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Time-Resolved Resonance Raman Study of the Reaction of Isodiiodomethane with Cyclohexene: Implications for the Mechanism of Photocyclopropanation of Olefins Using Ultraviolet Photolysis of Diiodomethane

Yun-Liang Li, King Hung Leung, and David Lee Phillips*

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong S. A. R., P. R. China

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We examine the chemical reaction of isodiiodomethane (CH_2I-I) with cyclohexene using time-resolved resonance Raman spectroscopy. Our results indicate that CH_2I-I reacts with cyclohexene to produce an iodine molecule leaving group on the 5−10 ns time scale which then almost immediately forms a I_2:cyclohexene complex. This in conjunction with previous results from photochemistry experiments and recent density functional theory calculations indicates that isodiiodomethane is the methylene transfer agent mainly responsible for cyclopropanation of olefins when using ultraviolet photolysis of diiodomethane. We present a mechanism for photocyclopropanation that is consistent with both experimental and theoretical characterization of reaction intermediates and products formed after ultraviolet photolysis of diiodomethane in a condensed phase environment. We briefly discuss the differences and similarities in the behavior of the isodiiodomethane and the Simmons−Smith carbenoids toward cyclopropanation reactions with olefins.

Introduction

Although cyclopropanation reactions are very important in organic and organometallic chemistry, the reaction mechanisms and the details of the structures and properties of the reaction intermediates are often not well understood. Diiodomethane has found utility as a reagent for cyclopropanation reactions with olefins. Diiodomethane can be activated by either a Zn−Cu couple in the Simmons−Smith reaction[1] or by ultraviolet photolysis.[2−5] Cyclopropanated products can be produced with high stereospecificity[2−5] upon ultraviolet photolysis of diiodomethane in solutions containing olefins. The lack of appreciable C−H insertion reaction and the high stereospecificity of the diiodomethane photocyclopropanation reaction indicate that the methylene transfer agent is not a free carbene. Several different reaction intermediates have been proposed to be the carbenoid that reacts with olefins to give a cyclopropanated product (proposed species have included an excited diiodomethane state, an iodocarbenium−iodide ion pair, and others).[1−5] However, the lack of direct observation of the reaction intermediates with experiments that can provide detailed structural information about the identity and properties of the carbenoid species have hampered work done to better understand the nature of the reaction intermediates and mechanism.

Excitation of diiodomethane by either ultraviolet light,[6−9] direct photoionization,[10] or pulsed radiolysis[11,12] in condensed phase environments all produce products that have characteristic transient absorption bands ∼385 nm (with strong intensity) and ∼570 nm (with weak intensity) that have been assigned to a variety of transient species such as trapped electrons,[6] the cation of diiodomethane[10,12] or the isomer of diiodomethane (CH_2I-I).[8,9] The condensed phase photolysis of diiodomethane has also been examined by several femtosecond transient absorption studies.[13−15] These femtosecond experiments displayed similar behavior for the most part of a fast rise of about several hundred femtoseconds that was then followed by a fast decay of several hundred femtoseconds and then a slower rise in the transient absorption on the 5−20 ps time scale. The fast rise in the transient absorption was agreed to be due to the initial C−I bond cleavage to give CH_2I and I or I•* fragments, and the fast decay was attributed to some recombination of the fragments within the solvent cage. However, three different interpretations for these femtosecond experiments were given depending on which product species was assigned to the transient absorption signal being followed in each experimental study.[13−15]

The ambiguity about the photoproduct species responsible for the characteristic ∼385 nm absorption band observed in both the photochemistry experiments[6−12] and the femtosecond transient absorption experiments[13−15] led us to employ transient resonance Raman spectroscopy to directly probe the identity of this photoproduct.[16] The vibrational frequencies observed in the transient resonance Raman spectra were compared to the calculated frequencies obtained from density functional theory (DFT) computations for several of the proposed photoproduct species, and this clearly showed that the isodiiodomethane (CH_2I-I) species is mostly responsible for the characteristic strong∼385 nm transient absorption band.[16] We subsequently used density functional theory computations to investigate the chemical reactivity of the CH_2I-I, $\bullet CH_2I$, and CH_2I^+ species[17] toward olefins (alkenes) and found that CH_2I-I easily reacts with ethylene to give formation of the cyclopropane product and an I_2 product via a one step reaction with a barrier height of ∼2.9 kcal/mol. However, the $\bullet CH_2I$ and CH_2I^+ species were found to have significantly more difficult pathways to react with ethylene via a two step reaction mechanism that had much larger barriers to reaction. These computational results combined with recent experimental results suggested that the CH_2I-I photoproduct species is likely the methylene transfer agent for photocyclopropanation reaction of olefins (alkenes) using diiodomethane, and a reaction mechanism was proposed.

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* To whom correspondence should be addressed.

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In this paper, we report a time-resolved resonance Raman experimental study to directly examine the reaction of isodiiodomethane with cyclohexene in room temperature solutions. We find that ultraviolet excitation of diiodomethane leads to formation of isodiiodomethane in both cyclohexane and cyclohexene solvents. The lifetime of isodiiodomethane is noticeably shorter in cyclohexene solvent compared to cyclohexane solvent due to reaction with cyclohexene to give an iodine molecule product that rapidly forms a complex with cyclohexene solvent molecules. We present a reaction mechanism for the cyclopropanation reactions of olefins that use ultraviolet excitation of diiodomethane that is consistent with both experimental and theoretical work characterizing the reaction intermediates produced following ultraviolet excitation of diiodomethane in condensed phase environments. We discuss the differences and similarities in the structure, properties, and carbenoid behavior of the isodiiodomethane species and the Simmons–Smith methylene transfer agent.

Experimental Section

Samples of diiodomethane (99% from Lancaster) were prepared with concentrations of approximately 0.24 M in cyclohexane (spectroscopic grade) and cyclohexene (99+%). The time-resolved resonance Raman spectroscopy experiments were done using an experimental apparatus and methods similar to those described previously for transient resonance Raman experiments[16,18–23] with the exception that the present experiments utilized a second nanosecond pulsed Nd:YAG laser which was electronically synchronized with the first laser. Excitation wavelengths for the pump and probe laser beams were generated using either the harmonics or the hydrogen Raman shifted lines from the two nanosecond pulsed Nd:YAG lasers (Spectra-Physics GCR-150-10 and LAB-170-10). Excitation wavelength combinations of 266 nm pump and 416.0 nm probe and 266 nm pump and 341.5 nm probe were used in the time-resolved resonance Raman experiments. The time delay between the pump and probe beams was synchronized using a pulse delay generator (Stanford Research Systems model DG-535) to control the timing of the two lasers (both firing of the lamp and Q-switch pulses). The relative timing of the pump and probe beams was monitored using the output from two fast photodiodes displayed on a 500 MHz oscilloscope (Hewlett-Packard 54522A), and the jitter observed was <5 ns between the two laser pulses. A near collinear geometry was utilized to lightly focus the pump and probe laser beams onto a flowing liquid stream of sample. Reflective optics were used to collect the Raman scattered light and image it through a polarization scrambler positioned at the entrance slit of a 0.5 m spectrograph (Acton model 505-F). The grating (blazed at 250 nm with 1200 grooves/mm) of the spectrograph dispersed the Raman signal onto a liquid nitrogen cooled CCD detector (Photometrics SDS9000) and was accumulated for ~300 s before being readout to an interfaced PC computer. Three to five of these of these readouts were summed to obtain a resonance Raman spectrum at each time delay. A pump only, probe only, and pump–probe spectrum were acquired at each time delay. A background scan was also obtained before and after an experimental trial. The known cyclohexane and cyclohexene Raman bands were used to calibrate the wavenumber shifts of the resonance Raman spectra. The solvent and parent diiodomethane Raman bands were removed from the pump–probe spectra by subtraction of the relevant probe only and pump only resonance Raman spectra in order to obtain the time-resolved resonance Raman spectra at each time delay.

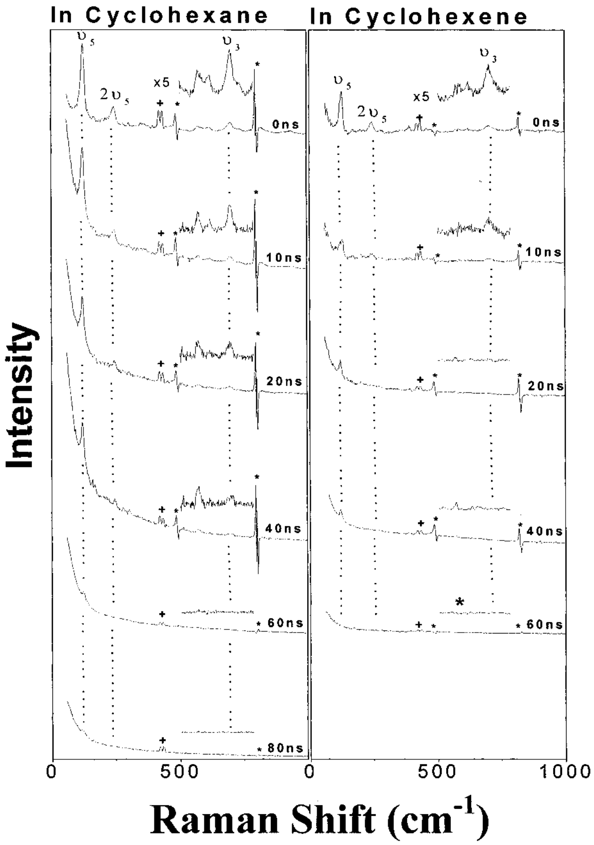

Figure 1. Time-resolved resonance Raman spectra of isodiiodomethane in cyclohexane (left) and cyclohexene (right) solvents obtained using 266 nm pump and 416.0 nm probe beams. The time delay between the pump and probe beams is indicated to the right of each spectrum. Some of the larger Raman bands are labeled with their assignments (ν_5, $2\nu_5$, and ν_3). The text and ref 16 provide more details of the vibrational assignments for isodiiodomethane. The 500–800 cm^{-1} region has been enlarged by a factor of 5 in the inset above each spectrum to make it easier to see changes in the intensity of the ν_3 Raman band as a function of time delay. Asterisks label places where solvent or parent Raman band subtraction artifacts are present. Crosses label stray light or ambient light artifacts.

Results and Discussion

Figure 1 presents time-resolved resonance Raman spectra of the isodiiodomethane species in cyclohexane and in cyclohexene solvents (using 266 nm pump and 416.0 nm probe excitation wavelengths). The resonance Raman spectra for isodiiodomethane shown in Figure 1 are essentially the same as those reported earlier for transient resonance Raman spectra using 309.1 nm pump and 416.0 nm probe excitation wavelengths.[16] The larger isodiiodomethane Raman bands include the nominal I–I stretch mode (ν_5) fundamental at 128 cm^{-1} and its overtones ($2\nu_5$ and $3\nu_5$) as well as the nominal C–I stretch mode (ν_3) fundamental at ~701 cm^{-1}, the nominal CH_2 wag (ν_4) fundamental at ~619 cm^{-1}, and the partially overlapped combination bands of $\nu_6 + 4\nu_5$ and $\nu_9 + \nu_5$ in the 580–600 cm^{-1} region. The reader is referred to ref 16 for more details of the assignment of the Raman vibrational bands to the isodiiodomethane species.

Inspection of Figure 1 shows that the isodiiodomethane species has a noticeably longer lifetime in cyclohexane solvent than in cyclohexene solvent. In addition, the transient isodiiodomethane signal appears somewhat weaker in the cyclohexene solvent although both experiments were done under virtually identical experimental conditions (i.e., done with the same beam alignment with only a change of the sample solutions). The shorter lifetime and smaller signal for the isodiiodomethane species in cyclohexene may be due to reaction of the isodiiodomethane species with the cyclohexene solvent on the 5−10 ns time scale. On the basis of recent density functional theory chemical reaction computations[17] and experimental results,[13−16,21,22,24−26] we proposed the following reaction mechanism for cyclopropanation of olefins using ultraviolet photolysis of diiodomethane in room-temperature solutions:

$$\text{initiation step}\qquad CH_2I_2 + h\nu \rightarrow \bullet CH_2I + I\bullet \qquad (1)$$

recombination to produce isomer

$$\bullet CH_2I + I\bullet \rightarrow CH_2I{-}I \qquad (2)$$

reaction of $CH_2I{-}I$ with olefin

$$CH_2I{-}I + \text{olefin} \rightarrow \text{cyclopropanated product} + I_2 \qquad (3)$$

formation of I_2−olefin complex

$$I_2 + \text{olefin} \rightleftharpoons I_2{-}\text{olefin complex} \qquad (4)$$

Several experiments[15,25] have unequivocally demonstrated that some of the initially formed $\bullet CH_2I$ and $I\bullet$ fragments in reaction step 1 can recombine within a few picoseconds to form the isodiiodomethane ($CH_2I{-}I$) photoproduct (this has a characteristic intense ~385 nm transient absorption band[15,16,25]) in reaction step 2. Our recent density functional theory computations[17] indicate that the $CH_2I{-}I$ species readily reacts with olefins to give cyclopropanated product and iodine molecule as in step 3. Brown and Simons[26] observed that the characteristic ~385 nm transient absorption formed after photoexcitation of diiodomethane in hydrocarbon glasses (that we[16] and Maier and co-workers[8,9] have assigned to isodiiodomethane) is quenched by alkenes to produce a new iodine molecule−alkene complex absorption band when the solid sample was allowed to warm and melt. This also suggests that isodiiodomethane may react with olefins to produce a cyclopropanated product and iodine molecule leaving group consistent with reaction step 3. In addition, halogen molecules are known to very easily react with olefins to form halogen molecule−olefin complexes as in step 4 for the I_2−olefin complex.[27−31]

To further investigate the potential reaction of isodiiodomethane with olefins in room-temperature solutions, we have done additional time-resolved resonance Raman experiments using 266 nm pump and 341.5 nm probe excitation wavelengths where the probe wavelength is near the isobestic point between the decay of the ~385 nm transient absorption band associated with isodiidodomethane and the formation of the ~320 nm absorption band due to I_2:olefin complex (see Figure 5 of reference 26). These experiments allow us to simultaneously monitor the formation and decay of the isodiiodomethane species and the potential iodine molecule product (in the form of its complex with cyclohexene) from cyclopropanation reaction of isodiiodomethane with cyclohexene.

Figure 2 presents the time-resolved resonance Raman spectra obtained for 266 nm photolysis of diiodomethane in cyclohexene solution using a 341.5 nm probe wavelength. Examination of Figure 2 shows that Raman bands associated with the isodiiodomethane molecule (ν_3 at ~700 cm^{-1}, $\nu_3 + \nu_5$ at ~830 cm^{-1}, and $\nu_4/\nu_3 - \nu_5/\nu_6 + 4\nu_5$ and $\nu_9 + \nu_5$ that are partially overlapped in the 580−620 cm^{-1} region) appear strongest at ~0 ns and then decrease in intensity between 0 and 20 ns. This decrease in intensity of the isodiiodomethane Raman bands in cyclohexene at the 341.5 nm probe wavelength in Figure 2 parallels that observed at the 416.0 nm probe wavelength shown in Figure 1. Over this same 0−20 ns region of time delay, new resonance

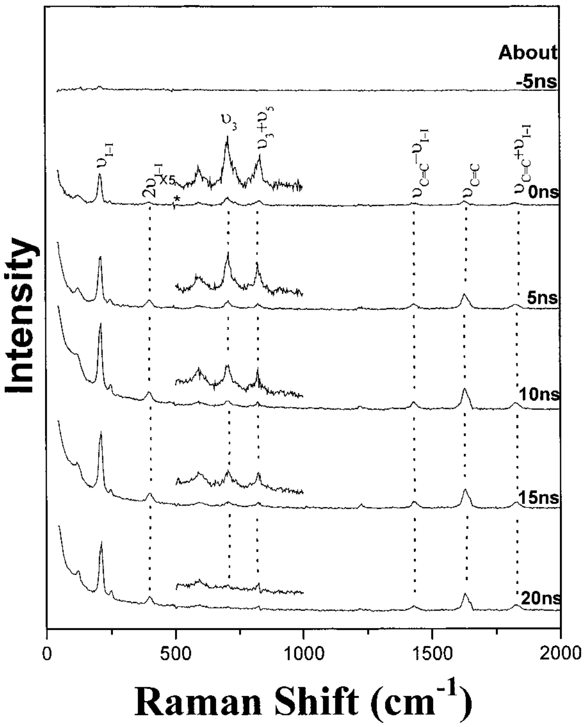

Figure 2. Time-resolved resonance Raman spectra of isodiiodomethane and I_2:cyclohexene complexes in cyclohexene solvent obtained using 266 nm pump and 341.5 nm probe beams. The time delay is indicated to the right of each spectrum. Some of the larger Raman bands are labeled with their assignments (ν_5, $2\nu_5$, and ν_3 for isodiiodomethane and the ν_{I-I}, $2\nu_{I-I}$, $\nu_{C=C}$, $\nu_{C=C}-\nu_{I-I}$, and $\nu_{C=C} + \nu_{I-I}$ for the I_2:cyclohexene complex). The reader is referred to the text for more details of the vibrational assignments for isodiiodomethane and I_2:cyclohexene complexes. The section 500−800 cm^{-1} has been expanded by a factor of 5 in the inset above each spectrum in order to more easily observe changes in the intensity of the ν_3 Raman band as a function of time delay. Asterisks label places where solvent or parent Raman band subtraction artifacts are present. Crosses label stray light or ambient light artifacts.

Raman bands appear at ~200, 395, ~1625, ~1425, and ~1825 cm^{-1} that are due to formation of an I_2:cyclohexene complex. Resonance Raman spectra of several I_2:alkene complexes[32] obtained with excitation in the absorption band around 300 nm were very similar to one another with most of their Raman intensity appearing in the overtones and combination bands of the nominal I−I stretch mode (fundamental ~200 cm^{-1}) and the C═C stretch mode (fundamental ~1620−1630 cm^{-1}). The fact that the I−I stretch mode forms combination bands with the nominal C═C stretch mode indicates these resonance Raman spectra and the associated absorption band in the 300 nm region are due to an I_2:alkene complex and not their separated species. Therefore, the new resonance Raman bands seen in Figure 2 are assigned to the I_2:cyclohexene complex as follows: the fundamental of the nominal I−I stretch to the band ~200 cm^{-1}, the first overtone of the I−I stretch to the band ~395 cm^{-1}, the nominal C═C stretch fundamental to the band ~1625 cm^{-1}, and the difference band and combination band of the C═C stretch and I−I stretch to the bands ~1425 cm^{-1} and ~1825 cm^{-1}, respectively. We note that the Raman bands due to the I_2:alkene complex are not present in the about −5 ns delay time between the pump and probe beams, and this indicates the new transient Raman bands are not due to an iodine impurity or due to iodine buildup of photoproducts in the bulk sample.

The new Raman bands in Figure 2 substantially increase in intensity from 0 to 10 ns at the same time the isodiiodomethane resonance Raman bands in the cyclohexene solvent decrease substantially in Figures 1 and 2 (probe wavelengths of 416.0 and 341.5 nm, respectively). This clearly suggests that isodiiodomethane reacts with cyclohexene very fast to give an iodine molecule leaving group that then forms the observed I_2:cyclohexene complex. There is noticeable intensity in the I_2:cycloexene complex Raman bands at the nominal 0 ns time delay between the pump and probe pulses, and this indicates the reaction between isodiiodomethane occurs on a similar time scale as the laser pulse-widths of about 4 ns (i.e., some reaction occurs between the rising edge of the pump pulse and the decaying edge of the probe pulse). This is consistent with the weaker isodiiodomethane intensity and shorter lifetime observed in cyclohexene compared to cyclohexane solutions observed in Figure 1. The original studies of Blomstrom et al.[2] found that ultraviolet photolysis of diiodomethane in a cyclohexene solution led to substantial conversion of the diiodomethane into norcane (the cyclopropanated cyclohexene product) and an iodine color that rapidly developed during the reaction. The key cyclopropanation reaction step 3 in our proposed reaction mechanism is consistent with the present nanosecond time-resolved resonance Raman spectroscopy results that show a very fast decay of the isodiiodomethane photoproduct giving rise almost immediately to formation of an I_2:cyclohexene complex, previous density functional theory computations that indicate isodiiodomethane can readily react with olefins to produce a cyclopropanated product and I_2 leaving group via a single step with a low barrier to reaction[17] and previous synthetic photochemical studies.[2−5]

Our present time-resolved resonance Raman spectroscopy experiments indicate that isodiiodomethane is the methylene transfer agent (or carbenoid) mainly responsible for the cyclopropanation reaction with olefins that employ ultraviolet photolysis of diiodomethane in room-temperature solutions. Understanding the identity and structure of the isodiiodomethane carbenoid leads to interesting chemical insight into the similarities and differences between activation of diiodomethane by a Zn(Cu) couple in the Simmons−Smith reaction[1] and by ultraviolet photolysis in the photocycloproanation reaction.[2−5] The Simmons−Smith "ICH_2ZnI" carbenoid reaction with ethylene has recently been studied using density functional theory computations.[33] This study obtained a calculated optimized geometry for the ICH_2ZnI species that displayed reasonable agreement with an X-ray crystal structure for the related bis(iodomethyl)zinc intermediate complexed with a glycolether.[34] The ICH_2ZnI carbenoid has its ZnI_2 leaving group attached to the methylene by two bonds (C−Zn and C−I), whereas the isodiiodomethane carbenoid has its I_2 leaving group attached by one bond (the lone C−I bond). This difference in structure and activation of the methylene moiety leads to significantly different chemical reactivity. For example, the photocycloproanation reaction associated with the isodiiodomethane carbenoid displays increasing reaction rates upon going from mono- to tetra-substituted alkenes, whereas the Simmons−Smith carbenoid (the diiodomethane−Zn complex) typically displays a reduced rate of reaction toward highly substituted alkenes.[1−5] This can largely be attributed to steric effects and a different mode of activation of the methylene group. The isodiiodomethane carbenoid has a much more open structure that is not much more sterically demanding than a CH_2I radical or methylene group. Therefore, it can much more easily approach and react with more highly substituted alkenes than the noticeably more bulky and sterically demanding Simmons−Smith carbenoid that has its ZnI_2 leaving group attached to the methylene moiety by two bonds. The rates of reaction for the two types of carbenoids are also affected by their different modes of activation. Density functional theory computational results for the Simmons−Smith (ICH_2ZnI) cyclopropanation reaction with ethylene found a barrier to reaction of about 11.5 to 14.6 kcal/mol[33] to 17 kcal/mol[35] depending on the level of theory and basis sets employed, whereas similar calculations for the cyclopropanation of isodiiodomethane with ethylene found much smaller barrier heights to reaction of about 2.9 kcal/mol. The Simmons−Smith reaction only occurs efficiently at high temperatures which is consistent with the large barriers to reaction observed in the DFT studies of this reaction.[33,35,36] However, the photocyclopropanation reaction occurs efficiently in room temperature solutions consistent with a methylene transfer agent that has a substantially lower barrier to reaction than the Simmons−Smith carbenoid. Although, the isodiiodomethane and Simmons−Smith ICH_2ZnI carbenoids have significantly different chemical reactivity and chemical structure, DFT studies[17,33,35,36] indicate that their reactions with the C═C bond of olefins are similar in that they both occur via a single reaction step and attack the C═C bond asymmetrically with weakening of the C═C bond accompanied by an asymmetric C−C bond formation.

Comparison of the structures and chemical reactivity of the isodiiodomethane and Simmons−Smith ICH_2ZnI carbenoids suggests a couple of strategies for finding better carbenoid agents for particular applications. For organometallic methylene transfer agents, it seems likely that activation of the methylene moiety in an organometallic carbenoid in which the molecular leaving group is attached by one bond (as in the organic isodiiodomethane carbenoid) could provide a methylene transfer agent that is much more reactive toward olefins as well as capable of efficiently cyclopropanating highly substituted alkenes. One could also try to tune the steric effects and the chemical reactivity of the carbenoid to optimize conditions for selecting cyclopropanation of particular C═C bonds. For example, it is already known that the photocycloproanation via ultraviolet photolysis of diiodomethane preferentially reacts at the more highly substituted cyclohexenyl double bond in limonene, whereas the Simmons−Smith carbenoid preferentially reacts with the less substituted isopropeneyl double bond.[4,5]

For cycloproanation reactions, we expect that both the lifetime and barrier to reaction with olefins to give cyclopropanated products and halogen molecule leaving groups would vary significantly with the type and number of halogen atoms attached to the carbon atom in isopolyhalomethane species. Thus, it may be worthwhile to systematically explore the carbenoid behavior of these species and seek improvements in photocyclopropanation reactions and also explore cyclopropanation reaction that add H−C−X or CX_2 groups to the C═C bond of the olefins. We have observed that ultraviolet photolysis of a number of different polyhalomethanes (such as CH_2Br_2, CH_2BrI, $CHBr_3$, $CFBr_3$, $CHBr_2Cl$, and $CBrCl_3$) in room solutions produce isomer photoproducts with at least nanosecond lifetimes[20−22,37,38] similar to diiodomethane.[16] We are currently exploring their photocyclopropanation reactions with olefins and results will be reported in due course.

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