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Photochemical generation and chemistry of α-Acetoxycarbene

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The Photochemical Generation and Chemistry of \( \alpha \)-Acetoxy carbene

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The Photochemical Generation and Chemistry of α-Acetoxycarbene

A thesis submitted to the chemistry department at Colby College as a requirement for graduation with honors in chemistry.

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Abstract

Efforts have been made at generating the parent α-acetoxy carbene from a non-nitrogenous precursor. Baeyer-Villiger oxidation of the ketone, 1-(1a,9b-dihydro-1H-cyclopropa[l]phenanthren-1-yl)-ethanone, available in two steps from phenanthrene, led to the ester, 1-(1a,9b-dihydro-1H-cyclopropa[l]phenanthren-1-yl)-acetate, which is a photochemical precursor of the parent α-acetoxy carbene intermediate. Photolysis of the ester in cyclohexene afforded an isomeric mixture of endo and exo acetates resulting from the carbene adding to the π-bond. Photolysis of the ester in trans-3-hexene yielded a single trans-cis acetate, a product of the same cycloaddition process. The formation of methyl glyoxal, via the 1,2-acyl shift of the carbene, is observed through its derivatives. Energy minimizations at the B3LYP/6-31G* level of theory located a singlet minimum that is significantly lower in energy than the corresponding triplet.
Introduction

Carbene chemistry has been an active field in chemical research for over sixteen decades. This research preceded both the term carbene and the chemical dogma that now defines stable carbon centers as quadrivalent. The initial research in 1836 attempted to synthesize the methylene group by dehydrating methanol, without oxidizing the carbon, via strong dehydrating agents. Other efforts included attempts to expel HCl from chloroform through pyrolysis and to reduce methyl iodide with copper powder. It was not until 1912, when Staudinger et al. published work on the decomposition of diazo compounds and ketenes, that the transient nature of the much-sought-after carbene was established, and the futility of trying to capture the carbene was realized.

Today, even a novice chemist would need just a moment to come to the conclusion that carbones are very unstable species. Carbones are molecules that have neutral divalent carbon centers. They are both electron deficient and possess two non-bonding electrons. The divalent carbon center can have both an empty atomic-orbital and a filled atomic-orbital, making the carbon susceptible to nucleophilic attacks as well as being capable of performing electrophillic attacks. Alternatively, each orbital can be half filled, making a diradical species, a family of molecules whose reactivity is uncontested. These two situations coincide with paired or unpaired configurations of the two non-bonding electrons, resulting in carbenes that exist in singlet or triplet multiplicity states, respectively. (Figure 1)

![Figure 1. Singlet carbenes have two paired electrons in an $sp^2$-orbital and an empty $p$-orbital. Triplet carbenes have one electron in each orbital, both with the same spin.](image)

By the 1960's enough research was ongoing that the literature included syntheses and reactive properties of alkyl and dialkylcarbenes, aminocarbenes, thiocarbenes, halo and dihalocarbenes, oxycarbenes and alkoxycarbenes, vinyl carbenes, phenyl carbenes, and, of course, the parent carbene, methylene. All of these carbenes can be added to another molecule, bringing with them their two substituents. They can maintain or scramble stereocenters depending on their multiplicity; they can undergo intra- or intermolecular
reactions depending on their environment, and some carbenes have even been shown to be stable molecules on which further chemistry can be done.  

Singlet carbenes classically undergo three kinds of reactions. These are $\sigma$-bond insertions, intramolecular rearrangements, and cycloadditions to $\pi$-bonds. $\sigma$-Bond insertions proceed by inserting the divalent carbon of the carbene between two atoms previously joined by a $\sigma$-bond, while rearrangements of carbenes usually involve sigmatropic migrations of a group near the divalent carbon, resulting in a unit of unsaturation. (Figure 2) Cycloadditions to $\pi$-bonds generate very predictable three-membered rings. Triplet carbenes can also add to $\pi$-bonds, but behave as radicals: ring formation occurs in a stepwise process. (Figure 3) Triplets also can be involved in other radical reactions such as hydrogen abstraction and dimerizations.

![Figure 2. Classic singlet carbene reactions: (I) $\sigma$-bond insertion, (II) intramolecular rearrangements (1,2-hydride migration).](image)

The multiplicity of the carbene is the determining factor in whether the stereochemistry of the trapping alkene is maintained in the product after cycloaddition to the $\pi$-bond. These intermolecular carbene reactions can be simplified to the interactions of four orbitals. Two orbitals are atomic orbitals on the divalent carbon, while the other two orbitals are the HOMO and the LUMO of the trapping agent. The electrons in a singlet carbene are paired in an $sp^2$-orbital, which can combine with the LUMO of the trapping agent to form a bonding molecular orbital in the adduct. Simultaneously, the filled HOMO in the trapping agent combines with the empty $p$-orbital remaining on the carbene to form a second bonding molecular orbital in the adduct. This concerted addition leaves no time for stereo centers in the trapping agent to undergo any isomerization. (Figure 3)
Triplet carbene additions, however, are not concerted. The electrons in a triplet carbene each occupy one of the atomic orbitals and have the same spin. One electron from either orbital pairs with one electron in the HOMO of the trapping agent, leaving the other electron to occupy a nonbonding SOMO of this high-energy intermediate. The orbital containing the remaining electron on each species cannot combine as these two electrons would have identical spins (a violation of Hund’s rule); no bond is formed. During the brief amount of time it takes for one electron to undergo a spin-flip, bond rotation can occur and result in scrambling of stereochemistry.\(^5\) (Figure 3)

![Figure 3. (I) Singlet carbenes add to \(\pi\)-bonds in a concerted fashion with stereochemistry maintained, while (II) triplet carbenes add to \(\pi\)-bonds in multiple steps during which stereochemistry can be lost.](image)

The multiplicity of the carbenes are determined largely by intramolecular characteristics rather than external factors. The spin states of these species are determined mostly by the nature of the groups neighboring the divalent carbon. Neighboring groups which have no ability to donate electrons to the electron deficient carbon result in the triplet state,\(^4\) which is favored in methylene. Groups that can donate electrons stabilize the singlet form of the carbene. This stabilization is the result of the singlet carbene having an empty orbital to accept electrons from the donor.
While the spin-state is not easily changed for a given carbene, the environment in which it is generated can be changed without difficulty. For most carbenes, generation in an unsaturated organic solution will result in very different products than if the same carbene were generated in a matrix of condensed argon. The environment in which carbenes are generated dictate, to an extent, what reaction will proceed. In the case of intramolecular reactions, the migration of large groups is very dependent on the viscosity or rigidity of the solution, while even in solid matrices hydride shifts still occur. The mechanism through which a carbene reacts can also be a function of the temperature at which it is generated. Palik and Platz have shown that as molecular movement becomes hindered at lower temperatures, the carbene is generated and remains in a similar configuration to its precursor, which may or may not favor intramolecular reactions. They go on to show that as the solvent becomes more inert, the composition of products shift back toward species resulting from intramolecular rearrangements.

Even the precursor from which the carbene is generated has some effect on the possible reactions the carbene will undergo. In order to promote the generation of such highly unstable species as carbenes, the initiation reaction must involve a thermodynamically favorable process. The production of a very stable species together with a very unstable species makes carbene synthesis possible. At the opposite end of the stability spectrum from radicals and carbenes, one would find nitrogen gas. Diazo and diazirinyl compounds have been used for nearly a hundred years in organic syntheses, and it was soon after that their application to carbene generation was realized. These compounds make nearly ideal systems for carbene generation for several reasons. First, the byproduct of the decomposition reaction is nitrogen gas, an unreactive species unlikely to recombine with the carbene. Instead, the carbene must react with either the matrix or itself. Perhaps more importantly, though, is that diazo and diazirinyl compounds dissociate easily; little energy needs to be added to these compounds to disrupt the structure and release the nitrogen gas. The decomposition of ketenes has been known as an additional method of generating carbenes for almost as long as the nitrogenous methods. (Figure 4) Ketene decomposition to make carbenes is promoted by a similar process to diazo decomposition, namely the production of thermodynamically stable carbon monoxide gas.
There are, however, known problems with using nitrogenous precursors as carbene sources. Much work has been done\(^7\) to show the diazo and diazirinyl compounds can often form carbene-like products via two separate pathways, one of which is not through a carbene intermediate. Unless special precautions are taken, distinguishing between these two pathways could be problematic. This is especially true for photochemical processes. To circumvent these problems, an alternative approach was chosen to generate the desired \(\alpha\)-acetoxy carbene from a reliable and proven nonnitrogenous source.

Heteroatoms have been shown to have a very substantial effect on the stability and reactivity of carbenes. Oxa-substituents, specifically, have two pairs of nonbonding electrons capable of interacting with the nonbonding orbitals of a divalent carbon in a carbene species. Work done with substituted methoxycarbenes\(^8\) has produced results which show that the oxygen neighboring the divalent carbon is sufficiently nucleophilic to cause the carbene to adopt the singlet configuration as the ground state. The increase in stability resulting from the additional bond character between the oxygen and the electron deficient carbon overcomes the decrease in stability resulting from pairing the electrons on that carbon. (Figure 5) The effect of various other groups on carbene stability have been studied in an effort to understand the interactions between these groups and this unusual carbon center. With continued efforts it should be possible to identify the properties of carbenes as a function of the nucleophilic nature of the neighboring groups.

Figure 4. Decompositions of (I) diazo compounds, (II) diazirinyl compounds, and (III) ketenes give stable gases and carbene species as products.

Figure 5. Electron donation from neighboring atoms stabilizes the carbene by increasing the bonding character. This stabilization is maximized when the accepting orbital on the carbon is empty.
Acyloxy substituted carbenes have been studied since 1966, but the more specific acetoxy group has been of particular interest in recent literature. The acetoxy moiety is a relatively weak electron donor compared to other oxygen substituents, and thus can be a unique aid in efforts made toward understanding how carbenes behave in the presence of groups of varying nucleophilicity. Moss has explored the chemistry of phenyl acetoxy carbene in great detail while chemistry of the parent species has yet to be investigated. It is the chemistry of this parent species that will most unambiguously display the effects of the acetoxy group on carbene stability.

Existing syntheses of acetoxy carbenes involve high temperature preparations and multiple byproducts. These conditions make it difficult to collect clear data on the carbene species and its products. Other generation processes include the nitrogenous precursors, and it is reported that these reactions proceed in low yield and may not actually involve free carbenes, but rather charged complexes resulting from incomplete or step-wise decomposition of the nitrogenous precursor. Furthermore, these mechanisms fail to be useful in generating the parent acetoxy carbene. When beginning this research, these methods were cast aside in favor of an alternative precursor.

Cyclopropanated phenanthrenes have been shown to effectively undergo chemical modifications which enable them to act as carbene precursors. These models have been used in earlier work to generate other carbenes as 2-hydroxy-2-methylpropylidine and oxiranyl carbene. (Figure 6)

These successes encourage the use of the phenanthrene backbone as the method to generate acetoxy carbene. Similar to the nitrogenous precursors, the decomposition of these molecules is driven by the generation of a very stable molecule and a very unstable molecule simultaneously. The nitrogenous processes clearly generate nitrogen gas, while these phenanthrene processes produce the very stable aromatic phenanthrene.
Figure 6. The phenanthrene system has been used to generate these parent carbene species when exposed to ultraviolet light: (I) 2-hydroxy-2-methylpropylidene and (II) oxiranylcarbene. The system has been extended to generate (III) acetoxycarbene.
Results and Discussion

Efforts on this project were first put into developing a successful synthesis of the precursor. Subsequently, the precursor was photolyzed and its chemistry was observed by means of trapping reactions. Finally, computational studies were performed on the carbene intermediate to compare with the results found experimentally. The results of these three general investigations follow with their discussion.

Synthesis: The synthesis of 1-(1a,9b-dihydro-1H-cyclopropa[7]phenanthrene-1-yl)-acetate (4), the precursor, can be accomplished in four steps from phenanthrene. The reagents used in the synthetic procedures are all commercially available. The precursor synthesis can be summarized by the addition of a cyclopropyl ring to phenanthrene. Several modifications are performed on the functional group on the cyclopropane before the desired precursor (4) to the parent acetoxy carbene is ready to undergo photolysis. (Figure 7)

\[
\text{phenanthrene} \xrightarrow{a} \text{(1)} \xrightarrow{b} \text{(2)} \xrightarrow{c} \text{(4)} \xleftarrow{d} \text{(3)}
\]

Figure 7. The synthesis of (4). a - ethyl diazoacetate, CuSO₄, heat; b - 1. EtOH, NaOEt; 2. HCl; c - MeLi, THF; d - MCPBA, CHCl₃.

The 9,10-π-bond in phenanthrene is most susceptible to cycloadditions. The reason for this is two fold: computational studies show this position to have more electron density than the others, and the reduction of this position gives a product with more aromaticity than does reduction of any other position. The reaction of molten phenanthrene with ethyl diazoacetate, catalyzed by anhydrous copper sulfate, afforded 1-(1a,9b-dihydro-1H-cyclopropa[7]phenanthrene-1)-carboxylic acid ethyl ester (1). The rate of addition of ethyl diazoacetate factors into the yield of the reaction; additions as slow as 4 mL/h were
used to achieve optimal results. In addition, maintaining the temperature within a few degrees of the melting temperature of phenanthrene was necessary to avoid charring the reaction. (Figure 7 - a) This resulting cyclopropyl ester was converted into the acid (2) by hydrolysis with 10% sodium hydroxide in ethanol followed by acidification with hydrochloric acid. It is this carboxylic acid product that is purified and characterized, rather than the ester due to the ease with which the acid can be removed from unreacted phenanthrene. The acid is also the functionality needed to advance to the next step. (Figure 7 - b) These two reactions together produce the acid in a low yield, which, at best, reaches 18%.

The infrared spectrum (Spectrum 1) of (2) confirms, with the presence of the broad hydroxyl band (2500-3300 cm⁻¹) and the carbonyl band (1697 cm⁻¹), that the product is a carboxylic acid. The broad peak downfield (11.7 ppm) in the proton NMR spectrum (Spectrum 2) and the peak downfield (168 ppm) in the 13C NMR spectrum (Spectrum 3) also reinforce the finding of the carboxylic acid. Further analysis of the proton NMR reveals large a J-coupling constant (8.8 Hz) of the protons on the cyclopropyl ring, suggesting the endo form is present.

In the presence of excess methyllicthium, the acid, (2), is easily reduced to the ketone, 1-(1a,9b-dihydro-1H-cyclopropa[I]phenanthren-1-yl)-ethanone, (3). The reaction is carried out in meticulously dry glassware under a flow of argon at 0°C. Again, the rate of addition of the methyllicthium has a similar effect on the yield of the reaction; these rates were on the order of 1 mL/min. (Figure 7 – c) This reaction is far more efficient than the acid synthesis, producing ketone in yields up as high as 64%. Successful conversion into the ketone can be verified by the lack of the hydroxyl vibration in the infrared spectrum of (3) (Spectrum 4) together with the absence of the broad resonance downfield in the proton NMR. (Spectrum 5) The presence of an intense singlet in the proton NMR (2.31 ppm) verifies that the methyl group has indeed been added to the compound. The coupling constant between the cyclopropyl hydrogens in the ketone is small (3.7 Hz), suggesting the exo structure is the preferred conformation.

The ketone is then oxidized via the Bayer-Villiger reaction with m-chloroperoxybenzoic acid to produce 1-(1a,9b-dihydro-1H-cyclopropa[I]phenanthren-1-yl)-acetate, (4). This reaction is very slow, taking about a week to approach completion. The reaction is
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degrees of the melting temperature of phenanthrene was necessary to avoid charring the
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reveals large a J-coupling constant (8.8 Hz) of the protons on the cyclopropyl ring,
suggesting\(^{14}\) the endo form is present.

In the presence of excess methyllithium, the acid, (2), is easily reduced to the ketone, 1-
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acid to produce 1-(1a,9b-dihydro-1H-cyclopropa[\(l\)]phenanthren-1-yl)-acetate, (4). This
reaction is very slow, taking about a week to approach completion. The reaction is
monitored by GCMS. The complete oxidation of the ketone is achieved by maintaining excess peracid throughout the course of the reaction. The Bayer-Villiger reaction could potentially oxidize either side of the ketone, but oxidation of the more substituted carbon occurs selectively, giving only the desired product. (Figure 7 - d) The yield of this reaction is very inconsistent, averaging near 15%.

The oxidation reaction’s success to form (4) is also evident in the spectra. The addition of the carbon-oxygen single bond stretch (1238 cm\(^{-1}\)) in the infrared spectrum strongly suggests ester formation. (Spectrum 8) The resonances resulting from the cyclopropyl hydrogens in the proton NMR (Spectrum 9) are further down field than the resonances of the cyclopropyl hydrogens of the ketone, a sign that an electron withdrawing moiety has been added to the ring. Similar small coupling constants (2.4 Hz) between cyclopropyl ring hydrogens show the molecule to prefer the **exo** formation as well.

**Photolysis:** Photolysis of (4) causes ring-scission of the cyclopropyl group to excise the parent acetoxy carbene. This regenerates the phenanthrene and releases the carbene (5). (Figure 8) The free carbene then has the opportunity to undergo the aforementioned reactions.

![Diagram](image)

Figure 8. The precursor decomposes to give the acetoxy carbene (5), and regenerate phenanthrene.

Initially, an effort was made to see if the carbene could be trapped with an alkene. A successful alkene for this task must not include a chromaphore, as the photolytic ring opening of the precursor would proceed in less efficient yields in that case. The alkene must also be manageable, preferably a liquid capable of dissolving the precursor. Such characteristics were found in cyclohexene. Photolysis in neat cyclohexene was attempted, and the GCMS spectrum of the photolysate showed adduct formation. The conditions caused the generated carbene to undergo a cycloaddition with the \(\pi\)-bond of the cyclohexene, yielding **exo** and **endo** acetic acid bicyclo[4.1.0]hept-7-yl ester (6). (Figure 9)
In order to get clean spectra of the adduct, the photolysate was vacuum distilled to separate the volatile components from the non-volatile impurities. The distillate was then purified by preparative GC to remove the adduct from the cyclohexene. A separate NMR study with an internal standard showed that the decomposition and trapping of the carbene in cyclohexene was in yields as high as 56%. The products' structures were confirmed by proton NMR (Spectrum 12), which included two distinctive triplets (3.98, 3.77 ppm). The cyclopropyl hydrogen not on the cyclohexene ring is shifted downfield by the near-by oxygen, and is found in an uncluttered region of the spectrum. This hydrogen is coupled to the two other protons on the cyclopropane in each compound. The coupling constant between hydrogens that are cis on a ring is larger than it is for trans, \(^{14}\) and the difference is enough to assign the triplet with larger coupling to the endo form of the adduct. Both NMR and GCMS indicate the ratio of the exo- and endo- products to be near 2:1.

Upon confirming that the carbene could be trapped through cycloadditions to an alkene, a stereochemically labeled alkene was chosen to produce results that would elucidate the multiplicity of the carbene. As mentioned earlier, singlet carbenes react in a concerted fashion in the cycloaddition to \(\pi\)-bonds, while triplets react in multiple steps. In an effort to maintain similar conditions as the previous trapping reaction, another hexene was chosen. Since an \((E)\)-isomer would react with a singlet carbene to give only one product, while a \((Z)\)-isomer would give two, and the carbene is suspected of being a singlet, trans-3-

![Figure 9. Photolysis of the precursor in neat cyclohexene give rise to two adducts resulting from the carbene performing a classical \(\pi\)-system cycloaddition.](image)

![Figure 10. Photolysis of the precursor in neat trans-3-hexene give rise to a single adduct, a product of a classical \(\pi\)-system cycloaddition.](image)
hexene was chosen as the labeled alkene. This reaction would give a single product if the carbene were indeed a singlet, but it would give an additional two isomers of that product if the carbene reacted as a triplet. Photolysis of the precursor in neat trans-3-hexene indeed gave only product: acetic acid 2,3-trans-diethyl-cyclopropyl ester (7). (Figure 10)

This adduct was also purified by vacuum distillation followed by preparative GC. Through another NMR experiment with an internal reference, it was shown that this reaction reached yields of 26%. This product, too, has a characteristic peak in the proton NMR (Spectrum 13), having been shifted downfield into an uncluttered region of the spectrum by the near-by oxygen. The analogous cyclopropyl hydrogen to those discussed earlier is cis to one hydrogen on the ring, and trans to another, making its signal a doublet of doublets. The lack of compounds isomeric to (7), as shown by no additional peaks in the 3-4 ppm region of the proton NMR, gives evidence to the singlet nature of the carbene. One product indicates that the cycloaddition is a concerted reaction, in which there is no opportunity to isomerize. Evidence from molecular orbital calculations to support this finding is discussed later.

Figure 11. (I) Acetoxycarbene undergoes an intramolecular 1,2-acyl shift to give methyl glyoxal (8). (II) Methyl glyoxal reacts with tertiary butyl amine to give both the mono, (9), and the diimine (10).

In an effort to observe the expected intramolecular 1,2-acyl shift of the carbene, the precursor was photolysed in solvents unsupportive of the cycloaddition reaction. These efforts were fruitless. It was later discovered that the product of the rearrangement, methyl glyoxal (8), is unstable in most organic solvents, and polymerizes rapidly. Efforts were then made to trap the dicarbonyl with primary amines, via the Shiff base reaction, before the polymerization could occur. The reaction with o-phenylenediamine would have yielded a known compound (2-methyl-quinoxaline), but the phenylenediamine proved to be
unstable in the presence of the ultraviolet light. The reaction with 1,2-diamino ethylene would have given a simple pyrazine, but this diamine, too, failed to be stable in the photochamber. The first attempt with a mono-amine, tertiary butylamine, gave a messy but unmistakable chromatogram. (Spectrum 16) The presence of the mono and diimines is clear evidence of the rearrangement. (Figure 11)

Aldehydes undergo the Schiff-base reaction very quickly while ketones are less reactive. It is therefore not unlikely that the energy applied in the photochamber may not have been sufficient to encourage the complete imination of the ketone. In lieu of being able to characterize the small quantities of adduct found in the photolysate by methods more rigorous than GCMS, another approach at verifying their identity was taken. Compound (9) can be synthesized by mixing commercial methyl glyoxal with tertiary butylamine, and a small addition of this material to the photolysate shows an unambiguous increase in intensity of the monoadduct peak, verifying its identity. (Spectrum 17)

**Computational Studies:** The singlet nature of the carbene is supported by computational studies performed using the B3LYP method with the 6-31G* basis set. This level of theory has proven to be sufficient when dealing with carbene systems.13a No efforts were made to relax or restrict any symmetry parameters for these calculations. Both optimized species are members of the C1 point group. The singlet acetoxycarbene adopts a coiled planar conformation, while the triplet carbene prefers an extended planar configuration. (Figure 12) The calculated energy minimia for this singlet lies 16.67 kcal/mol below the triplet minimia.

![singlet](image1.png)  
**singlet**  
![triplet](image2.png)  
**triplet**  

Figure 12. These planer conformations are the minimized structure of each carbene.

Through analysis of plots of energy surfaces as a function of molecular conformation, these studies also show that the barrier for rotation about the O-C: bond is a much easier process in the triplet species (6.3 kcal/mol), where there would be little π-interaction, than in the singlet species (17.3 kcal/mol), where there can be more extensive π-interaction.
The two bonds whose rotation changes the spatial configuration are the O-C bond and the C-O bond. The wide range of energies covered in the following plot (Figure 13) leaves no doubt that the dihedral angles around these two bonds play an important role in the energy of the singlet species. The analogous plot for the triplet carbene covers a much smaller range of energies, and averages 10 kcal/mol higher than the singlet over the whole plane. That is, computational data suggests even though the triplet species can adopt various conformations more easily than the singlet, the conformations the singlet does adopt are significantly more stable than the same conformations in the triplet. The following plot also shows that the singlet has several minimum energy conformations, two of which differ by as little as 1.55 kcal/mol.

Figure 13. Energy surface of the singlet carbene as a function of the two bonds free to rotate (shown relative to the global minimum 180° H-C-O-C, 0° C-O-C-C). The range of energies is near thirty kcal/mol for the singlet and near 12 kcal/mol for the triplet (not shown).
Conclusions

1-(1a,9b-dihydro-1H-cyclopropa[7]phenanthren-1-yl)-acetate, (4), can be synthesized in an overall yield of near 2% in three steps from phenanthrene. It is very stable and can be stored for extended periods of time without risk of decomposition. The ester is a successful precursor to the parent α-acetoxy carbene via photolysis. The carbene is shown to undergo the intramolecular 1,2-acyl shift reported of substituted α-acetoxy carbene to generate methyl glyoxal. Methyl glyoxal is unstable in organic solvents, and chemical evidence of its existence is only through its derivatives with tertiary butylamine. The mono- and diimine are seen in GCMS spectra. The carbene also undergoes cycloadditions with π-systems making cyclopropanes, similar to the substituted acetoxycarbene. This reaction was observed with cyclohexene and trans-3-hexene. The cyclohexene reaction gives both the endo- and exo- product, which were characterized, after purification by vacuum distillation and preparative GC, by proton NMR. The reaction with trans-3-hexene produces only acetic acid 2,3-trans-diethyl-cyclopropyl ester. This product is purified and characterized in the same manner. The lack of products isomeric to (7) indicates the multiplicity of the carbene is a singlet. Singlet carbenes cyclize with π-systems in a concerted manner while triplet reactions are multiple steps involving enough time for isomerization to occur. Computational data also suggests the carbene to be a singlet. The singlet is calculated to be considerably lower in energy than the triplet, and analysis of the carbon-oxygen bonds suggest the singlet is stabilized by additional bonding character, whereas the triplet is not.
Experimental

All GCMS data of synthesis intermediates and addition reactions were obtained on a Hewlett-Packard 5890 Gas Chromatograph/5891 mass selective detector. The column used was a Supelco 2-4028 SPB-1 fused silica column 30 m in length by 0.25 mm in diameter. GCMS data of rearrangement products were obtained on a Varian CP-3800 Gas Chromatograph/Saturn 2000 MS. This instrument was operating in chemical ionization mode with acetonitrile, and using a Chrompac CP Sil 8 CB capillary column 30 m in length by 0.25 mm in diameter. Preparative GC work was done on a GOW-MAC Gas Chromatograph series 5800 operating with a Supelco 3% SP2100 6" x ¼' column. All NMR data were collected on a Bruker Avance 400 spectrometer. CHN analysis were preformed on an Exeter CE-440 Elemental Analyzer. Infrared absorption data were collected on a Mattson 4020 Galaxy Series FT-IR. Photolysis was preformed in a Rayonet Photochamber (λ = 254 – 419 nm) at 250 watts. Column chromatography was preformed with 60-200 mesh silica gel. THF was dried by being passed through two columns (2' x 4") packed with alumina.

1-(1a,9b-dihydro-1H-cyclopenta[l]phenanthren-1-yl)-carboxylic acid:

Phenanthrene (30.2 g, 169 mmol) was steadily heated to melting with copper sulfate (0.612 g, 3.4 mmol) whereupon ethyl diazoacetate (20 mL, 190 mmol) was added drop wise over a period of 4½ hours. Heating was discontinued upon completion of addition and the contents of the flask were allowed to cool. Sodium hydroxide (10% in EtOH, 200 mL) was added and the reaction mixture was heated to reflux for 6 hours. Ethanol was removed under reduced pressure, and water (300 mL) was added. The reaction mixture was boiled for an additional hour. The reaction mixture was then filtered and the filtrate was cooled and acidified until no further precipitate formed. The tan, creamy precipitate was recrystallized from glacial acetic acid, reprecipitated by treatment with dilute aqueous NaOH followed by HCl, and recrystallized from acetic acid again to afford white crystals of the carboxylic acid in typical low yield (2.54 g, 18.5% yield). IR (KBr diffuse reflectance) 2400-3400 cm⁻¹, 1697 cm⁻¹; ¹H NMR (DMSO-d₆) δ 11.7 (s/b, 1H), 8.04 (m, 2H), 7.44 (m, 2H), 7.27 (m, 4H), 3.12 (d, J = 8.8 Hz, 2H), 2.26 (t, J = 8.8 Hz, 1H); ¹³C NMR (DMSO-d₆) δ 168.4, 132.4, 130.4, 130.1, 127.3, 126.6, 122.4, 25.5, 16.4.
1-(1a,9b-dihydro-1H-cyclopropa[1]phenanthren-1-yl)-ethanone:

The carboxylic acid (1.00 g, 4.25 mmol) was dissolved in anhydrous THF (30 mL) and cooled to 0°C under argon. To this solution was added CH₃Li (1.60 M in diethyl ether, 8 mL, 12.74 mmol) in a dropwise fashion and stirred overnight at room temperature. Saturated aqueous NH₄Cl (20 mL) was then added and layers were separated. The aqueous layer was extracted with CH₂Cl₂ (2 x 25 mL). The combined organics were washed with water (50 mL) and saturated NaCl (50 mL), dried over MgSO₄, filtered, and the solvent was removed under reduced pressure to give the crude ketone. This material was recrystallized from EtOH. (550 mg, 64% yield) IR (KBr diffuse reflectance) 1677 cm⁻¹; ¹H NMR (CDCl₃) δ 8.05 (m, 2 H), 7.48 (m, 2 H), 7.34 (m, 4 H), 3.29 (d, J = 3.7 Hz, 2 H), 2.31 (s, 3 H), 1.40 (t, J = 3.7 Hz, 1 H); ¹³C NMR (CDCl₃) δ 208.5, 133.7, 130.1, 130.0, 128.4, 127.5, 123.7, 34.6, 33.3, 31.9. Anal. Calcd for C₁₇H₁₄O: C, 87.15; H, 6.02. Found: C, 86.77; H, 6.08.

1-(1a,9b-dihydro-1H-cyclopropa[1]phenanthren-1-yl)-acetate:

The ketone (1.88 g, 8.04 mmol) was dissolved in chloroform (40 mL), to which was added m-chloroperoxybenzoic acid (10.17 g, 58.87 mmol) in four aliquots over a period of seven days. The mixture was allowed to sit for an additional three days at which point the remaining peracid was quenched with 10% Na₂S₂O₅ (80 mL). The reaction mixture was then filtered and the filtrate was washed with NaHCO₃ (3 x 15 mL) and water (2 x 15 mL). The reaction mixture was dried over MgSO₄, filtered, and the solvent removed under reduced pressure. The resulting solids were separated via column chromatography with 5% ether in hexanes. Product fractions were recrystallized from ether. (162 mg, 8% yield) IR (KBr diffuse reflectance) 1747 cm⁻¹, 1238 cm⁻¹; ¹H NMR (CDCl₃) δ 7.93 (m, 2 H), 7.44 (m, 2 H), 7.27 (m, 4 H), 3.50 (t, J = 2.4 Hz, 1 H), 2.81 (d, J = 2.4 Hz, 2 H), 2.12 (s, 3 H); ¹³C NMR (CDCl₃) δ 171.5, 131.6, 130.3, 129.8, 129.4, 127.3, 123.5, 59.3, 26.3, 21.4; Anal. Calcd for C₁₇H₁₄O₂: C, 81.58; H, 5.64. Found: C, 81.55; H, 5.67.
Acetic acid bicyclo[4.1.0]hept-7-yl ester:

The acetate (81 mg, 0.32 mmol) was dissolved in cyclohexene (1.2 mL) and THF (0.2 mL) in a sealed quartz tube under argon gas. The tube was irradiated for 72 hours, after which its contents were vacuum distilled. The distillate was purified by preparative gas chromatography. $^1$H NMR (CDCl₃, distinguishing peaks) endo- δ 3.98 (t, $J$=7.0 Hz, 1H), 2.11 (s, 3H), exo- δ 3.77 (t, $J$=2.8, 1H), 2.01 (s, 3H).

Acetic acid 2,3-trans-diethyl-cyclopropyl ester:

The acetate (75 mg, 0.30 mmol) was dissolved in trans-3-hexene (1.0 mL) in a sealed quartz tube under argon gas. The tube was irradiated for 50 hours, after which its contents were vacuum distilled. The distillate was purified by preparative gas chromatography. $^1$H NMR (CDCl₃) δ 3.85 (dd, $J$=3.0 Hz, 6.8 Hz, 1H), 2.04 (s, 3H), 1.43 (sex, $J$=7 Hz, 1H), 1.40 (sex, $J$=7 Hz, 1H), 1.28 (sex, $J$=7 Hz, 1H), 1.17 (sex, $J$=7 Hz, 1H), 0.98 (t, $J$=7.4 Hz, 3H), 0.96 (t, $J$=7.4 Hz, 3H) 0.68 (p, $J$=6.8 Hz, 1H), 0.63 (dq, $J$=3.0, 6.7 Hz, 1H).

2-tert-Butylimino-propionaldehyde and tert-Butyl-(2-tert-butylimino-1-methyl-ethylidene)-amine:

The acetate (15 mg, 0.06 mmol) was dissolved in tertiary butylamine (1.0 mL) in a sealed quartz tube under argon gas. The tube was irradiated for 14 hours, and its contents characterized by GCMS.
References


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Spectra

Spectrum 1. Infrared spectrum of 1-(1a,9b-dihydro-1H-cyclopropa[1]phenanthren-1-yl)-carboxylic acid.

Spectrum 2. Proton NMR of 1-(1a,9b-dihydro-1H-cyclopropa[1]phenanthren-1-yl)-carboxylic acid.


Spectrum 4. Infrared spectrum of 1-(1a,9b-dihydro-1H-cyclopropa[1]phenanthren-1-yl)-ethanone.

Spectrum 5. Proton NMR of 1-(1a,9b-dihydro-1H-cyclopropa[1]phenanthren-1-yl)-ethanone.


Spectrum 7. GCMS spectrum and TIC of 1-(1a,9b-dihydro-1H-cyclopropa[1]phenanthren-1-yl)-ethanone.

Spectrum 8. Infrared spectrum of 1-(1a,9b-dihydro-1H-cyclopropa[1]phenanthren-1-yl)-acetate.


Spectrum 11. GCMS spectrum and TIC of 1-(1a,9b-dihydro-1H-cyclopropa[1]phenanthren-1-yl)-acetate.

Spectrum 12. Proton NMR of the cyclohexene trapped products.

Spectrum 13. Proton NMR of the trans-3-hexene trapped product.

Spectrum 14. GCMS spectrum and TIC of the cyclohexene trapped products.

Spectrum 15. GCMS spectrum and TIC of the trans-3-hexene trapped product.

Spectrum 16. The GCMS plots of the trapped rearrangement products.

Spectrum 17. The GCMS plots of the rearrangement products spiked with 1-tert-Butylimino-propan-2-one.
Spectrum 1. Infrared spectrum of 1-(1a,9b-dihydro-1H-cyclopropa[1]phenanthren-1-yl)-carboxylic acid by diffuse reflectance in KBr.
Spectrum 2. Proton NMR of 1-(1a,9b-dihydro-1H-cycloprop[a]phenanthren-1-yl)-carboxylic acid in DMSO-d$_6$.

Spectrum 3. $^{13}$C NMR of 1-(1a,9b-dihydro-1H-cycloprop[a]phenanthren-1-yl)-carboxylic acid in DMSO-d$_6$.

*Acetic Acid
Spectrum 4. Infrared spectrum of 1-(1a,9b-dihydro-1H-cyclopenta[l]phenanthren-1-yl)-ethanone by diffuse reflectance in KBr.
Spectrum 5. Proton NMR of 1-(1a,9b-dihydro-1H-cyclopropa[1]phenanthren-1-yl)-ethanone in CDCl₃.

Spectrum 7. GCMS spectrum and TIC of 1-(1a,9b-dihydro-1H-cyclopropa[1]phenanthren-1-yl)-ethanone.
Spectrum 8. Infrared spectrum of 1-(1a,9b-dihydro-1H-cyclopropa[1]phenanthren-1-yl)-acetate by diffuse reflectance in KBr.

Spectrum 11. GCMS spectrum and TIC of 1-(1a,9b-dihydro-1H-cyclopropa[7]phenanthren-1-yl)-acetate.
Spectrum 12. Proton NMR of the cyclohexene trapped products in CDCl₃.

Spectrum 13. Proton NMR of the trans-3-hexene trapped product in CDCl₃.
Spectrum 14. GCMS spectrum and TIC of the cyclohexene trapped products.
File: C:\HPCHEM\1\DATA\TRANSADD.D
Operator: jonathan
Acquired: 30 Apr 102 11:28 pm using AcqMethod DAS
Instrument: 5970B
Sample Name: trans hexene addition product
Misc Info: 
Vial Number: 1

Abundance

Ion 127.00 (126.70 to 127.70): TRANSADD.D

Abundance

Scan 332 (3.742 min): TRANSADD.D

Spectrum 15. GCMS spectrum and TIC of the trans-3-hexene trapped product.
Spectrum 16. The GCMS plots of the trapped rearrangement products.
Spectrum 17. The GCMS plots of the rearrangement products spiked with 1-tert-butylimino-propan-2-one.