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DIRECT OBSERVATION OF THE YLIDES FORMED UPON REACTION OF CYCLOPENTADIENYLIDENE WITH ACETIC ANHYDRIDE, DIMETHYL CARBONATE, ETHYL ACETATE AND ACETONE

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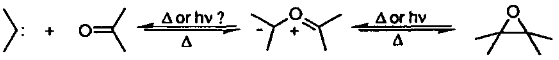
Cyclopentadienylidene was studied by laser flash photolysis (LFP) techniques. LFP of diazocyclopentadiene in acetic anhydride, acetaldehyde, acetone, dimethyl carbonate, ethyl acetate, acetonitrile, dimethyl sulfide and pyridine produces UV–visible active ylides. The first reports of the direct detection of carbene--anhydride, carbene–aldehyde, carbene–amide and carbene–carbonate ylides are presented. The spectra and the lifetimes of these ylides are reported.

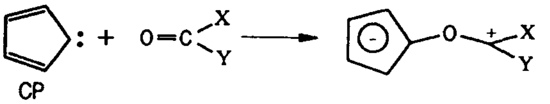
INTRODUCTION

Carbonyl ylides are useful reagents in dipolar cycloaddition reactions and in the synthesis of heterocyclic[1] and polycyclic compounds.[2] Methods of generating carbonyl ylides include the photolysis or thermolysis of oxiranes[1,3] or oxadiazolines.[4] Another method, which is the focus of this report, involves the reactions of carbenes with carbonyl compounds:[5,6]



Carbonyl ylides have been detected directly for carbenes produced in the laser flash photolysis of diazo compounds in the presence of ketones.[6] While evidence for carbonyl ylides derived from the reaction of carbenes with carboxylic acid derivatives has been found in some product studies,[4] attempts to directly observe carbonyl ylides derived from carbenes and carbonyl compounds such as anhydrides, amides and carbonates have generally failed with the exception of some stable intramolecular/cyclic cases[2] and the ylide formed between tetrakis(trifluoromethyl)cyclopentadienylidene and tetramethylurea.[7] The only previous report of spectroscopically detectable carbonyl ylides formed by reaction between an ester and a carbene is for (*p*-nitrophenyl)chlorocarbene generated in the presence of ethyl acetate.[8]

Simple theoretical considerations suggest that cyclopentadienylidene (CP) should readily form ylides to form an aromatic product:



Indeed, ylide formation is a consistent theme in the chemistry of CP.[9] These considerations prompted the present study of CP with a variety of carbonyl functional groups. We present here the first reports of UV–visible-active ylides derived from the reaction of a carbene with an anhydride, aldehyde, carbonate and amide. The lifetimes of these ylides are also presented.

RESULTS AND DISCUSSION

Laser flash photolysis (LFP) (XeCl excimer, 308 nm, or XeF excimer, 351 nm) of diazocyclopentadiene (DCP) in solvents containing the carbonyl functionality in acetic anhydride, acetaldehyde, acetone, dimethyl carbonate and ethyl acetate produces the transient spectra shown in Figures 1–5. The transient UV–visible spectra resulting from the LFP of DCP in acetonitrile, dimethyl sulfide and pyridine are shown in Figures 6–8. Likely structures of these transients are shown in Scheme 1 (structures **1**–**8**). The rates of formation of all of the transients in neat carbonyl compound were faster (≤20 ns) than the time resolution of the laser flash photolysis system used. The lifetimes of the proposed carbonyl ylides in neat ylide forming reagent range from 1 to 10 μs (Table 1). Lifetime values which have been measured previously for ketone–carbene ylides are also generally on the scale of microseconds.[6] The ylides formed by reaction of CP with pyridine and acetonitrile

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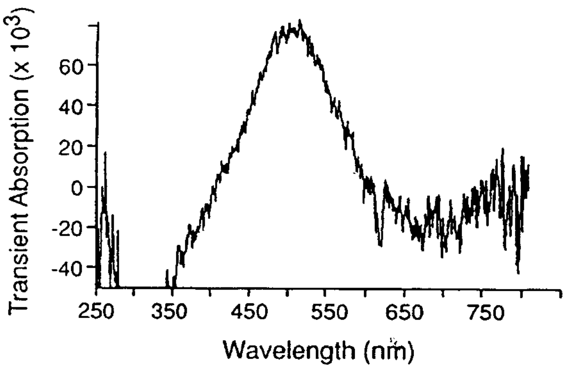


Figure 1. Transient spectrum produced by LFP of DCP in acetic anhydride. The spectrum was recorded 500 ns after a 308 nm laser pulse

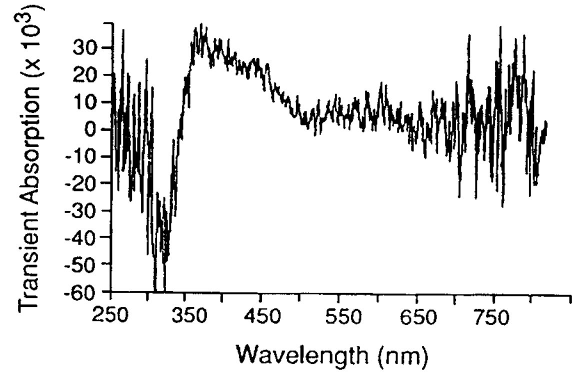


Figure 4. Transient spectrum produced by LFP of DCP in dimethyl carbonate. The spectrum was recorded 500 ns after a 308 nm laser pulse

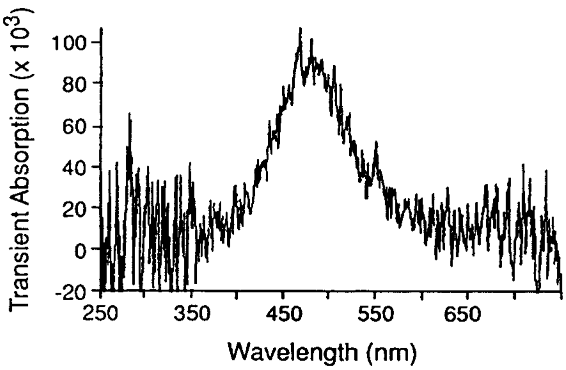


Figure 2. Transient spectrum produced by LFP of DCP in acetaldehyde. The spectrum was recorded 500 ns after a 308 nm laser pulse

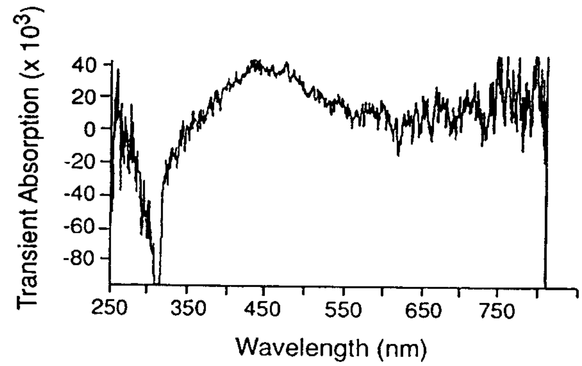


Figure 5. Transient spectrum produced by LFP of DCP in ethyl acetate. The spectrum was recorded 500 ns after a 308 nm laser pulse

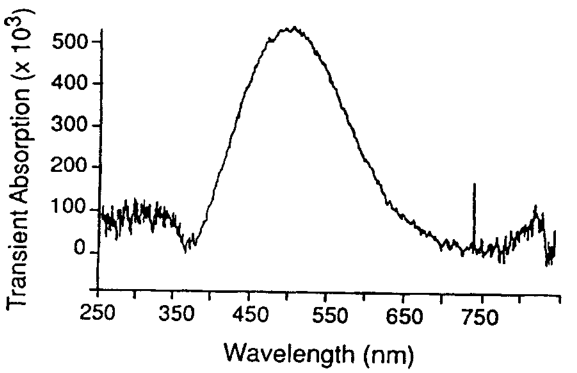


Figure 3. Transient spectrum produced by LFP of DCP in acetone. The spectrum was recorded 500 ns after a 308 nm laser pulse

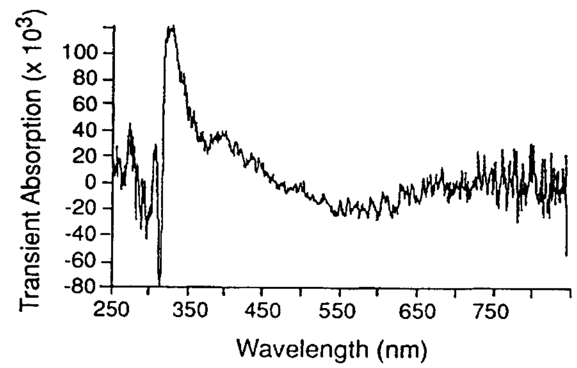


Figure 6. Transient spectrum produced by LFP of DCP in acetonitrile. The spectrum was recorded 500 ns after a 308 nm laser pulse

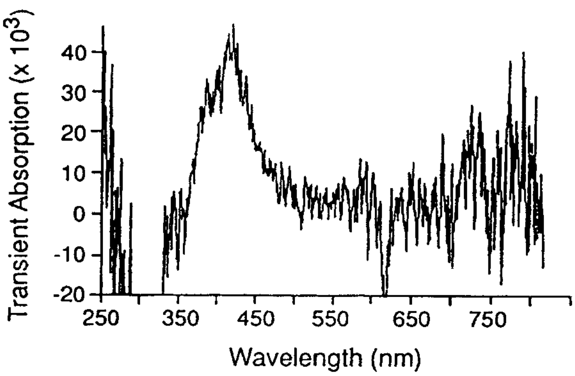


Figure 7. Transient spectrum produced by LFP of DCP in dimethyl sulfide. The spectrum was recorded 500 ns after a 308 nm laser pulse

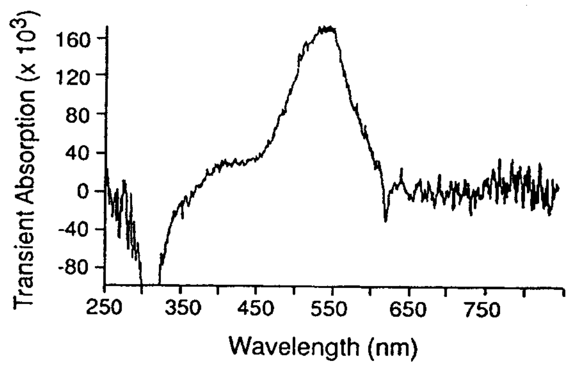


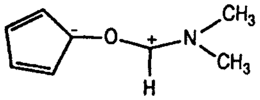
Figure 8. Transient spectrum produced by LFP of DCP in pyridine. The spectrum was recorded 500 ns after a 308 nm laser pulse

Table 1. Transient species observed upon laser (308 nm) flash photolysis of diazocyclopentadiene in various solvents

Carbonyl compounds	λ (nm)	Transient lifetime (µs)
Acetaldehyde	480	3·4
Acetic anhydride	500	0·9
Acetone	500	10
Dimethyl carbonate	360	3·4
Ethyl acetate	440	1·4
Pyridine	530	Long (min–h)
Acetonitrile	325	Long (min–h)
Dimethyl sulfide	420	10

have relatively long lifetimes, on the scale of minutes to hours, whereas that observed with dimethyl sulfide has a lifetime of 10 µs.

LFP of DCP in dimethylformamide also produces a UV–visible-active species. A transient spectrum recorded 500 ns after the laser pulse shows a transient absorption centered near 400 nm (Figure 9). The time evolution of this absorption band (Figure 10) indicates that it results from the absorption of at least two species, a contribution (ca. 30%) from a short lived (1 µs) transient and a larger contribution (70%) from a much longer lived species. Minutes after the laser flash a persistent increase is produced in the absorption of the sample at 400 nm. This suggests that a large component of the absorption present in Figure 9 may be due to a long lived (minutes) product while the smaller portion may be due to carbonyl ylide, **9**, derived from the immediate carbene reaction with the amide.



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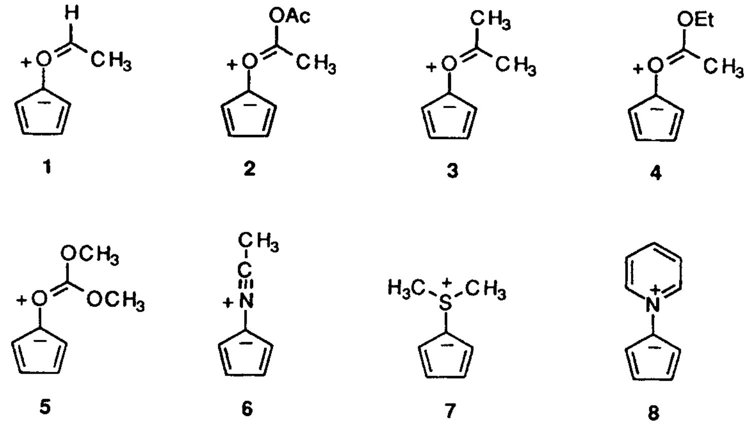


Scheme 1

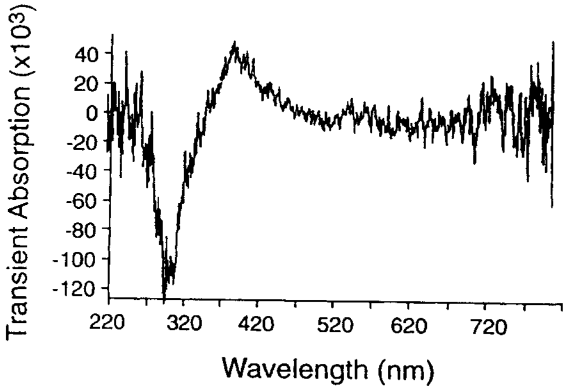
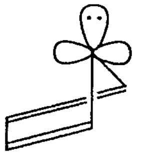


Figure 9. Transient spectrum produced by LFP of DCP in *N*,*N*-dimethylformamide. The spectrum was recorded 500 ns after a 308 nm laser pulse

Unlike CP, neither fluorenylidene nor tetrachlorocyclopentadienylidene produce observable carbonyl ylides with acetaldehyde, acetic anhydride, ethyl acetate and dimethylformamide (DMF). Furthermore, tetrachlorocyclopentadienylidene forms an observable ylide with pyridine but not with acetone or acetonitrile. The fluorenyl radical ($\lambda_{max} = 500$ nm)[10] produced by a hydrogen atom transfer reaction of triplet fluorenylidene was observed in ethyl acetate and DMF.

The greater facility of ylide formation with CP relative to fluorenylidene and tetrachlorocyclopentadienylidene may be due to the superior steric accessibility of the carbene center in CP or to electronic effects. Calculations[11] in fact reveal that the lowest closed-shell singlet configuration of CP is non-planar (e.g. **10**). Theory predicts that the empty-orbital of the carbene does not conjugate with the butadiene moiety and it receives no resonance stabilization. The lowest energy singlet state of CP is predicted, however, to be planar and to have an open-shell structure.



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11a **11b**

Planar, closed-shell structures such as **11a** and **b** of CP are not supported by theory. Substituted derivatives of CP such as fluorenylidene and tetrachlorocyclopentadienylidene may exist as planar singlet species which may change the predominant reactivity mode of these carbenes relative to the parent (CP) system.

The lifetime of the CP–acetone ylide (10 μs) is approximately three times that of its fluorenylidene counterpart (3·4 μs). This longer lifetime is probably related to the greater thermodynamic stability of the cyclopentadienyl anion than the fluorenyl anion.

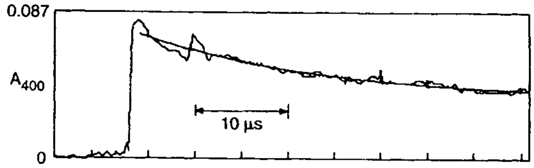
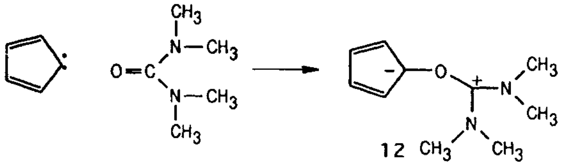


Figure 10. The decay of the short-lived transient produced upon LFP of DCP in *N*,*N*-dimethylformamide. Transient decays to a long-lived species which also absorbs at 400 nm

There are several possible fates for carbonyl ylides, including closure to form oxiranes, 1,3-dipolar cycloaddition to alkenes or carbonyls and fragmentation to form a carbonyl compound and a carbene.[1-6] Product studies have demonstrated that oxiranes are the major products of reaction of carbenes and ketones.[5,6] However, for certain carbonyl ylides derived from aldehydes, 1,3-dipolar cycloaddition to another molecule of aldehyde is observed.[1-6]

Another mechanism/mode of reaction worth considering is oxygen atom transfer. Calculations[12] suggest that certain carbonyl ylides bearing strong electron-donating substituents will fragment exothermically. Formal oxygen atom transfer consistent with this mechanism has been observed in the chemistry of 4,4-diphenylcyclohexadienylidene generated by thermolysis in DMSO,[13], in the reaction of fluorenylidene with oxiranes[14] and in the reaction of anthronylidene with pyridine *N*-oxide.[15] Oxygen transfer may become the dominant reaction of electrophilic carbenes with non-ketone carbonyl compounds and, if this is the case, then CP's facility for forming easily detected ylides may result, in part, from the carbonyl ylide's reluctance to fragment to form the unstable cyclopentadienone.

LFP of DCP in tetramethylurea fails to produce a detectable ylide (e.g. **12**), which is surprising because the structure of **12** implies unusual electronic stability.



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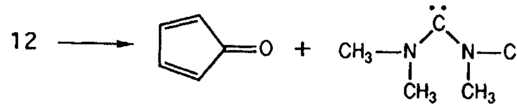
If this ylide is produced then either its chromophore is inconvenient or its lifetime is extremely short owing to rapid fragmentation to form a highly stabilized diaminocarbene (the authors are indebted to Professor Ned Jackson for bringing this possibility to their attention):



EXPERIMENTAL

Materials. Solvents were purified and dried by distillation from calcium hydride.

Diazocyclopentadiene (DCP). Diazocyclopentadiene was prepared and purified by literature procedures.[16] Because of the highly explosive nature of diazocyclopentadiene, distillation was performed under reduced pressure with heating not exceeding 60 °C; the resulting solid was dissolved in Freon 113 and stored in a freezer.

Tetrachlorodiazocyclopentadiene.[17] Activated' manganese dioxide[18] (3 g) was added to a solution of tetrachlorocyclopentadiene hydrazone[17] (1.2 g) in dry chloroform (20 ml) and stirred for 24 h, after which time TLC showed complete conversion. After removal of manganese dioxide by filtration, subsequent purification was performed as described in the literature.[17]

Laser flash photolysis (LFP). The LFP apparatus used has been described previously.[19] LFP was performed with 308 nm laser radiation generated from a Lambda Physik LPX 100 excimer laser (XeCl) or 351 nm laser radiation generated from a Lumonics TE 861 M-T excimer laser (XeF). The absorption of all samples used in the kinetic studies ranged from 0·4 to 0·9 at 308 nm or 351 nm depending on the wavelength employed. Laser samples were deaerated by bubbling with nitrogen for 2–3 min.

Transient spectra. Transient spectra were recorded 500 ns after a 308 nm wavelength laser pulse over a window of 500 ns using a EG&G Princeton Applied Research Model 1460 optical multichannel analyser.

Ylide lifetimes. Time-resolved spectra were measured at the λ_{max} of the various ylides over a window of 0·2 or 0·5 µs. The lifetimes of the growths of the ylides were shorter than the time resolution of *ac.* 20 ns. The lifetimes for the decay of the ylides were measured in neat ylide former and calculated with the aid of the Marquardt algorithm to fit the exponential decay (the Marquardt algorithm has been described.[20] The software in use at Ohio State University was written by Shamin Ahmed).

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