -45	Br -25	I -1.	F -31	CI -31	Br -31	I -31	CI -1-	Br -1	I -1	Br -45	I -45	I -25
A7	X		н	Ц	บ	Br	Π	Η	Η	Η	H	ц	щ	Ц	บ	บ	Br

158

path-I	S analy	vsis by use of	Marcus theory					
×	۲	ΔE	TSylide CX	20+CY2	E _{xy} calc.	$(E_{xx}+E_{yy})/2$	E _{xy} E	calc-
							Marcus _{Er}	Marcus
Η	Η		46.1	79.4	-33.3			
ц	ц		-182.4	-208.7	26.3			
บิ	บ		16.4	8.4	8.1			
Br	Br		79.9	79.6	0.3			
Ι	Ι		131.6	120.1	11.5			
Η	ц	68.1	-82.1	-98.7	16.6	-3.5	13.5	3.1
Η	บ	35.9	31.4	25.9	5.4	-12.6	-3.7	9.1
Η	Br	12.1	53.5	73.4	-19.9	-16.5	-13.5	-6.4
Η	Ι	19.4	94.5	90.1	4.4	-10.9	-6.1	10.5
ц	Ū	-32.2	-91.4	-84.1	-7.3	17.2	9.1	-16.4
ц	Br	-56	-60.9	-36.6	-24.3	13.3	-0.7	-23.6
ц	Ι	-48.7	-25.1	-19.9	-5.2	18.9	6.7	-11.9
C	Br	23.8	4	55.7	-6.9	4.2	10.1	-17.0
Ü	Ι	-16.5	86.4	72.5	13.9	9.8	5.6	8.2
Br	Ι	7.2	108.8	96.2	12.6	5.9	Τ.Τ	4.9

A8 Ylide p

$\Delta E (kcal/mol)^a$	HF	MP2	QCISD	B3LYP
Singlet ¹ C _{2v}	-3.1	-3.3		
Singlet ${}^{1}C_{1}$	-3.3		-4.3	
Triplet ³ C	-0.6	-1.1	-1.1	-1.1

B1 Calculated energies for $CO_2 + :CH_2$ complexes..

^a Calculated at the same level of theory, in respect with $CO_2 + \frac{1}{CH_2}$ or $\frac{3}{CH_2}$.

B2 Seleced IR frequencies (nm) of the possible intermediates.

1	1 2	³ 2a	³ 2s ^b	³ 3 p
1210	1168	1210 vs	1204	1225 vs
1456	1424	1425	1407	1408
1974 vs ^a	1949	1879 vs	1540 vs	1667 vs
2967	2991	2973	2987	2989
3058	3142	3103	3120	3099

^a very strong

	$v_{C=O}$ (cm ⁻¹))	v_{C-O} (cm ⁻¹)
di-Methyl α-lactone ^a	1900		
di-(Trifluoro) α -lactone ^a	1975		
di- <i>n</i> -Butyl- α -lactone ^a	1895		1163
$1 (\alpha$ -lactone)	1974 ^{HF} ; ¹	MP2	1210
³ 2a	1879 ^{HF} ; ¹	MP2	1210
³ 3p	1667 HF; 1	MP2	1225

B3 Experimental IR data existent in the literature.

^a From Chapman, O. L.; Wojtkowski, P. W.; Adam, W.; Rodriquez, O.; Rucktaschel, R. J. Am. Chem. Soc. **1972**, 94, 1365-1367.

	alfa-lactone	ylide	diradical	diradical	diradical
	1	¹ 2	³ 2a	³ 2s	³ 3p
Bond Length					
O(1)-C(2)	1.170;1.200	1.148;1.190	1.161;1.193	1.199;1.168	1.191;1.208
C(2)-O(3)	1.302;1.342	1.225;1.220	1.322;1.355	1.335;1.304	1.337;1.341
O(3)-C(4)	1.480;1.539	1.353;1.460	1.376;1.389	1.410;1.392	2.329;2.304
C(4)-H(5)	1.074;1.085	1.070;1.090	1.070;1.078	1.080;1.080	
C(4)-H(6)	1.074;1.085	1.069;1.090	1.073;1.080	1.080;1.071	
C(2)-C(4)	1.453;1.448		2.309;2.324	2.335;2.323	1.453;1.476
Bond Angle					
O(1)-C(2)-O(3)	139.5;138.9	146.4;152.0	128.1;126.4	129.9;130.8	121.1;122.6
O(1)-C(2)-C(4)	155.2;154.2				
O(3)-C(2)-C(4)	65.3;66.8				
C(2)-O(3)-C(4)	61.7;59.8	143.1;147.0	117.6;115.7	116.5;118.9	
C(2)-C(4)-O(3)	53.0; 53.3				
C(2)-C(4)-H(5)	120.7;120.9				
C(2)-C(4)-H(6)	120.7;120.9				
O(3)-C(4)-H(5)	113.8;113.2	113.0	111.8;111.8	116.5;115.7	
O(3)-C(4)-H(6)	113.8;113.2	110.3	116.8;117.1	116.1;115.7	
H(5)-C(4)-H(6)	116.7;116.6	124.4;114.0	121.5;123.0	123.9;122.7	120.8;120.9
Dihedral					
O(1),C(2),O(3),C(4)	180.0;180.0	130.6;134.0	178.6;177.9	0.0;0.0	
O(1), C(2), C(4), O(3)	180.0;180.0				
O(1),C(2),C(4)H(5)	81.9;82.7				
O(1),C(2),C(4),H(6)	-81.9;-				
	82.7				
O(3),C(2),C(4),H(5)	-98.1;97.3				
O(3),C(2),C(4),H(6)	98.1;-97.3				
C(2),O(3)-C(4),H(5)		62.7	174.8;167.9	79.3;76.98	
	111.5;112.2				
C(2),O(3)-C(4)-H(6)	111.5;112.2	152.9	28.2;18.2	79.3;76.98	

B4 Intermediates geometry data

^a values optimized at HF/6-31G* level ^b values optimized at MP2/6-31G*//MP2/6-31G* level

I aviv AJ.J. Calculation IIIIII	IIIA UIUIBIUS						-	
Ab initio method	11	31	$^{1}2 = TS3$	³ 2а	³ 2s	3 3p	3 3 8	¹ 3p ^a
NIMAG b	0		1	0	0	0	1	1
HF geometry HF/6-31G* HF/6-31G* with zpe corr. MP2/6-31G*//HF/6-31G* MP4/6-31G*//HF/6-31G*	-226.566756 -226.524435 -227.1701637 -227.2090601	.4706 .4309 .0172 .1655	.4125856 .37629 .055803 .1010932	.5220637 .484378 .0972632 .1395375	.5239637 .485846 .0979298 .1398913	.5538611 .511627 .0826197 .131944	.5397588 .5033448 .0702096 .1189609	.4758526 .4394910 .0563586 .1002004
MP2 geometry MP2/6-31G*//MP2/6-31G* MP2/6-31G* with zpe corr. MP4/6-31G*//MP2/6-31G*	-227.1753173 -227.136044 -227.2156467	.0859	.0471677 .012535 .0945938	.0859311 .05030 .1297811	.0863233 .050325 .1297636	.0840187 .0147875 .1337309	.0728282 .038610 .1223511	.0674556 .0349960 .1144999
G2 MP2(full)/6-31G* QCISD(T) G2	-227.1905005 -227.3284135 -227.4939909		.0622798 .2112663 .380767	.1006275 .2488095 .410324	.1010062 .2385126 .4093249	.0988036 .255366 .4157187	.087431 .2410656 .4016901	.0822282 .2296321
^a Acetoxyl staggered structure opt	imized at HF/6-31G*	level goe	s to alfa-lacto	ne (see text); ^b	Nimag =the nun	nber of imagina	ry frequencies o	btained by

Table A3.5: Calculated minima energies

vibrational analysis.

B6 Calculated Transition stat	es Energies							
	1ST ¹	¹ TS2	¹ TS3	³ TS4	³ TSa	³ TSs	3TS5	3TS6
	¹ R- ¹ 1	1– ¹ P	IR-IP	³ R_3 2	³ 2a- ³ 2s	³ 2rot	3 2 –3P	³ R- ³ 3p
HF geometry HF/6-31G* HF/6-31G* with zpe corr. MP2/6-31G*//HF/6-31G* MP4/6-31G*//HF/6-31G*	-226.5012 -226.5012 -226.4647 -227.0880 -227.1327	.50812 .47414 .11491 .15795	.412586 .37629 .055803 .101093	.420512 .385626 .997124 .044310	.509627 .47265 .067237 .110204	.518831 .481667 .075491 .117682	.494189 .459453 .062847 .113085	.5059613 .473143 .0698523 .1147002
MP2 geometry MP2/6-31G*//MP2/6-31G* MP2/6-31G* with zpe corr. MP4/6-31G*//MP2/6-31G*		.12079 .08436 .16609	.047168 .001253 .094594	.001823 266.9686 .048513	.070206 .03502 .114305	.078759 .04395 .122108	.044755 .01218 112243	.0643827 .031910 .113647
G2 MP2(full)/6-31G* QCISD(T) G2		.135640 .278700 .450427	.062280 .211266 .380767	.016468 .169032 .336395			.058918 .223022 .381868	.167889 .300741 .462341

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B7 Cartesian coordinates and energies for the species in Chapter 3

¹CH₂ singlet at G2:

Energy G2=-39.0583994; NImag=0 H 0.862245 0.000000 -0.523019 C 0.000000 0.000000 0.174340 H -0.862245 0.000000 -0.523019

³CH₂ triplet at G2:

Energy G2=-39.0690041; NImag=0 H 0.9823994481 0. -0.3313065703 C 0. 0. 0.1104355234 H -0.9823994481 0. -0.3313065703

CO singlet at G2:

Energy G2=-113.1774964; NImag=0 O 0. 0. 0.4929593158 C 0. 0.-0.6572790877

CO₂ singlet at G2:

Energy G2=-188.3613201; NImag=0 O 0. 0. 1.1432643 C 0. 0. 0. O 0. 0. -1.1432643

¹H₂CO singlet at G2:

Energy G2=-114.3389107; NImag=0 H 0. -0.9341725696 -1.1246980027 C 0. 0. -0.5364297749 O 0. 0. 0.6834968319 H 0. 0.9341725696 -1.1246980027

³H₂CO triplet at G2:

Energy G2=-114.2170052; NImag=0 H 0.961359272 0. -1.0956690211 C 0. 0. -0.6060668323 O 0. 0. 0.7284673795 H -0.961359272 0. -1.0956690211

$^{1}\alpha$ -Lactone singlet at G2:

Energy G2=-227.4939909; NImag=0 O,-0.8959712153,-0.5939595636,-0.1256176739 C,0.5837534797,-1.0105930933,-0.2137323168 H,0.891985264,-1.6711811933,0.5908347229
C,0.072856026,0.3155835795,0.0667433906 H,0.891985264,-1.2888680055,-1.2168613377 O,0.18051777,1.4852228488,0.3141126953

³α-Lactone triplet at HF/6-31G*

Energy HF=-226.4705866; NImag=0 O,-0.8242034733,-0.0359189632,-0.6370710623 C,-0.7831445652,-0.0538373395,0.781145306 C,0.3508133382,-0.4006542725,-0.0623133832 H,-1.3444676895,-0.8437410168,1.2450167176 H,-0.8304012471,0.9156196955,1.2435122308 O,1.4203105106,0.3678028374,-0.2131189983

³2anti triplet intermediate

Energy G2=-227.410324; NImag=0 0,3

H,-2.5023236365,-0.4823244738,0.1644361944 O,-0.4580683111,-0.4655363305,0.0093331549 C,-1.6849812127,0.1818084037,-0.065561153 C,0.6331566642,0.3367752059,-0.0118725154 O,1.7722841397,-0.0177147775,0.0072681338 H,-1.700455701,1.2368316795,0.1673555057

³2syn triplet intermediate

Energy G2=-227.4093249; NImag=0 0,3 0,1.4253821599,0.4630913079,-0.0071175146

C,0.7511984437,-0.5270083266,0.0074967265 O,-0.5832349449,-0.6654934857,0.0114303727 C,-1.336936391,0.5055555979,-0.0624886475 H,-0.836562224,1.4267137209,0.1973556742 H,-2.3861878121,0.3212200734,0.098092987

³3planar at G2

Energy G2=-227.4157187; NImag=0 0,3 O,-0.375442133,1.2846508313,0. O,1.2943980737,-0.2016641477,0. C,-0.0018625352,0.1358898973,0. C,-0.8374173368,-1.0784320707,0. H,-1.9083137909,-0.9381470621,0. H,-0.4076545035,-2.0704933663,0. ¹**3planar** optimized at HF 0,1 HF=-226.5667565 (α-lactone)

³3staggered at G2

Energy G2=-227.4016901; NImag=1 0,3 O,-1.3419580017,0.1055531533,0. O,0.6293799304,1.1559303504,0. C,0.0000595279,0.1110863865,0. C,0.6102690829,-1.2524322569,0. H,1.0193264527,-1.6218964033,0.9305417839. H,1.0193264527,-1.6218964033,-0.9305417839.

³C₁ triplet complex

Energy QCISD=-227.1295055; Nimag=0 0,3 O,0.8756760345,1.1886337984,-0.0270843777 C,0.8902423618,0.0157910339,-0.0284213522 O,0.917907612,-1.156811884,-0.0301776463 C,-2.3529340738,-0.0419490249,0.0763475906 H,-2.801982751,0.9429507083,0.084251884 H,-2.7705361489,-1.0405780772,0.086286877

Energy B3LYP=	Nimag=0
Energy MP2=	Nimag=0
0,3	
0,0,0.8539094176,1.184548	8299,0.0018501063
C,0,0.8918255514,0.011694	1918,0.001454723
O,0,0.942720152,-1.160735	4612,0.0020114075
C,0,-2.3756958447,-0.03030	045853,-0.0667543975
H,0,-2.7592109412,0.95146	44338,0.1820340007

H,0,-2.7106038559,-1.0303090223,0.1788719354

¹C_{2v} singlet complex at

Energy HF = -226.511438965 NImag=0 0,1

C,0,-0.8664454162,-0.0007494801,-0.0043767194 O,0,-0.9019260711,-0.0037133389,1.1388563473 O,0,-0.8904147086,0.0021623787,-1.1479086167 C,0,2.2729097566,0.0019757356,0.0114728044 H,0,2.9506799921,-0.8583854299,0.0126823019 H,0,2.9492602034,0.8634355788,0.0171593429

Energy MP2=-227.0830709 NImag=0 0,1

C,0,0.,0.,2.1881324482 C,0,0.,0.,-0.8360577795 O,0,0.,-1.1790122496,-0.867104503 O,0,0.,1.1790122496,-0.867104503 H,0,0.8646349464,0.,2.8806120176 H,0,-0.8646349464,0.,2.8806120176

¹C₁ singlet complex at

 $\begin{array}{l} HF\\ Energy HF = & -226.5114387; Nimag=0\\ 0,1\\ C & -0.0569508 & 0.0013784 & 0.8629406\\ O & 0.9029210 & 0.6165304 & 0.9550486\\ O & -1.0207462 & -0.6136905 & 0.8305619\\ C & 0.1492875 & -0.0035842 & -2.2639478\\ H & 0.6560849 & -0.7306272 & -2.9074249\\ H & -0.2675024 & 0.7211421 & -2.9714159\\ \end{array}$

¹TS1 singlet at HF/6-31G*

Energy HF=-226.5012017; NImag=1 0,1 O, 0.301752, 1.007470, 0.000018 C, 1.370051, -0.699051, -0.000038 C, -0.480738, 0.127541, -0.000013 H, 1.951778, -0.449479, 0.879895 H, -1.952125, -0.449226, -0.879668 O, -1.456724, -0.466499, -0.000008

¹TS2 singlet at G2

Energy G2=-227.4504276; NImag=1 0,1 O, 1.0392416675, -0.7871004626, 0.0000239426 C, 0.9280945472, 0.5364713846, 0.0000163445 C, -0.5694607556, 0.3557411034, -0.0000123948 H, 1.2145872439, 1.1227218537, -0.8977236483 H, 1.2145517058, 1.1227292398, 0.8977628512 O, -1.6118593799, -0.1627402901, -0.0000318053

¹TS3 singlet at G2

Energy G2=-227.3807067; NImag=1 0,1 O, -0.240963, -0.096460, 0.417699 C, -0.337004, 0.263084,1.830369 C, 0.304502, 0.077635, -0.662286 H, -0.142866, -0.685541, 2.325076 H, -1.364973, 0.607747, 1.913069 O, 0.453820, -0.149355, -1.823529

³TS4 triplet at G2

Energy G2=-227.3363951; NImag=1 0,3 O,-1.5945184263,-0.2392600717,0.0593604838 C,-0.4296289217,-0.0514933084,-0.0948726008 O,0.4664317236,0.8913497836,-0.0030400483 C,1.358916897,-0.5273222367,-0.0464221882 H,1.1859118274,-1.6038979562,-0.0095036595 H,2.2630539427,-0.1399264683,0.4067089096

³TS5 triplet at G2

Energy G2=-227.3818684; NImag=1 0,3 0,0.3707816098,-0.0124371966,-1.8868089525 C,0.0015124485,0.4183609418,-0.8833650152 0,0.1258129012,-0.5110845527,0.7155526436 C,-0.5185459254,0.1290582855,1.72403529 H,-0.6321331266,1.2030216962,1.643425476 H,-0.2384220999,-0.2993630649,2.6826033468

³TS6 triplet

Energy G2=-227, 381868; NImag=1 0,3 0,0,0.1356665204,1.2486699258,-0.1728921383 C,0,0.3010729725,0.0420102471,0.0158506409 0,0,1.0731065215,-0.8595885815,0.2161984005

C,0,-1.3321141239,-0.3664039992,-0.094549789 H,0,-2.1006874071,0.2782145297,0.2983021066 H,0,-1.383250019,-1.4445027711,-0.1725573147

³TS7 triplet

Energy HF=-226.5100422 NImag=1 0,3 0,0.5106279,-0.5643490667,-0.14254 C,1.5111329,0.3602559333,0.092737 H,1.2187859,1.3937119333,0.074726 H,2.4383529,0.0543259333,-0.346296 C,-0.6996251,-0.2594940667,0.350398 O,-1.5764011,0.3077729333,-0.155865 0,3

O,-0.6668743766,0.88697623,0.0001585899 H,-1.5427672282,-0.883307246,-0.9213850893 H,-1.5426362837,-0.8835181778,0.9214104737 C,-1.0557021867,-0.5607374519,0.000015085 C,0.297309263,-0.128236379,-0.0000383922 O,1.6213445084,-0.1493926788,-0.0001442825

³TSanti triplet at MP2

Energy MP2=-227.070205; NImag=1 0,3 H,-1.5474173587,-1.0004476722,0.8225714339 O,-0.5208772366,0.6087875765,-0.0928277669 C,-1.4946880499,-0.387360041,-0.0692186924 C,0.716961599,0.2086494615,0.3935135451 O,1.595608974,-0.340685056,-0.1791558531 H,-2.3840778348,-0.0721090141,-0.5924715899 HF=-226.5064849\MP2=-227.0702055\PUHF=-226.5118838 PMP2-0=-227.0741958\S2=2.039\S2-1=2.019\S2A=2.001\RMSD=4.

³TSsyn triplet at MP2

Energy MP2=-227.0787589 0,3 0,-1.3824336307,-0.5277808762,0. C,-0.7664381956,0.5018535002,0. 0,0.5528755691,0.7109712084,0. C,1.372114\6553,-0.4367343504,0. H,1.5012028674,-0.9281187787,-0.9531168462

H,1.5012028674,-0.9281187787,0.9531168462



	G2(0K)	77.185732									225.81516													
	zpe										43.3	43.5												
	MP2/6-31G*	77.066794 148.338643	833.264714	225.467216	910.330510	225.51921		225.434670	225.447693	225.500575	225.497927	225.434769					225.358461	225.396078	225.314516					
	MP4 sp	77.091829 148.369406	833.30757	255.522929	910.399881	225.570281		225.491290	225.505454	225.555663	225.550491	225.374552						225.450888	225.375986					
	MP2 sp	77.065258 148.335567	833.264004	225.464633	910.328877	225.516148		225.431483	225.443544	225.496760	225.492324	225.311467						225.39418	225.311461		-225.376539			
	zpe	18.5 22.0	45.7	48.4		44.5			45.6	46.4	46.3	41.9				23.8	42.3	44.2	41.5				41.9	15.0
Cliapici +	zpe	0.02945 0.03510	0.00728?	0.07705		0.0709			0.07259	0.07398	0.0	0.06684				0.03798	0.06750	0.07044	0.06609		0.07054		?0.06685	0 073 1 47
nic species in	HF/6-31G*	76.8178270 147.894914	832.884083	224.773007	909.706640	?224.814429		224.739129	224.756096	224.80701	224.805003	224.6249636	530.0652783	225.930079	756.085490	909.618579	224.6106635	224.681417	224.6231843	224.715788	-224.66247	224.5854255	224.69622	774 772025
BICS III	PM3	50.7 47.4	36.9	50.0	76.3	31.3		74.1	67.1	46.26	46.23		-104.9	79.8	-109.7	109.0	132.6	0.66		80.7	117.1		110.9	
מוכת בווכו	Exp	54.1	116.9			33.3±	0.45																	
I able A4.1 Calcul	Species	HCCH	CS2	Ncarbene	Scarebene	Imidazol	:	Azetidine	OpAzetidine	Plcis	PltransExp	zwt	DMAD	DiMeCDI	DiMeDiMeOCar	TS3+2Scarb	TS3+2Ncarb	TSHshiftNCcarb	TS stbyst	TS2+2	TSAzetROp	TSAzetROp*	TStoP1	TC AzetRiInvers

Table A4.1 Calculated energies fro the species in Chapter 4





