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## Reactions of Atomic Carbon with Acid Chlorides

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*Reactions of Atomic Carbon with Acid Chlorides*

Daniel B. Herrick '08

*A Thesis Presented to the Department of Chemistry,  
Colby College, Waterville, ME  
In Partial Fulfillment of the Requirements for Graduation  
With Honors in Chemistry*

Submitted May 25, 2008

*Reactions of Atomic Carbon with Acid Chlorides*

Daniel B. Herrick '08

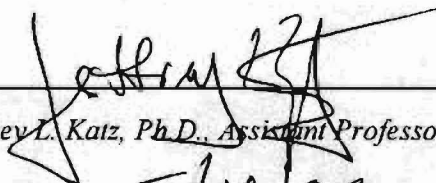
Approved:



\_\_\_\_\_  
(Dasan M. Thamattoor, Ph. D., Associate Professor of Chemistry)

May 19, 2008

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Date



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(Jeffrey L. Katz, Ph.D., Assistant Professor of Chemistry)

5/19/08

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Date

## VITAE

Daniel B. Herrick was born in the beautiful and liberal-minded town of Berkeley, California to Thomas and Christina Herrick on November 28, 1985. Raised in Orinda, California, he remembers spending long hot days at the pool swimming in the summers, and playing the piano, clarinet, and saxophone even through his college years. Daniel graduated from Miramonte high School in 2004, and embarked on a long and adventurous journey when he traveled across the country to spend four years as an undergraduate at Colby College in Maine.

He entered Colby College in September 2004 knowing well he wanted to study the sciences. During his sophomore year, Daniel took organic chemistry with Professor Thamattoor, and found the subject matter both interesting and challenging. Beginning in his junior year, Daniel began working for Professor Thamattoor in his research lab investigating reactions of atomic carbon. It was the work done in the laboratory that made Daniel realize that he wanted to continue to conduct research in chemistry. He will graduate Colby College on May 25, 2008 with a B.A. in Chemistry. In June 2008, he will begin work with Dr. Daniel Hanley at The Johns Hopkins Medical School conducting neurological research. Daniel aspires to obtain his M.D./Ph.D and return to the laboratory.

## ACKNOWLEDGMENTS

I thank my parents, Tom and Chris Herrick, for supporting me through my education throughout my childhood and at Colby. They have encouraged me to strive for success. I also thank my brother, Ben Herrick, for guiding me through my college years, and understanding me when the parents don't.

I also thank Dasan Thamattoor, who, through giving me the opportunity to work in his lab, has given me the most rewarding experience I have had at Colby. He has made me realize the joys of research, and he has provided me with the necessary tools for success as a future scientist. Das has pushed me to excel in science and research, and I am grateful to have had the chance to work with such a fine academic.

Professor Phil Shevlin has also made this research possible. Without his time and energy spent helping us set up this reactor and giving us advice, we would not have the command of the carbon atom reactor that we now have. His trips to Colby were also very helpful in starting our research that this thesis reports.

My friends have also played a key role in my success at Colby. Without them being so understanding of my second life in Keyes, I would not have the support necessary to face the daily struggles in lab.

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## ABSTRACT

This thesis is the first report of reactions of atomic carbon with acid chlorides. Carbon is known to react with phosgene to afford dichlorocarbene. We report a similar reaction with carbon and acid chlorides, generating alkylchlorocarbenes. We examine both the nature of the carbene products generated through deoxygenation and the general reactivity of carbon with the acid chlorides.

We report two ways in which carbon reacts with acid chlorides. First, as expected from prior work with phosgene, carbon deoxygenates the carbonyl group yielding alkylchlorocarbenes, which rearrange as expected. Second, carbon abstracts the chlorine, and generates the acyl radical, which, in the case of pivaloyl chloride and isobutyryl chloride, decarbonylates and a free radical chain reaction mechanism generates the alkyl halide. The reaction of isobutyryl chloride and carbon demonstrates that both the deoxygenation and chlorine abstraction mechanisms compete, as there is a 2:1 ratio of the two processes, respectively.

## INTRODUCTION

### 1.1 History of Atomic Carbon Chemistry

Many of the reactive intermediates in organic chemistry derive their high reactivity from the fact that they involve low-valent forms of carbon that are thermodynamically driven to form four bonds.<sup>1</sup> In the process of forming four bonds, if done in a consecutive and not concerted fashion, atomic carbon traverses other reactive intermediates. For example, as carbon acquires tetravalency, it first takes the form of a carbene, then a carbene, and finally a free radical before becoming tetravalent.

Skell and Harris developed the use of the carbon arc in 1965 to generate and study the reactions of atomic carbon with organic substrates.<sup>2</sup> Since then, both Skell and Shevlin have dominated the field of atomic carbon chemistry, publishing a plethora of papers describing reactions of atomic carbon with numerous substrates. At the conclusion of Professor Shevlin's career in 2003, and thus his atomic carbon research at Auburn University, the Thamattoor group at Colby College with the help of Professor Shevlin adopted the novel research. Working with one of only two functioning atomic carbon reactors in the world, the Thamattoor group has continued atomic carbon chemistry research in the United States. Our group is particularly interested in reactions involving atomic carbon because it provides an alternate method of generating and studying the reactivity of carbenes.



## 1.2 Generating Atomic Carbon

The carbon arc has been used extensively since 1965 to generate atomic carbon by vaporizing graphite. The Thamattoor group utilizes the electric arc to generate carbon atoms. A schematic diagram of the reactor at Colby College is presented in Figure 1.

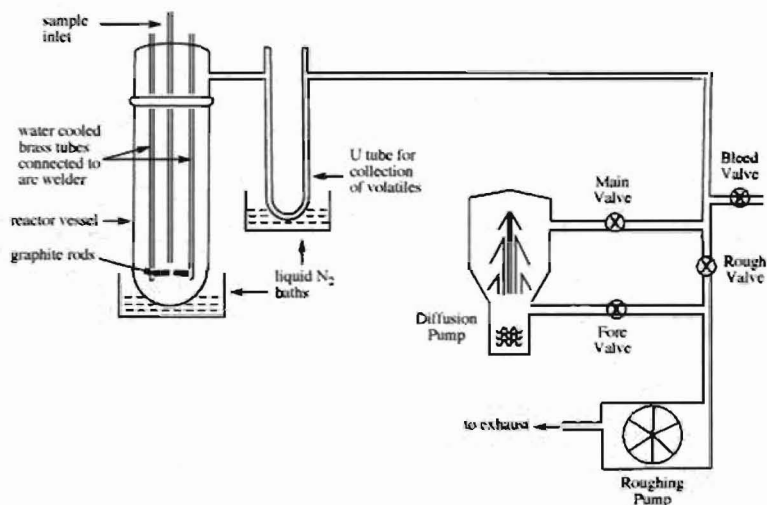


Figure 1 A diagram of the atomic carbon reactor at Colby College

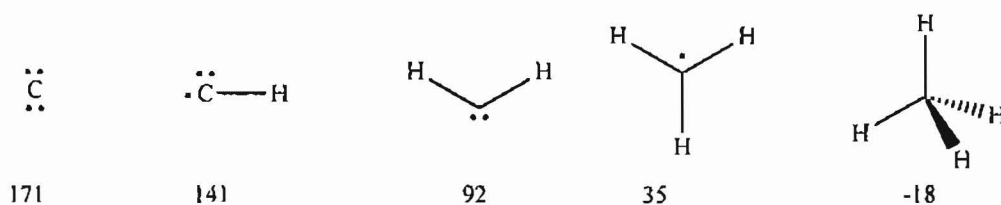
The reactor is evacuated to approximately  $10^{-5}$  torr and an arc is struck between two graphite rods. Each graphite rod is attached to the end of a water-cooled brass electrode, and the electrodes are connected to the arc welder. The arc welder, at low voltage, arcs a current of approximately 90 Amperes between the graphite rods, and vaporizes atomic carbon. The walls of the reactor vessel are cooled to 77K in liquid nitrogen. The organic substrate, introduced through the inlet tube, and atomic carbon are cocondensed on the walls of the reactor vessel. After the reaction is complete, the liquid nitrogen bath is removed and the reactor vessel is warmed to room temperature. The volatile products are trapped in a liquid nitrogen cooled U-tube. The products are removed from the U-tube

and are characterized by gas chromatography-mass spectrometry, nuclear magnetic resonance spectroscopy, and gas-phase infrared spectroscopy.

To perform a mechanistic study on the reaction of carbon with a substrate,  $^{13}\text{C}$  may be packed into holes bored in the ends of the graphite rods and atomic  $^{13}\text{C}$  is generated when the arc is struck. The position at which the carbon atom is incorporated into the products is enriched with  $^{13}\text{C}$ , and  $^{13}\text{C}$  NMR spectroscopy labels the position at which the carbon incorporates itself into the organic substrate.

### 1.3 Energies and Spin States in Atomic Carbon Reactions

A unique quality of atomic carbon chemistry is the abundance of energy the species brings to every reaction it is involved in. The heats of formation demonstrate the capacity atomic carbon has to react with nearly any substrate (Figure 2).<sup>3</sup> There is an inverse relationship between the number of bonds made to the central carbon and the energy of the species, and zero-valent carbon is the most energetic in this series.



**Figure 2** The heats of formation (kcal/mol) of carbon centered reactive intermediates

The ground state of atomic carbon is a triplet [ $\text{C}(^3\text{P})\pi\text{H}_f^\circ = 171$  kcal/mol] with two metastable singlet excited states [ $\text{C}(^1\text{D})\pi\text{H}_f^\circ = 201$  kcal/mol] and [ $\text{C}(^1\text{S})\pi\text{H}_f^\circ = 233$  kcal/mol]. Many of the reactions reported, and the reactions of interest to the Thamattoor

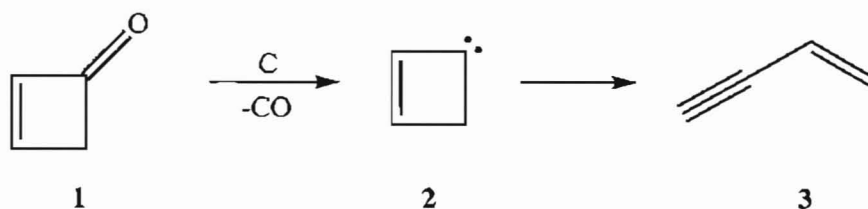
group, involve the  $^1D$  state, which brings with it an additional 30 kcal/mol of energy to its reactions.<sup>4</sup> The singlet state of carbon is thought to deoxygenate carbonyl compounds to afford the often difficult to generate singlet, not triplet, carbenes. Because carbon is such an energetic species, there is often no enthalpic barrier to reactivity between atomic carbon and organic substrates, and reactions are often “downhill” from the time the reaction begins to its completion.

#### **1.4 History of Carbenes**

Carbenes are characterized as highly reactive intermediates containing neutral divalent carbon atoms. Carbene chemistry has an exciting history, beginning with the French chemists Dumas and Regnaults' attempts to prepare methylene by dehydrating methanol with phosphorus pentoxide or concentrated sulfuric acid.<sup>5</sup> In 1862, Geuther proposed that the hydrolysis of chloroform generated dichloromethylene, and this reaction is now a common method used to generate dihalocarbenes.<sup>6</sup> Because of their relatively short lifetimes, in the order of milliseconds to nanoseconds, carbenes were nearly impossible to isolate decades ago. It was not until recently that Arduengo generated, isolated, and obtained an X-ray structure of the first stable carbene.<sup>7</sup> Carbene chemistry is now considered an important area of research in organic chemistry.

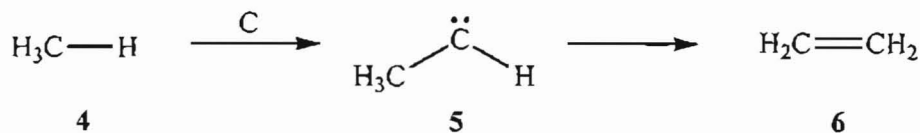
## 1.5 Generating Carbenes By Atomic Carbon Reactions

As atomic carbon achieves tetravalency, it often traverses other reactive intermediates including carbenes. Common reactions of atomic carbon with organic substrates that generate carbenes are deoxygenation, carbon insertion into a sigma bond, and carbon addition to a pi bond. Skell and Plonka were the first to report that deoxygenation of carbonyl compounds by arc-generated carbon is an effective method of preparing carbenes (Scheme 1).<sup>8</sup> When cyclobut-2-enone (1) is reacted with carbon, cyclobutenylidene (2) is formed, and rearranges to but-1-en-3-yne (3).<sup>9</sup>



Scheme 1

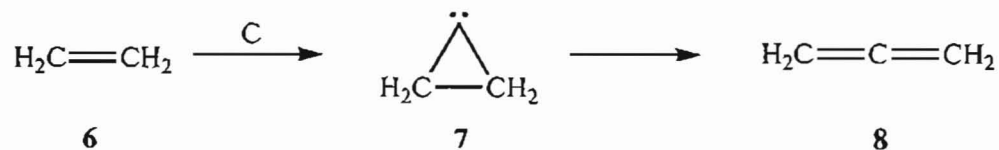
In 1989, Shevlin et. al. reported on atomic carbon, parallel to the reactivity of a singlet carbene, inserting into a C-H bond in methane (4), yielding a carbene intermediate (5) which rearranges to ethylene (6) as a result of a 1,2 H shift (Scheme 2).<sup>10</sup>



Scheme 2

Also imitating the reactivity of a carbene, atomic carbon undergoes  $\pi$ -bond addition to afford cyclopropenylidenes. As Skell et al.<sup>11</sup> demonstrated, the reaction of atomic

carbon with ethylene (6) gives cyclopropenylidene (7), which is known to undergo ring opening to form allene (8) (Scheme 3).



Scheme 3

It should be noted that the same carbene can be generated by reacting atomic carbon with different substrates. For example, deoxygenating an aldehyde and inserting carbon into the C-H bond of a different substrate can afford the same carbene (Figure 3).

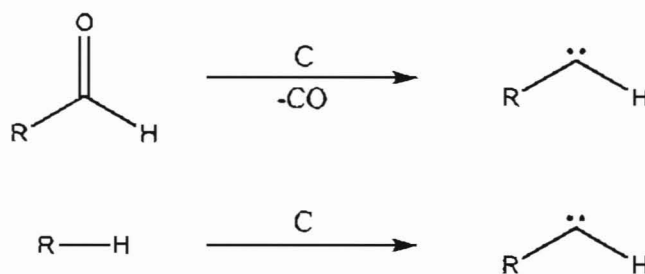


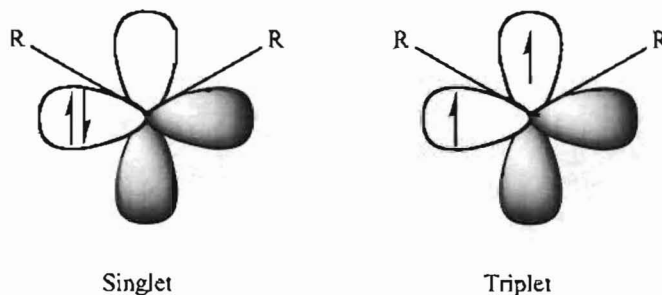
Figure 3 Reactions of carbon with different substrates can yield the same carbene

However, when atomic carbon deoxygenates a molecule, the carbon atom is not incorporated into the substrate as it is with sigma bond insertion and pi bond addition. In a deoxygenation reaction, carbon generated from the arc is lost as carbon monoxide.

### 1.6 Structure and Reactivity of Carbenes

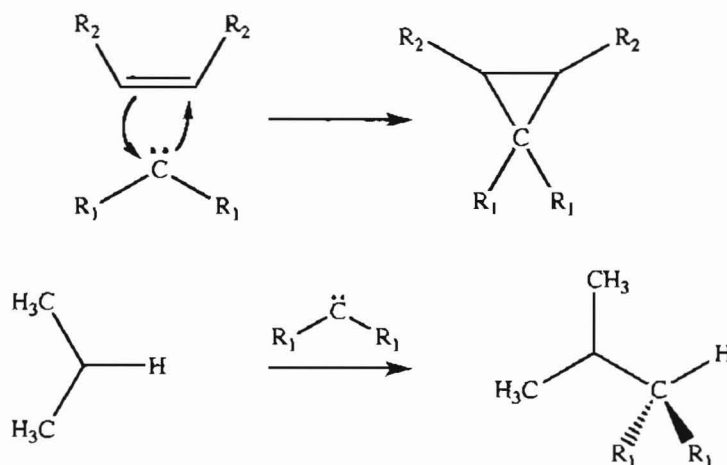
The carbene generated by the reaction of atomic carbon with an organic substrate is characterized by the location of the two non-bonding electrons associated with the central neutral carbon atom. If the electrons are paired, the carbene is in the singlet state, and if the electrons are unpaired, the carbene is in the triplet state (Figure 4). As mentioned

previously, we are most interested in the excited singlet-state ( $^1D$ ) carbon atom, which generates singlet carbenes.



**Figure 4** The singlet and triplet state carbenes

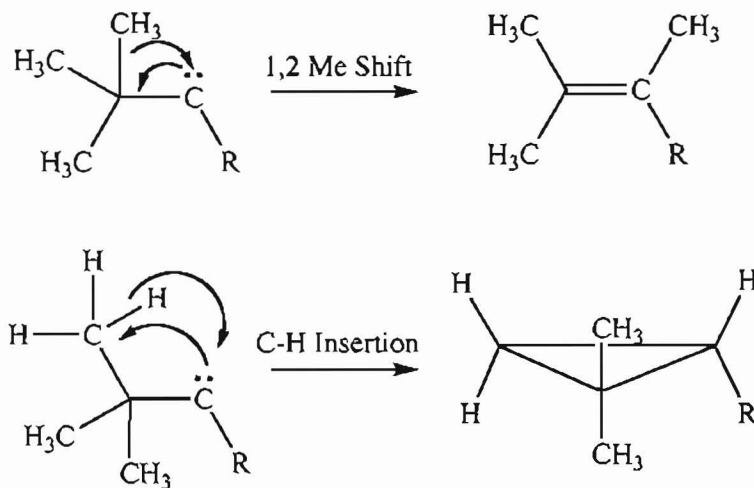
The reactivity of carbenes is similar to the reactivity of atomic carbon, which is predominantly characterized by bond insertion. Addition to the carbon-carbon pi bond is a common route to generating cyclopropanes, and insertion into sigma bonds is also typical of carbene reactivity (Figure 5).



**Figure 5** Carbenes undergoing pi bond addition (top) and sigma bond insertion (bottom)

Intramolecular reactions that carbenes usually undergo are 1,2 and 1,3 C-H insertion, depending on the proximity of C-H bonds to the carbene. Energetically, a 1,2 hydrogen

shift is more favorable than a 1,3 hydrogen shift, and the 1,2 methyl shift, which is especially unfavorable happens to a lesser extent (Figure 6).



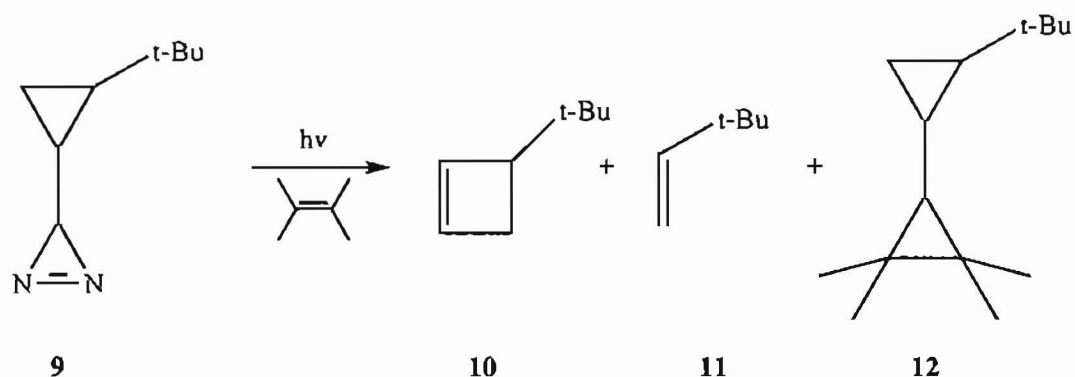
**Figure 6** Intramolecular rearrangements of carbenes. A 1,2 Me shift (top) and a 1,3 C-H insertion (bottom)

Kinetically, intramolecular rearrangement is often favored over intermolecular rearrangement.

### 1.7 Problems with Traditional Carbene Precursors

Although diazirines and diazo compounds are known to generate carbenes upon thermal decomposition, it is sometimes the case that it is the reaction of the precursor itself rather than the free carbene that is being studied. The precursor, in either its ground or excited state, can yield what were thought to be carbene products. Platz and Huang have shown in their trapping studies of the *t*-butylcyclopropylcarbene generated from its diazirine precursor, that the products formed from the experiment are not generated from the carbene intermediate exclusively (Scheme 4).<sup>12</sup> The carbene generated from the thermolysis of the diazirine precursor (9) was trapped by tetramethylethylene (TME).

However, as the concentration of TME was increased, the yield of **12** increased, but the concentrations of the other two products, **10** and **11**, remained the same, therefore demonstrating that they were formed through different intermediates other than the *t*-butylcyclopropyl carbene intermediate.



**Scheme 4**

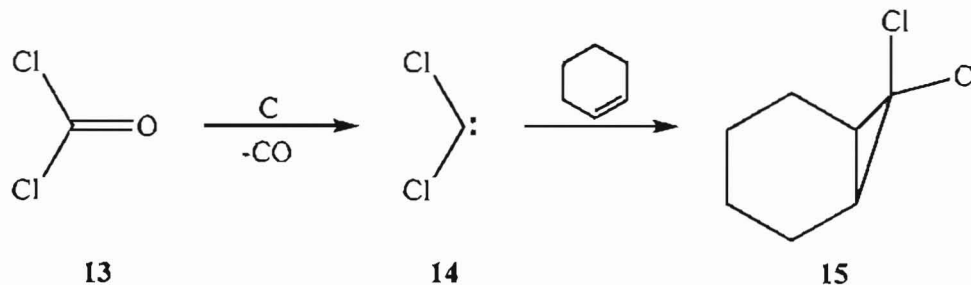
Platz and Huang's experiment shows that generation of carbenes cannot always be accomplished solely with traditional diazo and diazirine precursors, and alternative methods to generate carbenes must be used to verify products resulting from putative carbene reactivity. Because of this uncertainty in the generation of the free carbene through diazirine and diazo precursors, generating carbenes through deoxygenation of carbonyl compounds by atomic carbon has proven to be fruitful.

### 1.8 Reactions of Atomic Carbon with Acid Chlorides

In this study, reactions of atomic carbon with acid chlorides have been explored. There is only one report that describes the deoxygenation of phosgene (**13**) by carbon atoms to

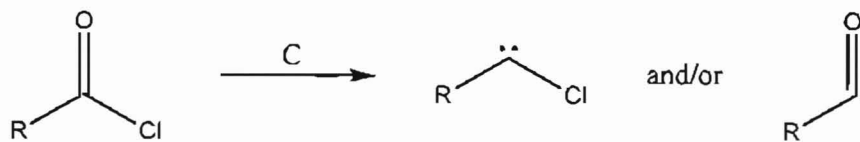


produce dichlorocarbene (**14**), which can be trapped by cyclohexene to afford adduct **15** (Scheme 5).<sup>13</sup>



Scheme 5

We were curious to see if the deoxygenation of phosgene by carbon to form dichlorocarbene can be extended to generate alkylchlorocarbenes from the corresponding acid chlorides. Overall, this study focuses on the reactions of carbon with acid chlorides and the reactivity of the *t*-butyl-, isopropyl-, and methyl- chlorocarbenes resulting from deoxygenation of the corresponding substrate. Because carbon atoms are extremely electrophilic and high in energy, the carbonyl oxygen is not the only site of attack for carbon. We report that the reactions of carbon atoms with acid chlorides proceed by two distinct mechanistic pathways, deoxygenation and chlorine abstraction, depending on the nature of the alkyl group in the substrate (Scheme 6).



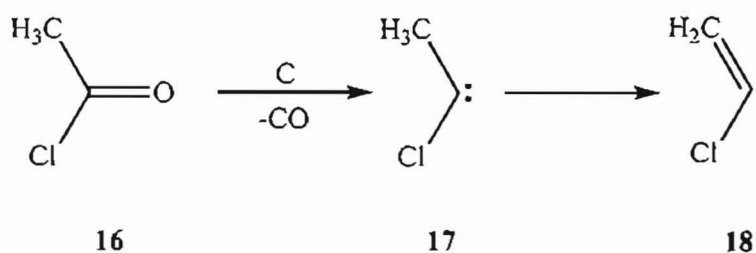
Scheme 6

## RESULTS & DISCUSSION

### 2.1 Reactions of Atomic Carbon with Acid Chlorides

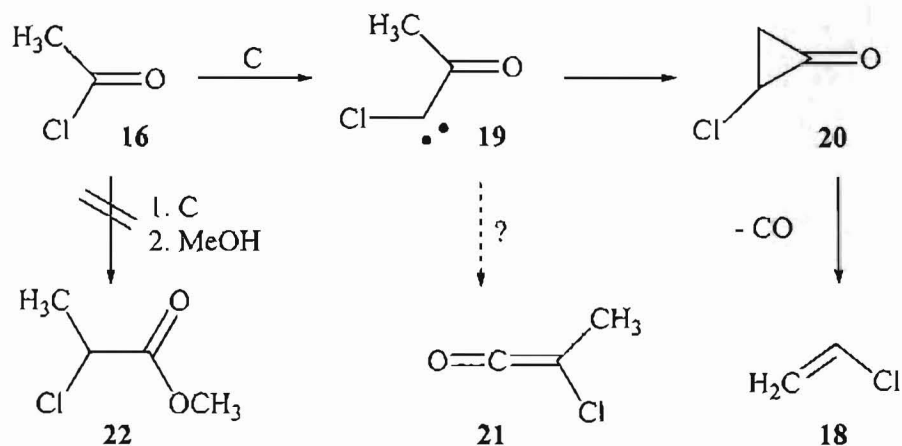
#### 2.1.1 Acetyl Chloride

When arc generated carbon is cocondensed with acetyl chloride (**16**) at 77K, the reaction does produce vinyl chloride (**18**), which we attribute to an intramolecular hydrogen shift of the chloromethylcarbene intermediate (**17**) that results from deoxygenation (Scheme 7).



Scheme 7

It is possible, however, that the carbon could insert into the carbon chlorine bond in **16** to produce acetylchlorocarbene (**19**) (Scheme 8). This insertion is analogous to the reaction of carbon with acid halides to produce alkylhalocarbenes.<sup>14</sup> Intramolecular insertion into a C-H bond could then convert the carbene into the cyclopropanone derivative (**20**), which can lose carbon monoxide to yield **18**.

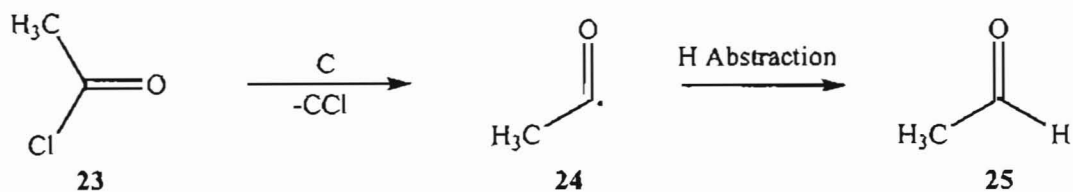


Scheme 8

Although we cannot rule out this mechanism, our attempts to trap chloromethylketene (21), a potential intermediate in the event of a Wolff rearrangement in 20, as the ester 22 were unsuccessful.

Throughout the time the arc was struck, the pressure increased from about  $10^{-5}$  torr to about  $10^{-2}$  torr. Once carbon generation ceased, the pressure quickly decreased to the initial pressure. The pressure change results from the formation of carbon monoxide after deoxygenation of the acid chloride.

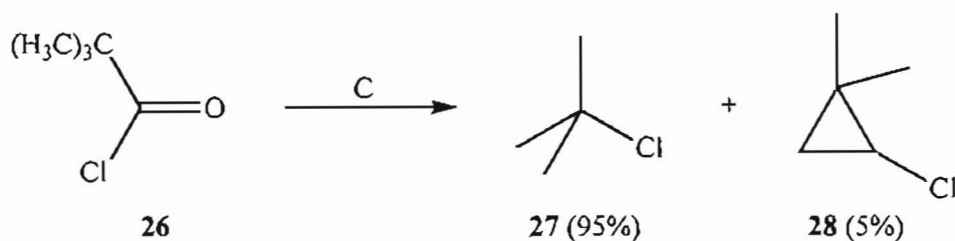
We cannot overlook the possibility of carbon abstracting chlorine from acetyl chloride (23), generating the acyl radical (24) (Scheme 9). If generated, 24 could undergo several processes including decarbonylation, yielding the energetically unfavorable methyl radical, abstraction of hydrogen, yielding acetaldehyde (25), or dimerization, to form biacetyl. The reaction mixture was collected in a gas-phase IR cell, and the IR spectrum did not reveal the presence of acetaldehyde or biacetyl (See Spectra). Also, we were unable to detect chloromethane by GC/MS, which would result from the methyl radical abstracting chlorine from 23 (See Spectra). Another event that could occur is the interconversion of 23 and 24 by a degenerate chlorine exchange.



Scheme 9

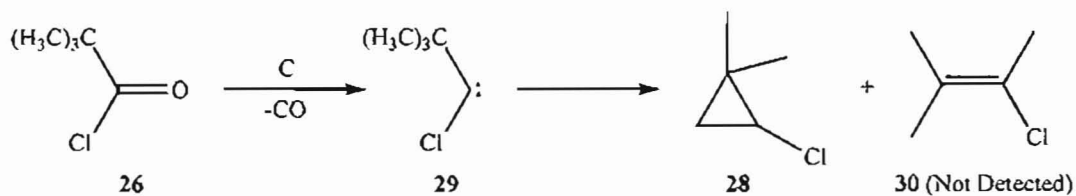
### 2.1.2 Pivaloyl Chloride

The reaction of pivaloyl chloride (**26**) with atomic carbon proceeds by two distinct mechanistic pathways. The major product formed was *t*-butyl chloride (**27**), and only small amounts of 1-chloro-2,2-dimethylcyclopropane (**28**) was produced (Scheme 10).



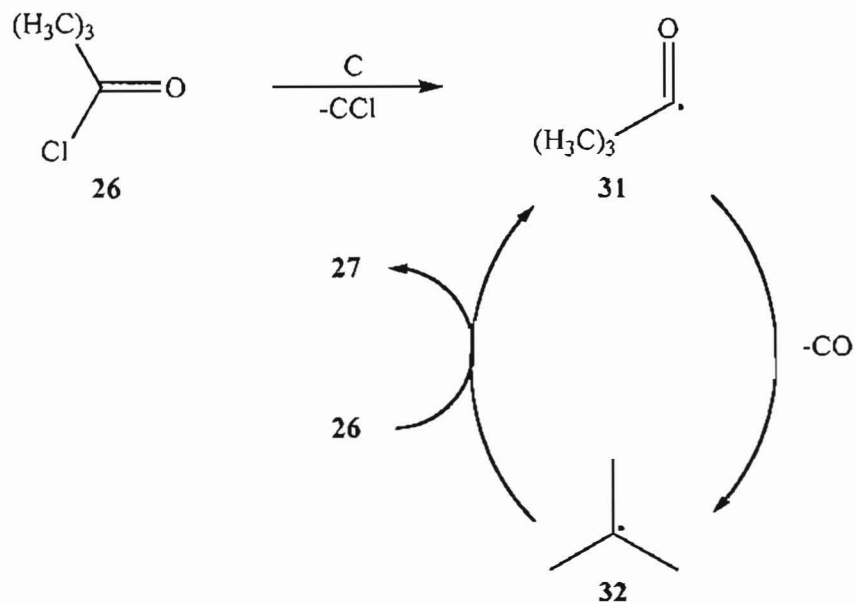
Scheme 10

We attribute the formation of **28** to the deoxygenation of **26**, followed by a known C-H insertion in the *tert*-butylchlorocarbene (Scheme 11).<sup>15</sup> We were not able to detect 2-chloro-3-methyl-2-butene (**30**), which sometimes results from the rearrangement of **29**.<sup>16</sup> However, this does not always occur.<sup>17</sup>



Scheme 11

The deoxygenation pathway in this reaction only accounts for a small percentage of the products resulting from the reaction, and the initially unexpected abundance of **27** in the reaction mixture requires an explanation. We propose a mechanism that involves a free radical chain reaction, which is initiated by atomic carbon abstracting chlorine (Scheme 12).

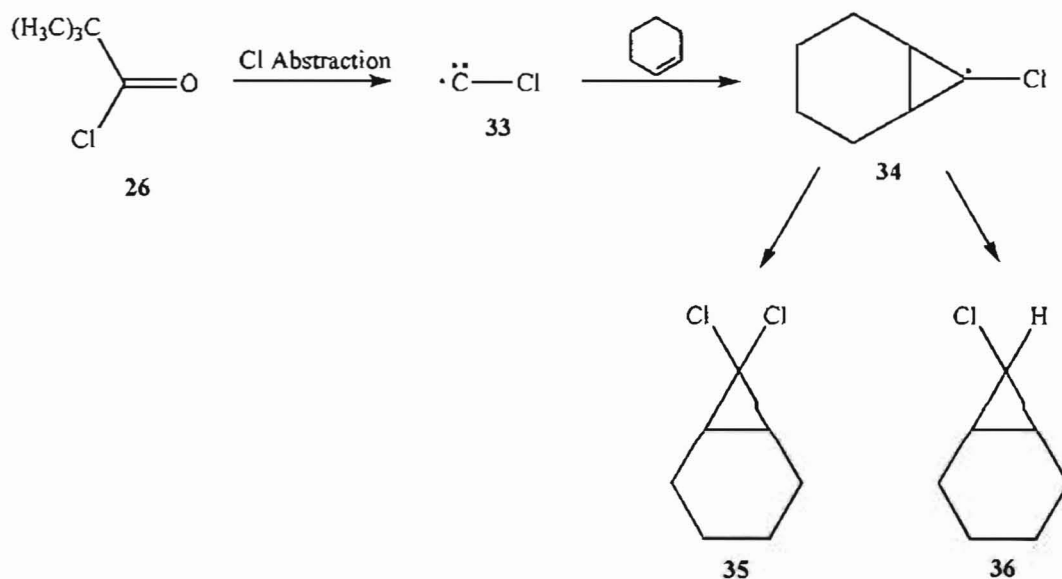


Scheme 12

Chlorine abstraction by atomic carbon generates the pivaloyl radical (**31**). This is similar to halogen abstraction from alkyl halides by atomic carbon, which generates the stable tertiary radical in addition to inserting into the carbon-halogen bond.<sup>18</sup> Decarbonylation of the acyl radical generates **32**, a stable tertiary radical. Chlorine abstraction from **26** by **32** affords **27** and regenerates **31**. This hypothesis is consistent with the observations made in the pressure changes throughout the reaction. When the arc is struck, the initial pressure is approximately  $10^{-5}$  torr, and there is an increase in pressure to about  $10^{-2}$  torr as a result of the formation of carbon monoxide as the deoxygenation mechanism

proceeds. When we stop striking the arc, however, the pressure does not recover quickly in comparison to the reaction of carbon with acetyl chloride. This demonstrates that there is carbon monoxide being released after carbon generation has ceased, and the generation of carbon monoxide in this case is not directly related to the interaction between carbon and the substrate.

We also attempted to trap the carbon-chlorine carbene species (33) with cyclohexene, which would generate a radical intermediate (34) after addition to the pi bond (Scheme 13). 34 could then either abstract chlorine affording 35, or hydrogen affording 36. Both the U-tube and reactor vessel were checked, however neither 35 nor 36 could be detected by GC/MS.

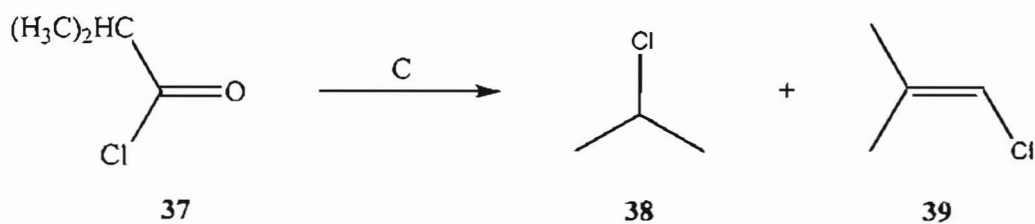


Scheme 13

We would not expect to trap the carbon-chlorine carbene species if the reaction is proceeding through a free radical chain reaction mechanism because this species results from the initiation step in the reaction.

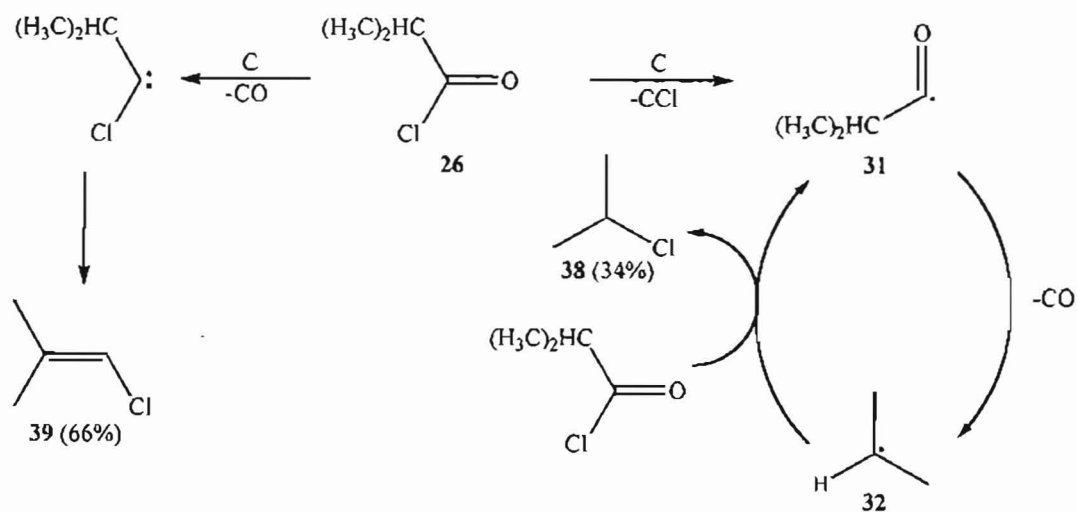
### 2.1.3 Isobutyryl Chloride

The size of the isopropyl group represents an intermediate between the *t*-butyl and methyl groups of the two previous experiments with pivaloyl chloride and acetyl chloride. When cocondensed with atomic carbon, the reaction with isobutyryl chloride (**37**) proceeds through both the free radical chain reaction mechanism and the deoxygenation mechanism, affording 2-chloropropane (**38**) and 1-chloro-2-methylpropene (**39**), respectively (Scheme 14).



Scheme 14

The ratio of **38** to **39** when samples of the neat liquid are analyzed by GC/MS is approximately 1:2 (See Spectra). The intermediate sized alkyl group seems to prompt strong competition between the radical mechanism and the deoxygenation mechanism (Scheme 15).



Scheme 15

The relative ratios of the alkane and alkene demand further investigation into how the nature of the alkyl group affects the reactivity of the substrate with carbon. It is apparent that deoxygenation is favored for smaller alkyl groups, and chlorine abstraction is favored for acid chlorides with larger alkyl groups. Future studies need to focus on computational modeling and reactions of  $^{13}\text{C}$  with acid chlorides to detect if carbon is in any way incorporated into the product.



## METHODS AND MATERIALS

### 3.1 Generating and Reacting Organic Substrates With Atomic Carbon

#### *Assembly of the Carbon Reactor System*

The reactor vessel was removed from the circular cut-out in the reactor cart if it was already in place. Two pre-weighed graphite rods, approximately 2" in length, were secured to each water-cooled electrode, and 1/8" of each graphite rod was allowed to extend out from each electrode towards the walls of the reactor vessel. The sample inlet Y-tube was placed above the graphite rods, perpendicular to the plane of the rods. It was made certain the rods did not come in contact with the inlet tube. The reactor head was then sealed to the reaction vessel, placing the large o-ring between the two glass units. Using the ultratorrs, the U-tube was connected to the reactor head and the flex-hose vacuum line.

#### *Evacuating the Carbon Reactor System*

After opening the bleed valve on the roughing pump, the roughing pump was turned on, and the bleed valve was closed. After assuring the main bleed valve was closed, the roughing valve was opened to begin evacuating the entire reactor. The work dropped to zero, and the fore valve was opened to rough the fore line to the diffusion pump. Once both work gauges dropped to zero, the diffusion pump fan, and then the diffusion pump, were turned on to begin heating the oil in the pump. The substrate was added to the substrate inlet bulb and the inlet bulb remained isolated from the main system. The U-tube was cooled in liquid nitrogen, and the substrate was freeze-pump-thawed. The

roughing valve was then closed and the main valve was opened. The roughing valve and the main valve were never open simultaneously. The cold cathode pressure gauge was turned on and the sample was freeze-pump-thawed an additional two times. Once the pressure dropped below  $10^{-4}$  torr, the reactor vessel was cooled in liquid nitrogen. Water was turned on to cool the electrodes for when the arc was struck. The two electrode leads were plugged into the AC power of the arc welder.

#### *Generating Atomic Carbon and Executing the Reaction*

At the beginning of a striking interval, the pressure was no higher than  $10^{-4}$  torr. The pressure increased to at least  $10^{-3}$  torr by the end of a 10 second striking interval if CO gas was produced in a deoxygenation reaction, or otherwise extruded from the substrate. The substrate inlet valve was opened to introduce the substrate to the well, and if the substrate was not volatile enough to enter the reactor vessel under room temperature, heat was applied with a heat gun. The arc was struck in 10-second intervals while introducing the substrate and the liquid nitrogen level in the Dewar was kept high, as liquid nitrogen boiled off quickly while the arc was being struck. The graphite rods were allowed to cool between each striking interval. To run a control to confirm the products were not formed via pyrolysis as the substrate is entering the well, the substrate was condense on the sides of the well, and then the arc was struck. The arc was not struck while the sample bulb was exposed to the system. Yields were much lower.

### *Post Reaction Procedure*

The arc welder was turned off and the reaction vessel was allowed to cool in liquid nitrogen for an additional 5 minutes. The liquid nitrogen bath was removed from underneath the reaction vessel and the vessel warmed to room temperature while the system was still evacuated using the diffusion pump. The U-tube was kept in liquid nitrogen. After the reactor vessel warmed to room temperature, the system was isolated from the pumps by closing the main valve. The liquid nitrogen under the U-tube trap was changed to a dry ice/acetone bath and the system returned to atmospheric pressure after the bleed valve was opened. The U-tube warmed to room temperature after removing the dry ice/acetone bath; the products that condensed in the U-tube were collected. If the products expected to form were extremely volatile, the U-tube was kept in the dry ice/acetone bath and the cold products were extracted. This was especially important when attempting to quantify, not just detect, reaction products.

## **3.2 Isolating and Analyzing the Products**

### *Isolating Solid Products in the Reactor Vessel*

Products that were not volatile enough to be condensed in the U-tube remained in the reactor vessel. After the reaction was complete, the reactor vessel was removed from the reactor head. The reaction vessel was extracted twice with two 20 mL portions of methylene chloride. The solid carbon was filtered from the mixture using a fitted filter, and excess solvent was removed under reduced pressure.

### *Isolating Liquid Products*

If the products were extremely volatile and not isolable in the U-tube once it returned to atmospheric pressure and warmed to room temperature, a small 5-15 ml flask was attached at the screw-top entry point to access the U-tube to collect the volatiles. After closing the main valve and isolating the system, the small flask was cooled in liquid nitrogen, and the bottom of the U-tube was slowly warmed to room temperature. The flask condensed the volatiles after they were warmed to room temperature. The reactor was returned to atmospheric pressure and the small flask was removed before it was warmed to room temperature. Samples for NMR and GC/MS were taken while the products were cold.

### *Isolating Gaseous Products*

To isolate volatiles in the gas phase, the above procedure was repeated, except the small flask was replaced with a gas-phase infrared cell. The finger extending from the cell was cooled in liquid nitrogen to condense a small amount of sample. Saturating the cell and trapping liquid in the cell negatively affected the spectral data. Before returning the system to atmospheric pressure, the valve on the gas-phase IR cell was closed to keep it evacuated. Once the cell was isolated, the remainder of the system was returned to atmospheric pressure and the cell was removed.

## **3.3 General Reactions of Atomic Carbon With Acid Chlorides**

Using the procedure described above to operate the carbon reactor with organic substrates, acid chlorides, varying by the alkyl group, were reacted with atomic carbon.

Three general reactions were carried out in attempt to generate differently substituted chlorocarbenes, varying by alkyl group. Acetyl chloride, isobutyryl chloride, and *t*-butyl acetyl chloride were each reacted with atomic carbon to generate the *t*-butyl chlorocarbene, the isopropyl chlorocarbene, and the methylchlorocarbene.

### 3.4 Syntheses of Carbon Reaction Products

#### *General Procedures*

Standard synthetic techniques were employed throughout with commercially available starting materials and solvents (Aldrich and Acros). All glassware for the moisture sensitive reactions were oven dried and the reactions ran under dry argon atmosphere. GC/MS data was collected on a Varian 3900 Gas Chromatograph (Factor Four capillary column, VF-5 ms, 30 m, 0.25 mm, 0.25  $\mu$ m) attached to a Saturn 2100T ion trap Mass Spectrometer.  $^1\text{H}$  NMR spectra were obtained on a Varian spectrometer, referenced relative to TMS at 500 MHz. Gas-Phase Infrared spectroscopy data was obtained on a Perkin Elmer spectrometer, using NaCl windows.

#### *Synthesis*

**2-Chloro-1,1-dimethylcyclopropane (28):** The product was prepared by the method of G. L. Closs and L. E. Closs.<sup>19</sup> Isobutylene (30 g, 0.54 mole), condensed from gas in the canister using a dry ice finger, and methylene chloride (18.8, 0.28 mole) were added to a 250 mL three-neck round bottom flask equipped with a stir bar, addition funnel, and low temperature thermometer. The solution was cooled to  $-45^\circ\text{C}$  using a dry ice/acetone bath. Using the addition funnel, methyllithium (110 mL, 0.14 mole) was added over 30

minutes to the stirred solution. Throughout the addition, the temperature remained between  $-50^{\circ}\text{C}$  and  $-40^{\circ}\text{C}$ . The solution was hydrolyzed with 15 mL of water, and then warmed to room temperature. The product was purified using preparative gas chromatography.

***t*-Butyl hypochlorite:** The product was prepared by the method of Mintz and Walling.<sup>20</sup> 500 mL of commercial household bleach was added to a 1-L Round-bottom flask equipped with a mechanical stirrer. The flask was placed in an ice bath with minimal exposure to light, and the temperature was lowered to  $10^{\circ}\text{C}$ . A solution of *t*-butyl alcohol (37 mL, 0.39 mole) and glacial acetic acid (24.5 mL, 0.43 mole) is added at once to the stirred bleach solution. The solution was stirred for an additional 3 minutes after the addition of the *t*-butyl alcohol and acetic acid solution is added.

The reaction mixture is poured into a 1-L separatory funnel, and the aqueous layer is discarded. The organic layer, a yellow oil, is washed with a 50-mL portion of 10% aqueous sodium carbonate, and washed a second time with 50 mL of water. The product is dried over 1 g of calcium chloride and filtered. The product is stored in an amber glass bottle and cooled in the refrigerator.

**2-Chloro-3-methyl-2-butene (30):** The product was prepared by the method of Irwin and Hennion.<sup>21</sup> A 3-neck round-bottom flask equipped with a reflux condenser and a liquid addition funnel was charged with acetic acid (27 mL, 0.47 mole) and 2-methyl-2-butene (25 mL, 0.24 mole). *t*-butyl hypochlorite (6), was added to the reaction mixture over 45 minutes at  $20^{\circ}\text{C}$ . The solution was washed three times, first with water (50 mL),

next with 10% aqueous sodium carbonate (50 mL), and again with water (50 mL). The organic layer is dried over calcium chloride, and 2-chloro-3-methyl-2-butene was isolated using preparative gas chromatography.

**7-Chlorobicyclo[4.1.0]heptane (36):** The product was prepared by the method of G. L. Closs and L. E. Closs.<sup>22</sup> Cyclohexene (33 g, 0.4 mole) and methylene chloride (17 g, 0.2 mole) were added to a 250 mL three-neck round bottom flask equipped with a stir bar, addition funnel, and low temperature thermometer. The solution was cooled to  $-45^{\circ}\text{C}$  using a dry ice/acetone bath. Using the addition funnel, methyllithium (62.5 mL, 0.1 mole) was added over 45 minutes to the stirred solution. Throughout the addition, the temperature remained between  $-50^{\circ}\text{C}$  and  $-40^{\circ}\text{C}$ . The solution was hydrolyzed with 15 mL of water, and then warmed to room temperature. The product was purified using preparative gas chromatography.

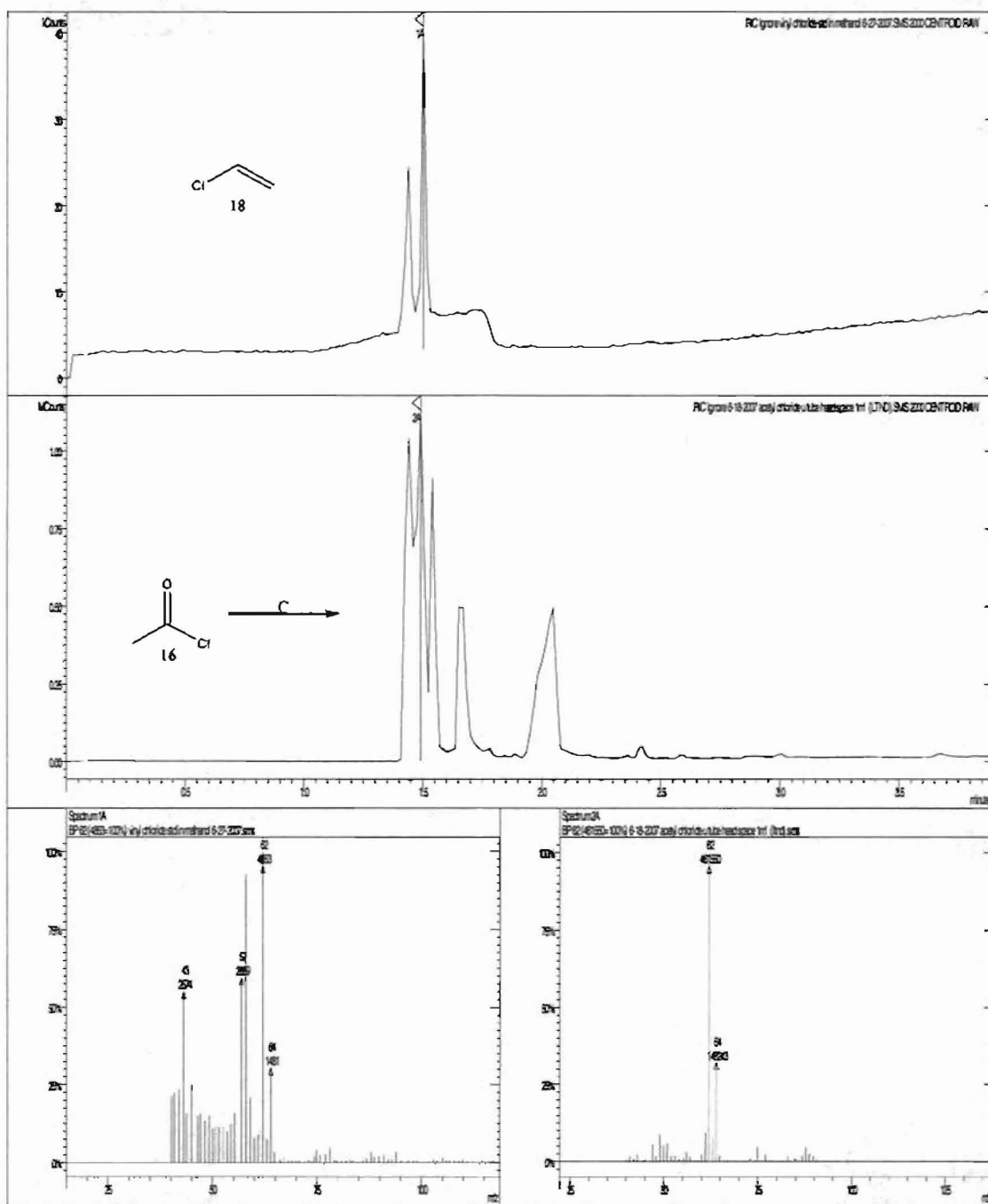
**7,7-Dichlorobicyclo[4.1.0]heptane (35):** The product was prepared by the method of Goh.<sup>23</sup> To a 250-mL round bottom flask equipped with a water condenser, cyclohexene (8.2 g, 10 mmole), chloroform (24.3 mL, 30 mmole), and benzyl triethyl ammonium chloride (1 g) were added. The solution was warmed with a hot water bath. While stirring with a magnetic stir bar, 50% NaOH (32 mL, 80 mmole) was added down the condenser over one half hour. The reaction mixture was refluxed for an additional hour following the addition of NaOH. After cooling the reaction mixture, water (30 mL) and petroleum ether (30 mL) were added in separate portions down the condenser while continuing to stir. The reaction mixture was transferred to a separatory funnel and the lower aqueous

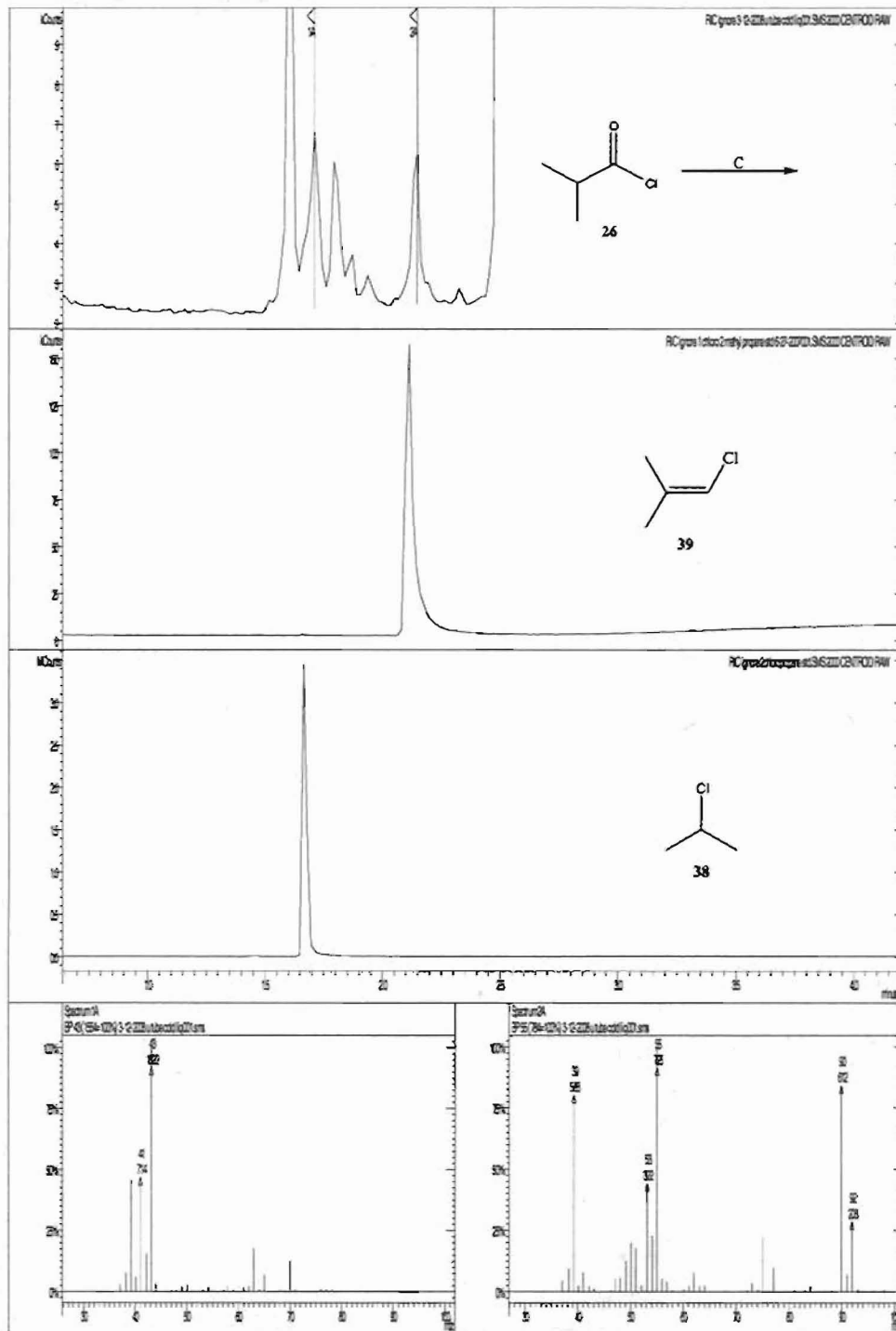
layer was separated. The crude organic layer was dried with sodium hydroxide pellets (5g) for 15 minutes. The organic solution was separated by preparative gas chromatography.

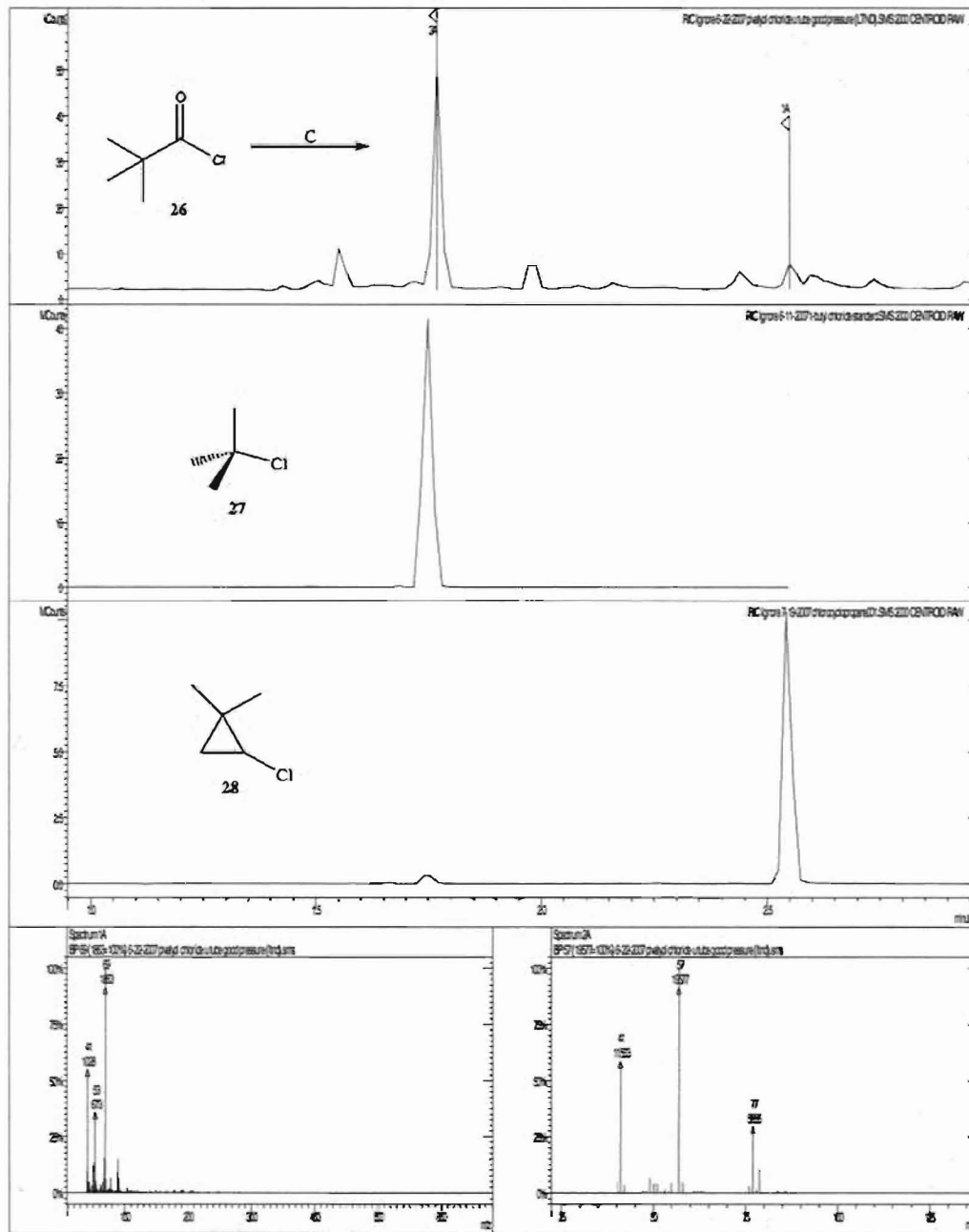


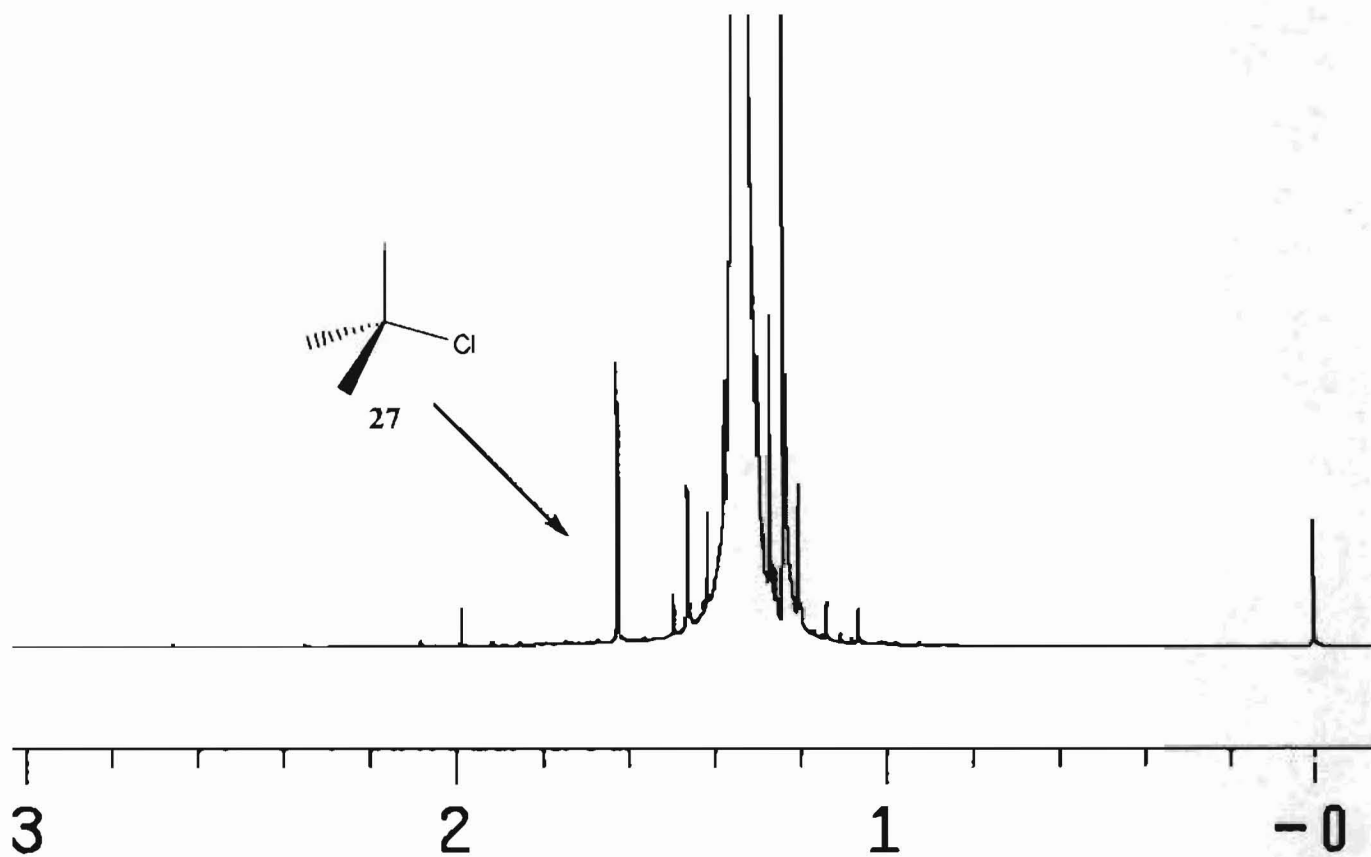
## SPECTRA

Acetyl Chloride (16) + C [GC/MS].....	33
Isobutyryl Chloride (37) + C [GC/MS].....	34
Pivaloyl Chloride (26) + C [GC/MS].....	35
Pivaloyl Chloride (26) + C [ <sup>1</sup> H NMR].....	36
Acetyl Chloride (16) + C + MeOH [GC/MS].....	37
Acetyl Chloride (16) + C, Chloromethane, Vinyl Chloride (18) [GC/MS].....	38
Acetyl Chloride (16) + C and Acetaldehyde (25) [FT-IR].....	39
2-Chloro-1,1-dimethylcyclopropane (28) [ <sup>1</sup> H NMR].....	40



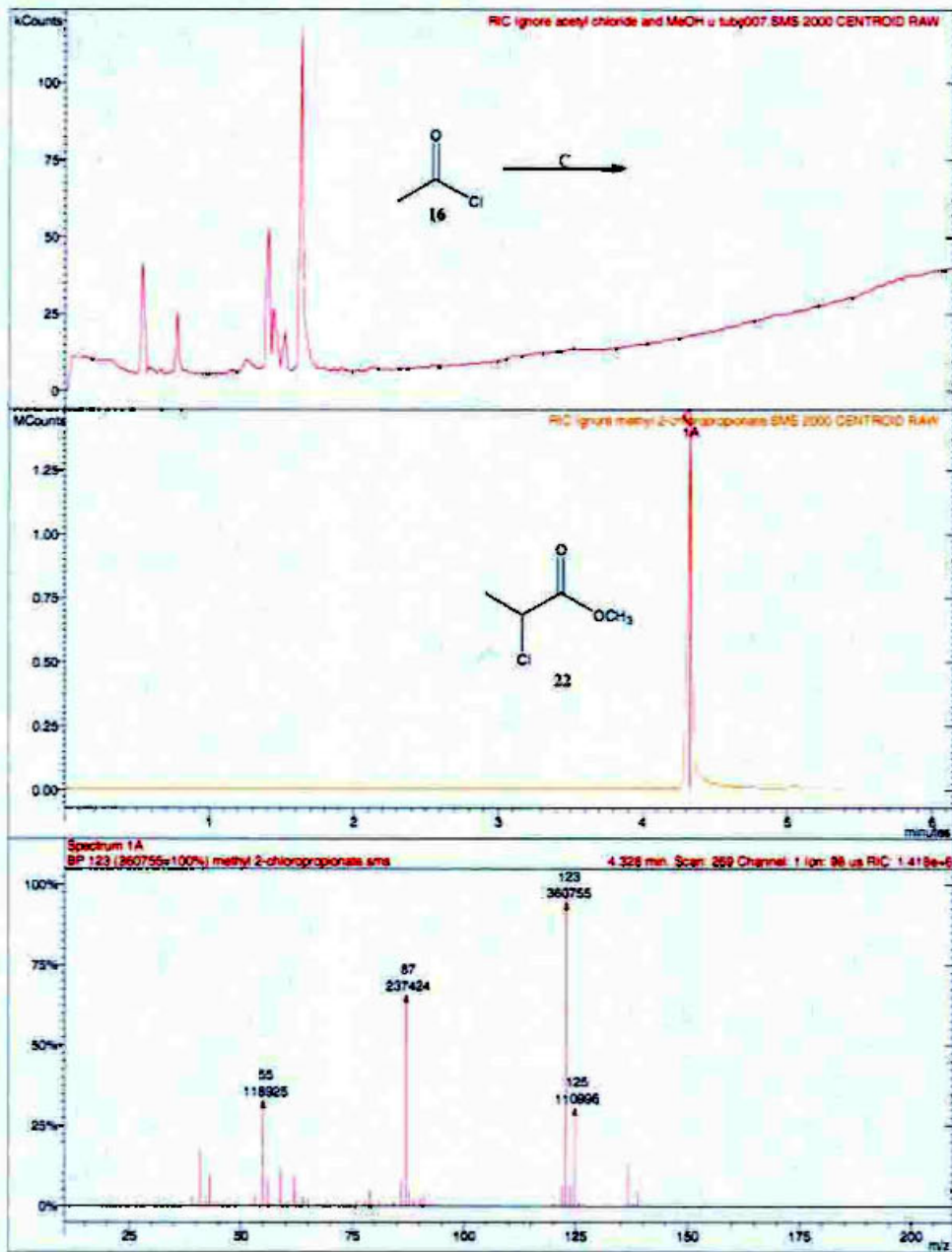




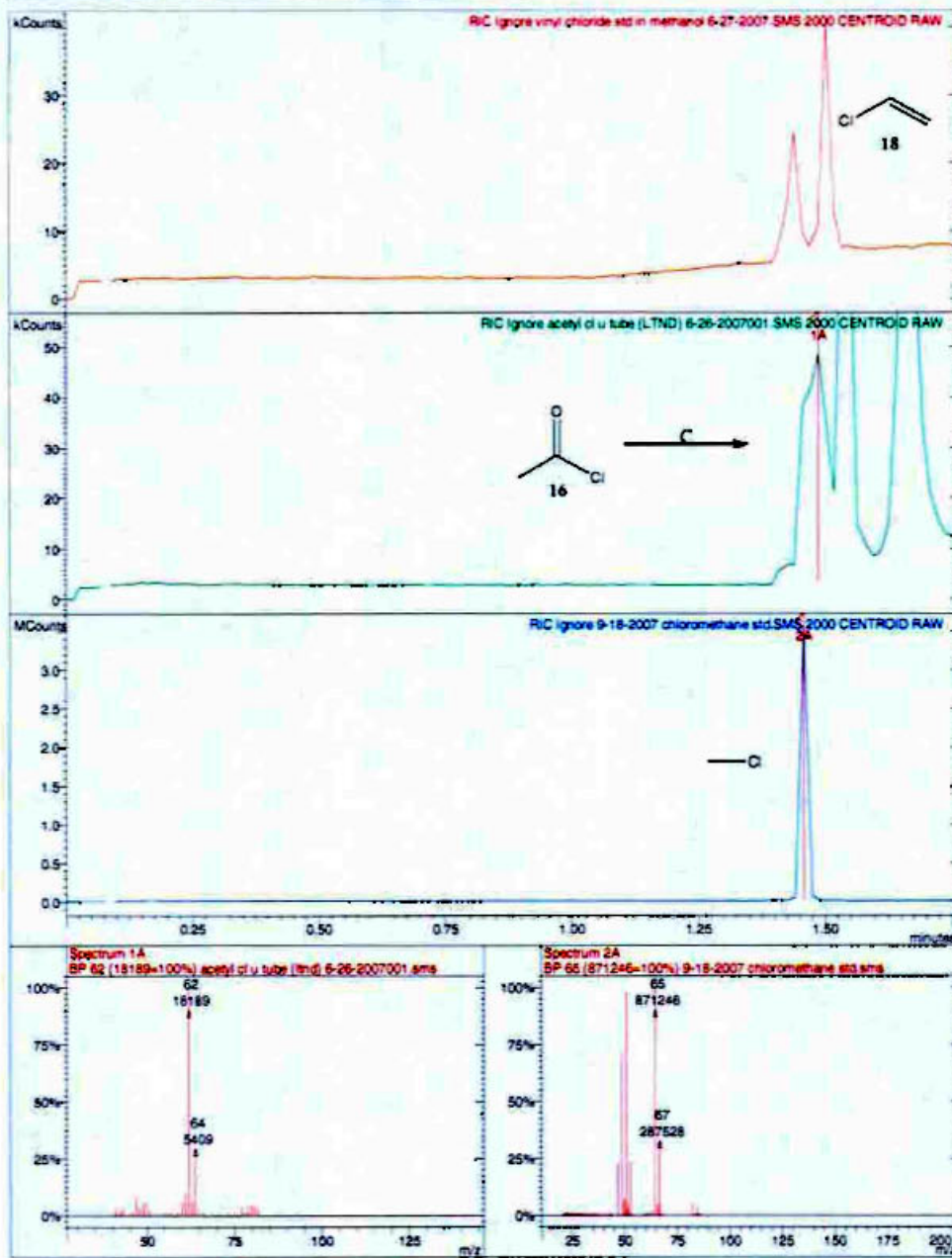


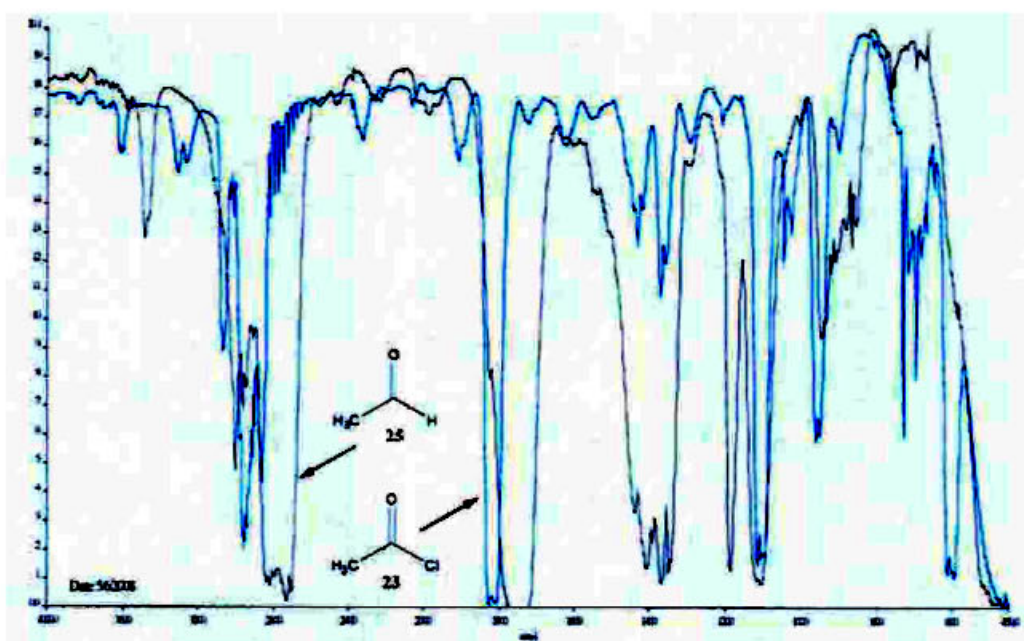
Pivaloyl Chloride + C

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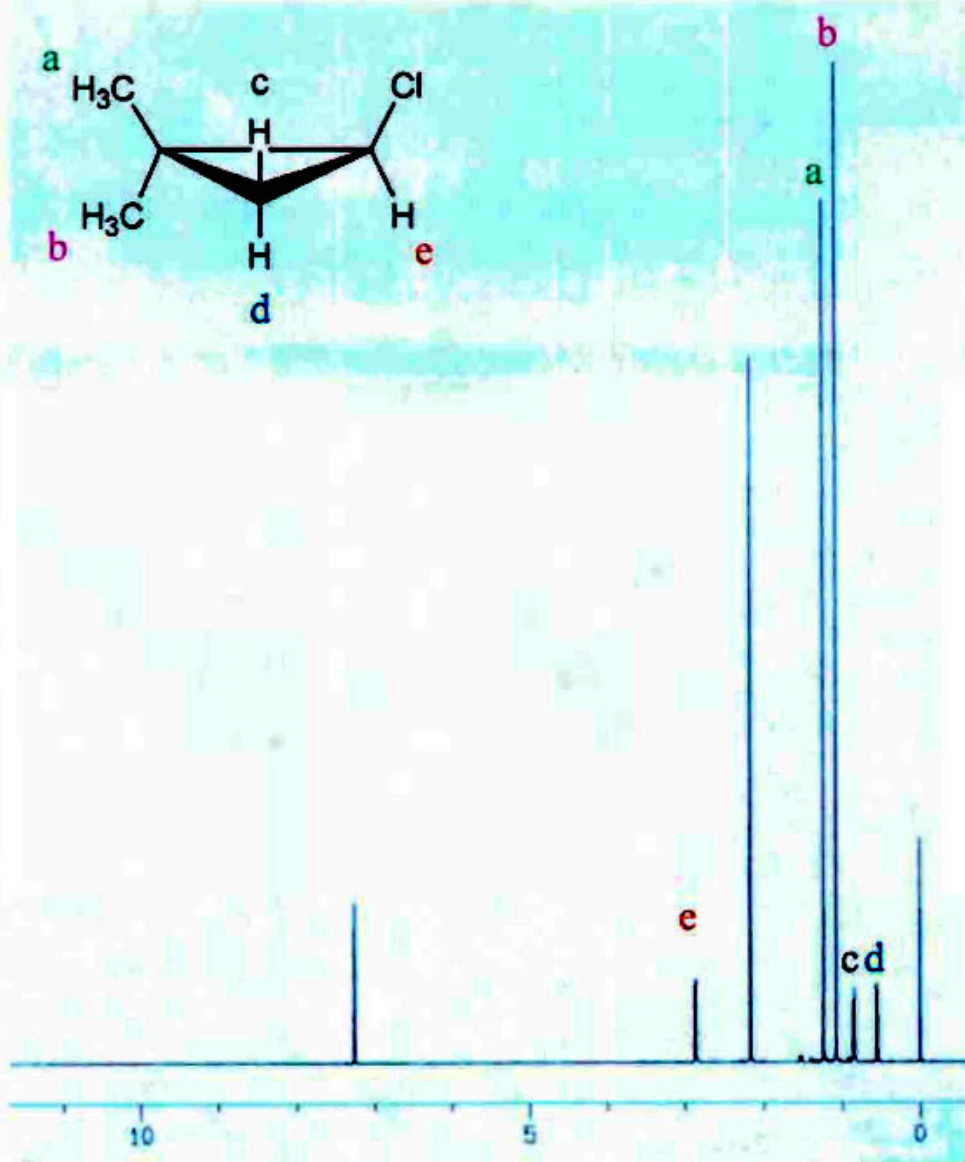


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