

One- vs Two-Photon Processes in the Photochemistry of 1,*n*-Dihaloalkanes

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ABSTRACT

1,*n*-Dihaloalkanes can be photochemical precursors of *n*-haloalkyl and -allyl radicals and cations, which are generated via one-photon processes. Time-resolved techniques have provided considerable information on the structures and reactivity of these intermediates. Low-temperature matrix isolation, two-laser two-color, laser-drop, and laser-jet photolysis techniques are powerful tools to photolyze haloalkyl radicals and to generate carbenes or biradicals via two-photon processes.

Introduction

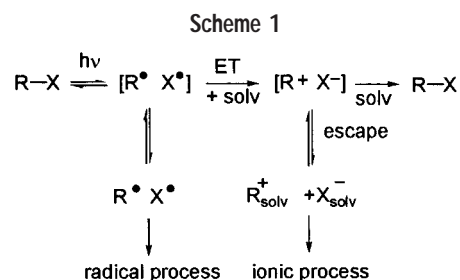
The lowest energy transition of haloalkanes involves promotion of one of the *n* electrons of the halogen to the σ^* orbital of the carbon–halogen (C–X) bond. The wavelength of the light absorption by this chromophore depends on both the nature of the halogen atom and the

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substituent on the carbon atom. For simple chloro- and fluoroalkanes, such absorptions occur below 200 nm, but increasing atomic number of the halogen and aromatic substitution cause a bathochromic shift of the absorption maximum.¹ Absorption of light by monohaloalkanes usually induces carbon–halogen bond cleavage; the ease of homolysis is opposite to the order of the C–X bond strength, C–F < C–Cl < C–Br < C–I.¹ Although direct photolysis of the C–F bond is extremely rare, all the benzylic halides undergo light-induced cleavage. Previous studies have shown that the initially formed radical pair can escape from the cage to participate in radical processes or undergo electron transfer to generate ionic intermediates (Scheme 1). The type of products obtained depends on the polarity of the solvent and the nature of the leaving group. Thus, carbocationic reactions are favored in polar solvents and compete more effectively with radical processes in the case of iodoalkanes than with the equivalent bromides.² The heterolysis/homolysis ratio correlates with the pK_a values of the conjugate acids HX and not with the electron affinities of X[•]. Solvation of the incipient ions seems to be concerted with the electron transfer; so the reduction potentials of the halides will determine the driving force for the electron transfer.³

Dihaloalkanes are interesting substrates due to their bichromophoric nature. Photolysis of the first C–X bond gives rise to the one-photon transients, namely haloalkyl radicals or cations. Such species have been postulated in many interesting thermal and photochemical reactions (radical halogenation of alkanes, addition of halogens to double bonds, photocyclopropanation of alkenes). In some cases, time-resolved laser techniques allow one to generate haloalkyl radicals in solution and perform reactivity studies. Furthermore, these techniques have been used to detect new species (such as biradicals and biradicaloids) through absorption of a second photon by the initially generated haloalkyl radical (Scheme 2). On the other hand, low-temperature matrix isolation techniques have provided considerable structural and mechanistic information on two-photon intermediates generated

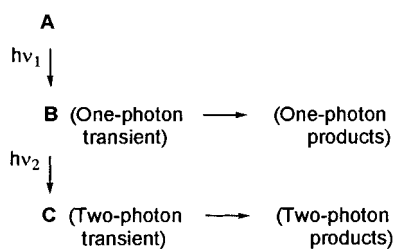
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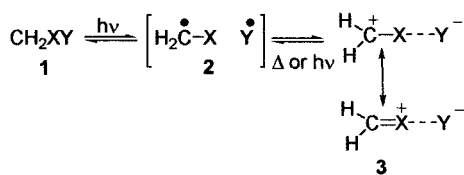
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Scheme 2



Scheme 3



1a: X = I, Y = I	X = Y = I	370 nm, 545 nm
1b: X = Br, Y = I	X = Br, Y = I	403 nm, 660 nm
1c: X = Cl, Y = I	X = Cl, Y = I	438 nm, 745 nm
1d: X = F, Y = I		

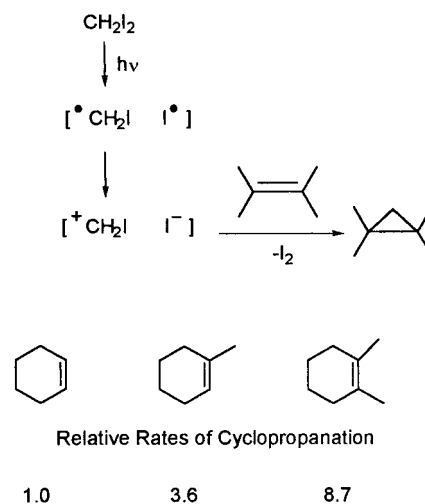
using dihaloalkanes as precursors. Thus, carbenes, biradicals, and biradicaloids have been detected and characterized by photolysis of dihalides at 77 K. The essence of this technique is the generation of reactive intermediates in frozen, inert medium; the low temperature prevents bimolecular reactions. In this case, difficulties are associated with detection of the photolabile one-photon haloalkyl intermediate.

This Account deals with the photochemistry of dihaloalkanes from the point of view of the nature of the intermediates generated. Special emphasis is placed on the latest developments, based on applying modern two-laser two-color techniques to generate and detect 1,*n*-biradicals. These species have been postulated as intermediates in many interesting reactions, such as dimerization of styrenes, isomerization of cyclopropanes, di- π -methane rearrangement, and extrusion of small molecules (nitrogen, carbon monoxide, SO₂, etc.) from cyclic azoalkanes, ketones, sulfones, or other precursors.

Photochemistry of 1,1-Dihaloalkanes

Generation of Isodihaloalkanes. Photolysis of dihalomethanes **1** in an argon matrix at 12 K gives rise to an equilibrium with their isomeric species **3**; if two different halogen atoms are present, it is the heavier one that migrates (Scheme 3).⁴ Homolytic cleavage of the weaker carbon–halogen bond (C–Y) seems to be the primary step. The generated radical pair **2** cannot dissociate in the solid matrix and collapses to the starting dihaloalkane or to the isodihaloalkane. Isomerization of diiodomethanes is easier than that of dibromo-, bromochloro-, or dichloromethanes since only the iodinated compounds show absorption bands in the UV region between 295 and 255 nm. Interestingly, fluoroiodomethane (**1d**) does not afford the photoisomer.

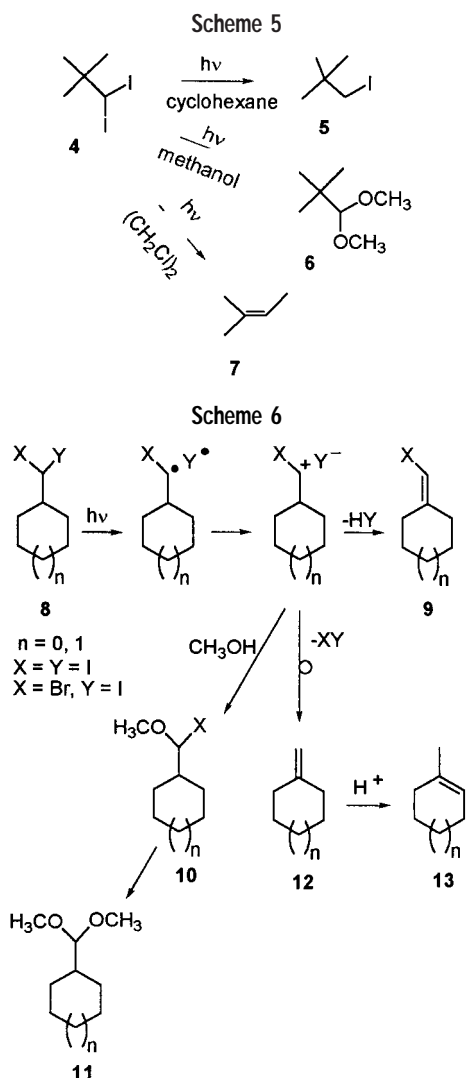
Scheme 4



When the matrixes containing compounds **1a–c** are irradiated with monochromatic light corresponding to the long-wavelength component of each absorption band, they become colored because of the formation of the isodihalomethanes, which have UV spectra with a weak long-wavelength band ($\epsilon \sim 1300$) and a stronger band ($\epsilon \sim 10000$) at higher energy. The reverse reaction (**3** \rightarrow **1**) can be induced by irradiation with light having the same wavelength as one of the UV maxima. This reaction also occurs upon warming to 26–30 K. It is believed that isodihaloalkanes play an important role in the photochemistry of all dihalomethanes.

Generation of α -Halocations. In solution, irradiation of dibromo- and diiodomethane in the presence of olefins yields cyclopropanes. It has been suggested that the initially generated α -iodoradical in the photolysis of 1,1-diiodomethane undergoes electron transfer to afford the α -iodocation, which is able to achieve cyclopropanation (Scheme 4).^{5,6} Two facts agree with the electrophilic nature of the reactive intermediate: (a) trapping occurs in the presence of lithium bromide to afford bromoiodomethane and (b) the reaction rates increase with the nucleophilicity of the alkene from mono- to tetrasubstituted derivatives. This cyclopropanation procedure is less sensitive to steric effects than the Simmons–Smith method, therefore, being particularly useful with congested olefins. For instance, 2,2,5,5-tetramethyl-3-hexene affords no adduct when using the Simmons–Smith method,⁶ while the photocyclopropanation yield is 30%. The same applies to 2,3-dimethyl-2-butene (42% yield with the Simmons–Smith method versus 83% yield of photocyclopropanation).

On the other hand, irradiation of 1,1-diiodo-2,2-dimethylpropane (**4**) affords 1-iodo-2,2-dimethylpropane (**5**) in cyclohexane, 1,1-dimethoxy-2,2-dimethylpropane (**6**) in methanol, and 2-methyl-2-butene (**7**) in 1,2-dichloroethane (Scheme 5).^{7,8} While product **5** could be explained through the intermediacy of an α -iodo radical, the formation of **6** and **7** could involve a iodonium intermediate. However, attempts to achieve cyclopropanation of olefins failed. For instance, after irradiation of **4** in cyclohexene, the only products were compounds **5** and **7**.

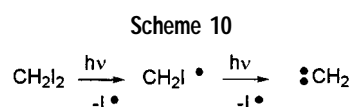
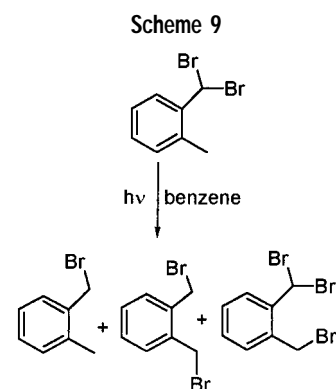
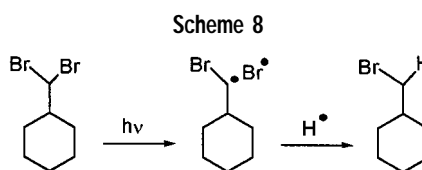
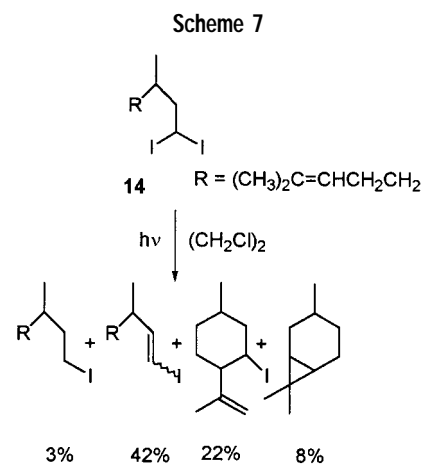


The photobehavior of other 1,1-diiodo- and 1,1-bromoalkanes **8** has been studied and compared with that observed for **4**. The corresponding vinyl halide **9**, (di)methoxyalkanes **10** and **11** (when methanol is the solvent), and olefins **12** and **13** are suggested to arise from the α -halo cation (Scheme 6).⁵

The finding that 8,8-diiodo-2,6-dimethyl-2-octene (**14**) gives some cyclopropanation⁵ suggests that this reaction is limited to intramolecular systems or to intermolecular processes with simple diiodides, such as diiodomethane, which have no β carbon atom (Scheme 7).

Generation of α -Haloradicals. Contrary to the iodo analogues, 1,1-dibromomethylcyclohexane gives predominantly radical behavior,⁵ leading to the reduction product even in polar solvents such as 1,2-dichloroethane (Scheme 8). This behavior is consistent with the finding that alkyl iodides afford predominantly ionic products, whereas bromides give rise predominantly to radical processes. One of the reasons may be that hydrogen abstraction by bromine atoms competes favorably with electron transfer within the initially formed radical pair.

Similarly, in the case of α, α -dibromo-*o*-xylene, homolysis of the C–Br bond is followed by a series of

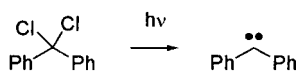


hydrogen abstraction and radical recombination reactions (Scheme 9).⁹

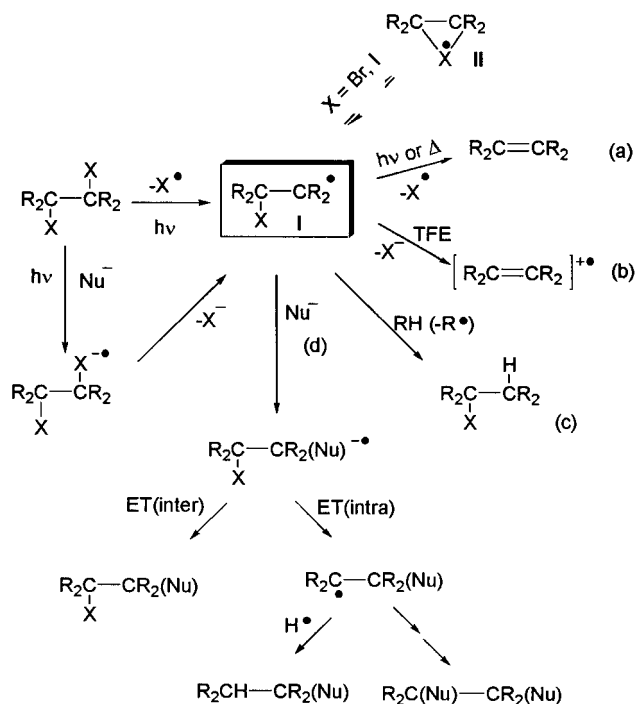
Generation of Carbenes. As stated above, diiodomethane can photoisomerize to isodiiodomethane in an argon matrix. On the other hand, diiodomethane is a reagent for cyclopropanation in solution, whereby an iodocarbenium–iodide ion pair is proposed as the reactive intermediate. These observations demonstrate that the mechanism of the photolysis of diiodomethane might be different in both condensed phases. In the gas phase, formation of iodomethyl radical and iodine atom is the primary step; the main reaction is re-formation of the parent molecule.¹⁰ On the other hand, photofragmentation spectroscopy of diiodomethane at 266 nm evidences a two-photon, two-step dissociation process. The first photon affords the α -iodoradical, which may absorb a second photon and dissociate to CH_2 and another iodine atom (Scheme 10).¹¹

Photolysis of glassy matrixes of 1,1,2,2-tetrakis(dimethylamino)ethene containing 1,1-dichloro-1,1-diphenylmethane produces diphenylcarbene (Scheme 11)

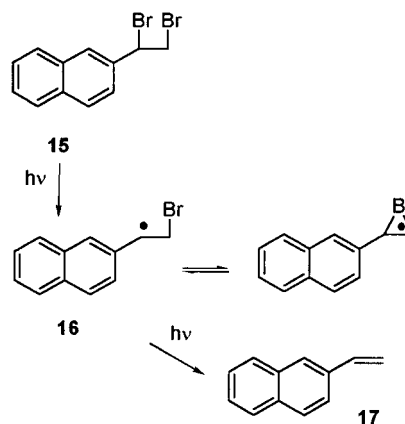
Scheme 11



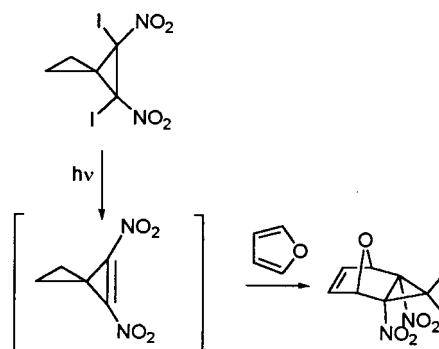
Scheme 12



Scheme 13



Scheme 14



through an electron-transfer mechanism. This intermediate has been detected by EPR.¹²

Photochemistry of 1,2-Dihaloalkanes

Generation of β -Haloradicals. Photolysis of the first C–X bond of 1,2-dihalides gives rise to β -haloalkyl radicals. Their role in the control of the stereochemistry during the halogenation of alkenes and haloalkanes is bound to the existence of an equilibrium between open (**I**) and bridged (**II**) structures.¹³ Theoretical calculations have found that the bridged structures are strongly favored for $CH_2BrCH_2^\bullet$ and $CH_2ICH_2^\bullet$ radicals. In the case of $CH_2ClCH_2^\bullet$ and $CH_2FCH_2^\bullet$, both structures have similar energy, while $CH_2FCH_2^\bullet$ prefers the open structure.¹⁴ In agreement with these studies, loss of the β -bromine atom of the $(CH_2BrCHBr)_3SiCHBrCH_2^\bullet$ radical, obtained in the photolysis of tetrakis(1,2-dibromoethyl)silane, appears to be insensitive to the presence of oxygen, suggesting that bromine bridging plays an important role.¹⁵ Furthermore, although β -chloroethyl aryl radicals have UV spectra with λ_{max} ca. 320 nm and are quenched by oxygen at the diffusion rate (general features of benzylic radicals), the analogous β -bromo radicals show low reactivity toward oxygen; this supports the predominance of the bridged structure for the latter.¹⁶

In low-polarity solvents (benzene, acetonitrile), β -bromoalkyl radicals lose bromine atoms thermally (Scheme 12, pathway a). Thus, 1,2-dibromides photodecompose to give bromine atoms with a quantum yield of ca. 2. In the presence of a donor, hydrogen abstraction by bromine atom yields HBr. The photolytically controlled generation

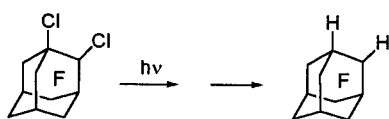
of this strong acid is of great interest in the photoresist and photolithography industries.^{17–19}

By contrast, 2-bromo-1-(2-naphthyl)ethyl radical (**16**), generated by UV laser photolysis of 2-(1,2-dibromoethyl)naphthalene (**15**), does not debrominate thermally. This behavior has been attributed to the stability of the intermediate naphthylethyl radical (Scheme 13).¹⁶ However, photolysis of radical **16** using a second laser pulse leads to further C–Br cleavage and enhances production of 2-vinylnaphthalene (**17**).

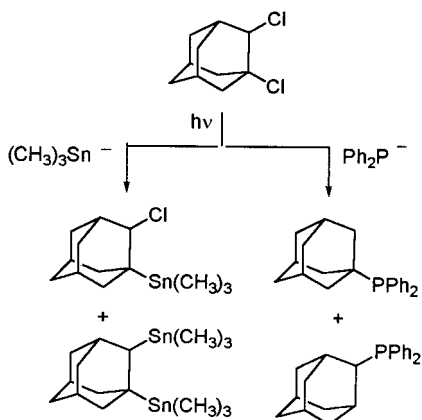
Dehalogenation of 1,2-dihaloalkanes has been used for synthetic purposes. Thus, loss of two iodine atoms in 1,2-diiodoalkanes has been envisioned as a route to synthesize reactive dienophiles (Scheme 14).²⁰

On the other hand, in highly polar solvents such as 2,2,2-trifluoroethanol, 1-arylalkyl radicals with bromine or chlorine atoms attached to the carbon adjacent to the radical center decay mainly through heterolysis of the remaining C–X bond, to give styrene radical cations (Scheme 12, pathway b).²¹ The rate of heterolysis is influenced by the nature of the leaving group, the ionizing ability of the solvent, and the structure of the initially generated radical intermediate. The accelerating effect of electron-donor substituents at the para position of the aromatic ring evidences the direct participation of the radical in the heterolysis process. An additional phenyl group at the β -position facilitates the heterolysis, leading to stilbene radical cations. It has been suggested that stabilization of the positive charge by the phenyl group as the heterolysis process proceeds may be responsible for such an effect.²¹

Scheme 15



Scheme 16



In the presence of hydrogen donors, β -chloroalkyl radicals can abstract H atoms (Scheme 12, pathway c). Polychloroperfluoroadamantanes dissolved in CFCl_3 are photodehalogenated in the presence of methanol, hexane, or other hydrogen donor cosolvents. Thus, in 1,2-dichloroperfluoroadamantanes, chlorine atoms can be replaced by hydrogen atoms in a stepwise manner using a simple photochemical reduction (Scheme 15). This provides an inexpensive method for the synthesis of perfluoroadamantyl derivatives.²²

Finally, haloalkanes with low reactivity toward polar nucleophilic substitution, such as the bridgehead halo-compounds, can react with nucleophiles by photostimulated radical nucleophilic substitution ($\text{S}_{\text{RN}}1$).^{23,24} It has been postulated that electron transfer (ET) between the nucleophile and haloalkane generates a radical anion

which dissociates, leading to a radical. Thus, β -haloalkyl radicals are postulated as intermediates in the photolysis of such 1,2-dihaloalkanes. Their coupling with the nucleophile (Scheme 12, pathway d) would give rise to a new radical anion, where intramolecular ET to the remaining C–X bond may compete with the intermolecular process. Thus, the monosubstituted products may not be intermediates in the formation of the sometimes observed disubstituted compounds. Several studies have shown that the rate of intramolecular ET depends on the energy difference between the molecular orbitals involved, as well as the size and flexibility of the bridge. Reactions of this type have been used for the synthesis of mono- and disubstituted adamantane derivatives (Scheme 16).

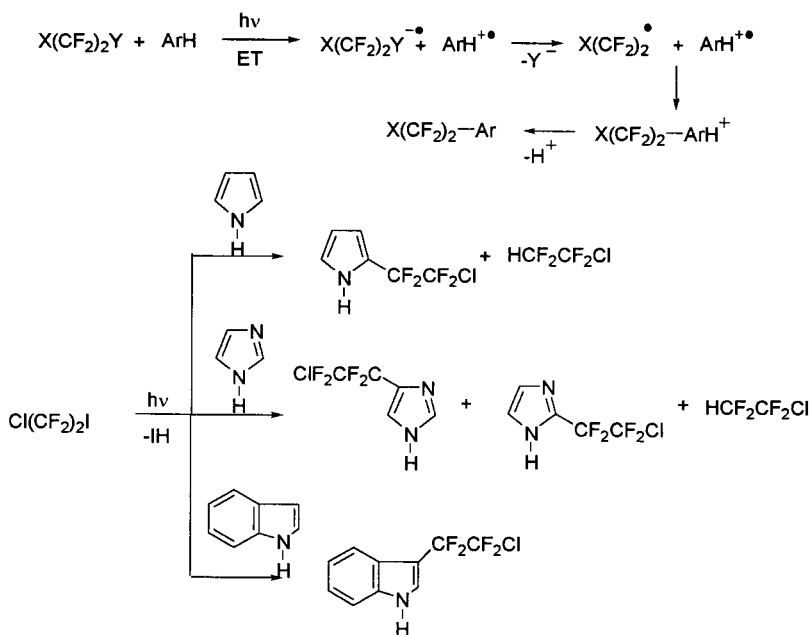
On the other hand, photoinduced electron transfer between aromatic amines and 1,2-dihaloalkanes allows the preparation of fluorine-containing heteroaromatic compounds.^{25,26} The mechanism of this reaction does not appear to be $\text{S}_{\text{RN}}1$; however, there is evidence for the formation of an aromatic radical cation and a perfluoroalkyl radical. Their coupling would afford the observed product (Scheme 17).

Photochemistry of 1,*n*-Dihaloalkanes ($n > 2$): Connection through an Aromatic Ring

Generation of Biradicaloids. Photolysis at 254 nm of an alkane matrix containing 1,2-bis(chloromethyl)benzene (**18**, X = Cl) produces *o*-xylylene (**20**) detected by its fluorescence spectrum.¹² In solution, both 1,2-bis(chloromethyl)benzene and 1,2-bis(bromomethyl)benzene (**18**, X = Br) have been shown to be photochemical precursors of *o*-xylylene (Scheme 18).²⁷

Laser flash photolysis of deaerated solutions of **18** (X = Cl) in cyclohexane at 266 nm gives rise to the formation of two transients: the 2-(chloromethyl)benzyl radical (**19**) and *o*-xylylene (**20**), with absorption maxima at 330 and

Scheme 17



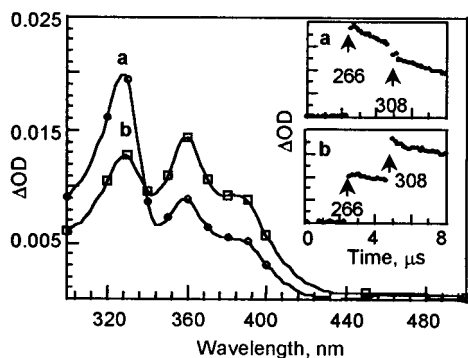
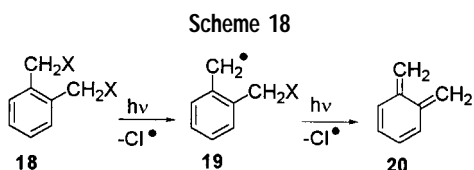


FIGURE 1. (a) Transient absorption spectrum recorded following laser excitation (266 nm) of 1,2-bis(chloromethyl)benzene under nitrogen 1.12 μs after laser pulse. (b) Transient absorption spectrum obtained after two-laser two-color excitation of 1,2-bis(chloromethyl)benzene. The intermediate generated by means of a 266 nm laser pulse is photolyzed after 2 μs by a second laser at 308 nm. Inset: Kinetic trace at 330 (a) and 360 nm (b). The bleaching at 330 nm corresponds to the disappearance of the benzylic radical, and the jump at 360 nm corresponds to the formation of *o*-xylylene.



360 nm, respectively (Figure 1, spectrum a).^{27,28} As expected, only radical **19** was sensitive to the presence of oxygen in the recorded time scale (data not shown). Two-laser two-color techniques have proved that the 2-(chloromethyl)benzyl radical, generated by means of a 266 nm laser pulse, is photolyzed by a second laser at 308 nm, leading to xylene; this shows the two-photon origin of this transient from 1,2-di(chloromethyl)benzene and confirms that the benzyl radical **19** is the key light-absorbing precursor (Figure 1, spectrum b and inset).²⁸

Similarly, laser flash photolysis of 1,4-bis(chloromethyl)benzene (**21**) leads to the formation of two transients: the 4-(chloromethyl)benzyl radical (**22**) and *p*-xylylene (**23**), with absorption maxima at 320 and 290 nm, respectively (Figure 2). Again, two-laser two-color flash experiments have been used to demonstrate the sequential two-photon generation of *p*-xylylene from 1,4-bis(chloromethyl)benzene (Scheme 19).²⁸

Generation of Biradicals (Non-Kekulé Structures).

Non-Kekulé hydrocarbons have been obtained by photolysis of bis(halomethyl)aromatic compounds. Thus, 254 nm photolysis of 1,3-bis(chloromethyl)benzene (**24**, X = Cl) in glassy ethanol gives rise to benzyl-type monoradicals and *m*-xylylene biradical (**26**), which have been detected by their fluorescence spectra (Scheme 20, equation a). Similar results have been obtained by solution-phase-induced fluorescence experiments performed at room temperature. The mechanism of formation of *m*-xylylene is not known. It is not clear whether a single 248 nm photon has sufficient energy to cleave both carbon-chloride bonds of **24**. Alternatively, formation of a light-sensitive intermediate, the *m*-(chloromethyl)benzyl radical

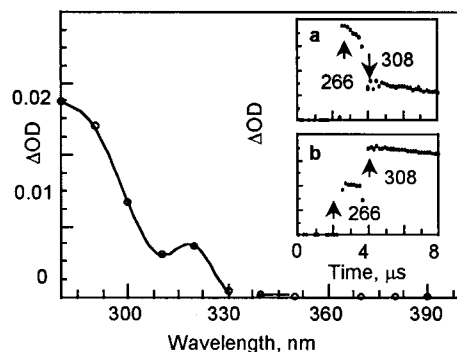
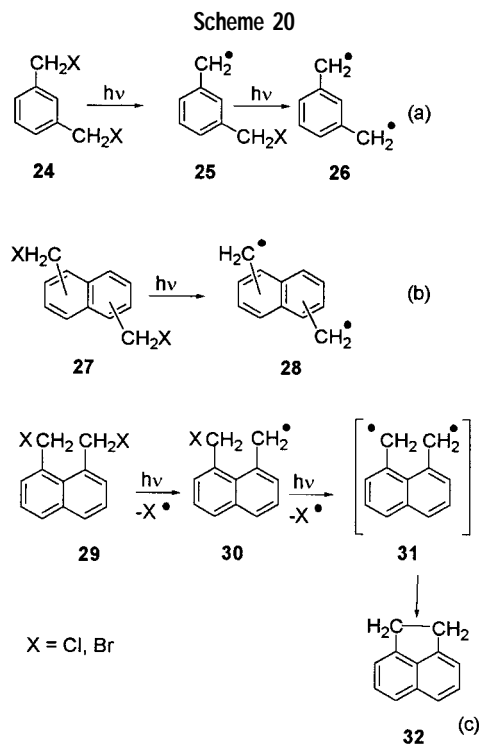
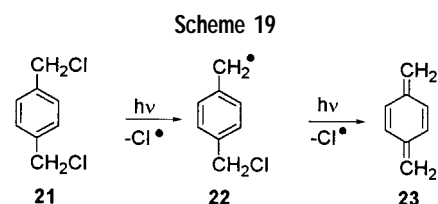
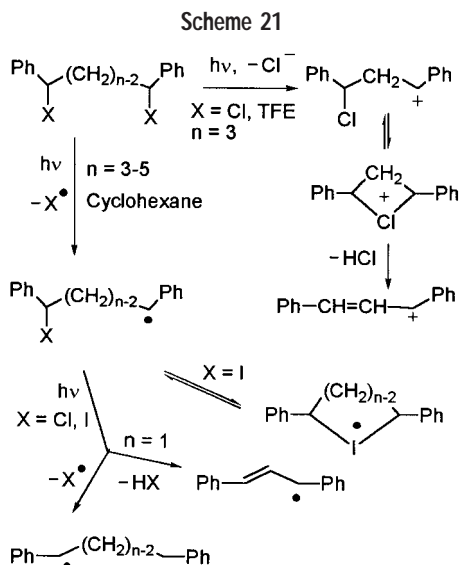


FIGURE 2. Transient absorption spectrum recorded following laser excitation (266 nm) of 1,4-bis(chloromethyl)benzene under nitrogen 0.8 μs after laser pulse. Inset: Kinetic trace at 320 (a) and 290 nm (b). The bleaching at 320 nm corresponds to the disappearance of the benzylic radical, and the jump at 290 nm corresponds to the formation of *p*-xylylene.



(**25**), which absorbs a second photon could lead to *m*-xylylene.^{12,29}

Naphthoquinodimethanes **28** have been detected in the photolysis (254 nm) of 1,3-, 1,6-, and 2,7-bis(chloromethyl)naphthalenes (**27**, X = Cl) in matrix media or laser flash photolysis (KrF, 248 nm) in solution at room temperature (Scheme 20, equation b).³⁰ In solution, dibromo derivatives (**27**, X = Br) also produce the biradicals, though the spectra are poorly resolved; by contrast, their photolysis in ethanol at 77 K does not produce naphthoquin-



odimethanes. This has been interpreted as being due to radical recombination within the radical pair initially generated after photolysis of the first C–Br bond, to regenerate the starting material. In the case of the dichlorides, the chlorine atom can abstract a hydrogen from the matrix more rapidly than the bromine atom. Finally, laser-jet photolysis studies have demonstrated the two-photon generation of acenaphthene (**32**) from 1,8-bis-(halomethyl)naphthalenes **29**; the one-photon intermediate **30** is photolyzed to acenaphthene (Scheme 20, equation c).³¹ However, the intermediacy of the non-Kekulé type biradical **31** in this reaction is still unclear.

Photochemistry of 1,*n*-Dihaloalkanes (*n* > 2): Bichromophores Connected through an Aliphatic Chain

Irradiation of 1,*n*-dihalo compounds in solution leads to different intermediates depending on the nature of the halogen, the chain length, the solvent polarity, and the light intensity. In general, the generation of cationic intermediates needs polar media, while a low-polarity solvent, such as cyclohexane, allows the detection of monoradicals (*n*-chloroalkyl, cyclic hypervalent iodine, allyl, etc.) and 1,*n*-biradicals (Scheme 21).

Generation of *n*-Haloradicals and 1,*n*-Biradicals. Low-intensity irradiation of 1,*n*-dichloro-1,*n*-diphenylalkanes in cyclohexane gives rise to products arising from the one-photon transient *n*-chloroalkyl radical, through hydrogen abstraction from the medium or coupling with cyclohexyl radicals (Scheme 22). The solvent-derived radicals are formed due to efficient hydrogen abstraction by the generated chlorine atoms.

Laser flash photolysis experiments have shown that these chloroalkyl radicals have the characteristic features of benzylic radicals: absorption with λ_{\max} at 320 nm, lifetimes in the microsecond time scale, and quenching by oxygen at close to the diffusion-controlled limit^{32,33} (for the 4-chloro-1,4-diphenylbutyl radical, see Figure 3). Two-laser two-color techniques have been used to demonstrate that *n*-chloro-1,*n*-diphenylalkyl radicals photolyze to 1,*n*-

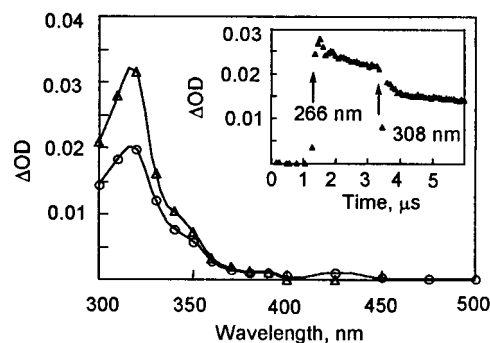
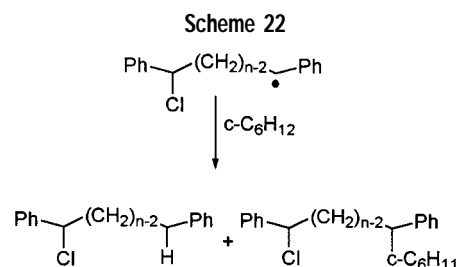


FIGURE 3. Transient absorption spectra recorded following laser excitation of 1,4-dichloro-1,4-diphenylbutane under nitrogen 3.12 (Δ) and 17.0 μs (O) after the laser (266 nm) pulse. Inset: Kinetic trace at 320 nm. The bleaching of the signal assigned to the 4-chloro-1,4-diphenylbutyl radical is followed by the formation of the 1,4-diphenyl-1,4-butanediyl biradical.



diphenylalkane diyl biradicals when irradiated at a wavelength matching their optical absorption. Thus, 4-chloro-1,4-diphenylbutyl radical, obtained by irradiation of 1,4-dichloro-1,4-diphenylbutane with a first laser pulse at 266 nm (synthesis laser), can be excited by a second laser at 308 nm (photolysis laser). Bleaching of the characteristic signal of the benzyl radical is accompanied by the formation of a shorter-lived transient (lifetime 200 ns) absorbing also at 320 nm, namely the 1,4-diphenyl-1,4-butanediyl biradical (inset in Figure 3).

The laser-drop technique provides a way of performing product studies under high-intensity irradiation conditions while minimizing the amounts of secondary products.^{34,35} Such studies have shown that 1,*n*-diphenyl-1,*n*-alkane diyl biradicals cyclize to 1,2-diphenylcycloalkanes. Alternatively, the biradicals undergo either fragmentation or disproportionation to produce olefins as byproducts (Scheme 23).^{36–38}

Generation of 1,3-Diphenylallyl Radical. High-intensity irradiation of cyclohexane solutions of 1,3-dichloro-1,3-diphenylpropane leads mainly to 1,2-diphenylcyclopropanes as major products, together with significant amounts of 1,3-diphenylpropene, 1-phenylindane, and 3-cyclohexyl-*trans*-1,3-diphenylpropene.³⁹ As stated above, intermediacy of the two-photon transient 1,3-diphenyl-1,3-propanediyl biradical explains the formation of all products except 3-cyclohexyl-*trans*-1,3-diphenylpropene. Laser flash photolysis experiments (Figure 4) show that the one-photon transient 3-chloro-1,3-diphenylpropyl radical photolyzes, leading not only to the 1,3-diphenyl-1,3-propanediyl biradical (which is not detectable due to its short lifetime, 15 ns) but also to the longer lived 1,3-diphenyl-2-propenyl radical ($\tau = 10 \mu\text{s}$) (Scheme 24). This

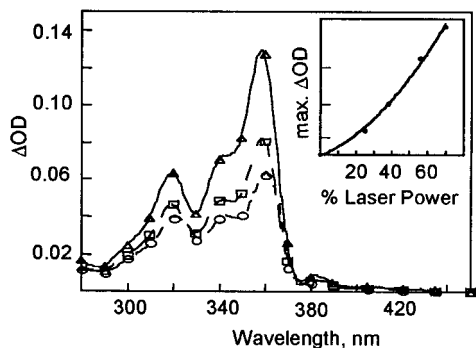
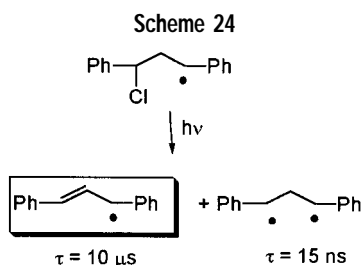
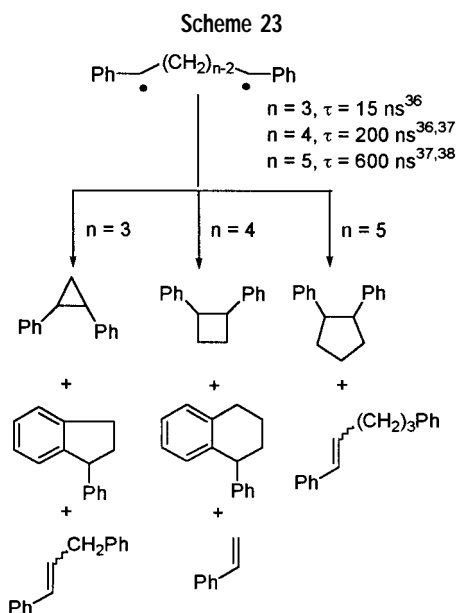


FIGURE 4. Transient absorption spectra recorded following laser excitation (266 nm) of 1,3-dichloro-1,3-diphenylpropane under nitrogen 0.72 (Δ), 8.48 (\square), and 15 μ s (\circ) after the laser pulse. Inset: Effect of laser power on signal intensity monitored at 360 nm.



intermediate has an absorption spectrum with maxima at 320 (weak), 340 (weak), and 360 nm (strong) and is completely trapped by the cyclohexyl radicals generated in the medium to produce 3-cyclohexyl-*trans*-1,3-diphenylpropene. Investigation of the effects of light intensity on the size of the signal at 360 nm is consistent with its two-photon origin (inset in Figure 4).^{39,40}

Generation of Cyclic Hypervalent Iodine Radicals. Photolysis of 1,*n*-diiodo-1,*n*-diphenylalkanes with a medium-pressure mercury lamp in cyclohexane gives rise to products arising from the haloalkyl radical, either by radical disproportionation ($n = 5$)⁴¹ or by rearrangement with loss of iodine ($n = 3$) (Scheme 25).⁴²

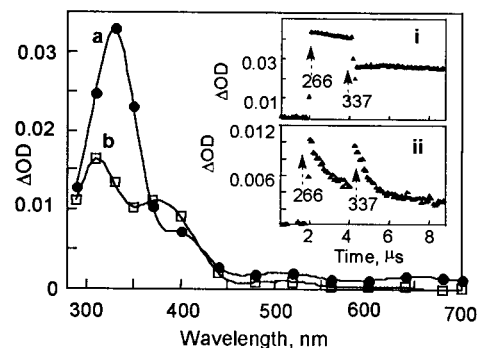
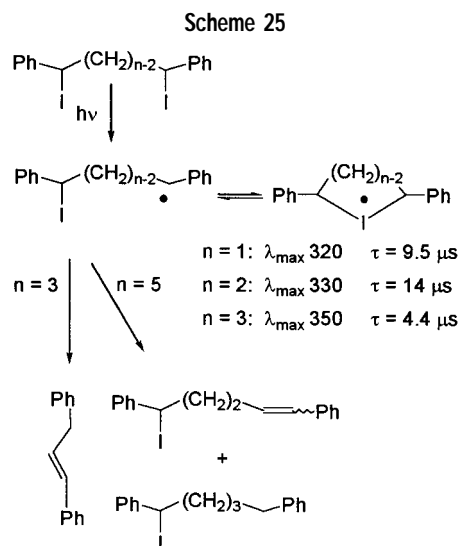


FIGURE 5. (a) Transient absorption spectrum recorded following laser excitation (266 nm) of 1,4-diiodo-1,4-diphenylbutane under nitrogen 0.2 μ s after the laser pulse. (b) Transient absorption spectrum obtained upon two-laser two-color excitation of 1,4-diiodo-1,4-diphenylbutane. The intermediate generated by means of a 266 nm laser pulse is photolyzed after 2.1 μ s by a second laser at 337 nm. Inset: Kinetic trace at 330 (i) and 380 nm (ii); the bleaching at 330 nm corresponds to the disappearance of the hypervalent iodine radical, and the new jump at 380 nm corresponds to formation of more $\text{RI}_2 \cdots \text{I}^{\cdot}$ complex.



Laser flash photolysis of 1,*n*-diiodo-1,*n*-diphenylalkanes^{41–43} (deaerated cyclohexane solutions), using either a Nd:YAG laser (266 nm) or a XeCl excimer laser (308 nm), leads to the formation of two transients with low reactivity toward oxygen (for the 1,4-diiodo-1,4-diphenylbutane, see Figure 5 and insets). One of them has been assigned to the cyclic hypervalent 9-I-2 iodine radical (Scheme 25) with absorption maxima and lifetime depending on the ring size; its nature and behavior are due to spin delocalization in the *n*-iodoalkyl radicals with participation of the remaining iodine atom. The other transient has a weaker broad UV band extending from ca. 370 to 450 nm and has been ascribed to $\text{RI}_2 \cdots \text{I}^{\cdot}$ complex.

Two-laser two-color flash photolysis of these diiodoalkanes has been performed using 266 nm pulses to produce the cyclic hypervalent 9-I-2 iodine radicals, and a second laser pulse (nitrogen laser at 337 nm or excimer laser at 308 nm) has been used to irradiate them. A permanent and irreversible bleaching of the signal of the cyclic hypervalent 9-I-2 iodine radicals is concomitant

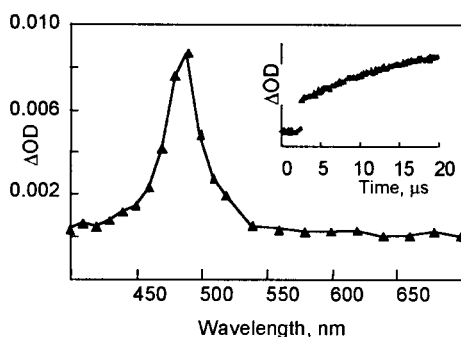
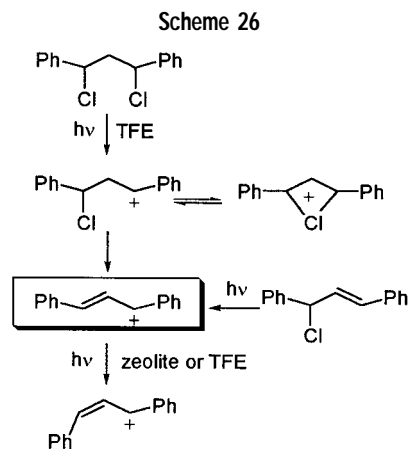


FIGURE 6. Transient absorption spectrum obtained upon 266 nm laser flash photolysis of 1,3-dichloro-1,3-diphenylpropane in TFE 720 ns after the laser pulse. The inset shows the growth as monitored at 490 nm.

with the formation of more $RI_2 \cdots I^\cdot$ complex (Figure 5 and insets),⁴³ which agrees with the photoextrusion of iodine atom from the cyclic hypervalent radical. Product studies on the photolysis of 1,*n*-diiodo-1,*n*-diphenylalkanes under high-intensity irradiation conditions have shown the formation of products that can be considered fingerprints for the intermediacy of the corresponding 1,*n*-diphenyl-1,*n*-alkanediyl biradicals.

Generation of the 3-Chloro-1,3-diphenylpropyl and 1,3-Diphenylpropenyl Cations. Photolysis of 1,3-dichloro-1,3-diphenylpropane in 2,2,2-trifluoroethanol (TFE) at 266 nm leads to the γ -chloroalkyl cation. Similarly to other γ -chloroalkyl cations,⁴⁴ this species thermally loses hydrogen chloride, leading to the (*E,E*)-1,3-diphenylpropenyl cation with characteristic absorption at λ_{\max} 490 nm (Figure 6).⁴⁵ The possibility of two-photon generation of the latter from the dichloride has been ruled out by studying its formation at different laser intensities. Alternatively, the propenyl cation can be generated upon photolysis of 3-chloro-1,3-diphenylpropene in TFE solutions. The lack of a power dependence in the photoheterolysis of the 1,3-dichloro-1,3-diphenylpropane implies that 3-chloro-1,3-diphenylpropene is not a necessary intermediate in the conversion of the 3-chloro-1,3-diphenylpropyl cation to the (*E,E*)-1,3-diphenylpropenyl cation.

Other haloalkyl cations (β -, δ -, and ϵ -) have been generated by thermal heterolysis of the corresponding dihalide in superacid media;⁴⁶ their NMR data have evidenced the interaction between the vacant orbital of the cationic center and the lone electron pair of the halogen atom. In the case of the 3-chloro-1,3-diphenylpropyl cation, there is kinetic evidence for interconversion between the open chain cation and the corresponding cyclic chloronium ion (Scheme 26). Thus, though their UV spectra have not been recorded, these species give rise to the formation of the allyl cation in two stages ("instant" and "slow", see trace in the inset in Figure 6). This kinetic behavior is in agreement with the open cation partitioning between efficient loss of hydrogen chloride and reversible cyclization to chloronium ion. The latter, acting as a reservoir, allows the slow formation of the allyl cation. The equilibrium between open-chain and cyclic forms explains the long lifetime of this cation (125 μ s) in comparison with those of typical benzylic cations.



Finally, the (*E,E*)-1,3-diphenylpropenyl cation photoisomerizes to its (*Z,E*) stereoisomer either in rigid media⁴⁷ or in solution.⁴⁵ In TFE, (*Z,E*)-1,3-diphenylpropenyl cation undergoes thermal reversion with a lifetime of 3.5 μ s at room temperature.

Conclusions

1,*n*-Dihalocompounds have been demonstrated to be suitable photochemical precursors of a wide variety of reactive intermediates. Due to their bichromophoric nature, 1,*n*-dihalocompounds can be photolyzed by either one- or two-photon processes. The first photon affords haloradicals, which may undergo electron transfer to generate the corresponding halocations; both intermediates, radicals and cations, can decay to give the one-photon products. In a solid matrix or under high-intensity irradiation conditions, the initially generated haloradicals may absorb a second photon and dissociate to carbenes, non-Kekulé hydrocarbons, biradicaloids, or biradicals, depending on the nature of the starting compound. Laser-drop and laser-jet photolysis techniques provide a way of studying the two-photon products, minimizing the amounts of secondary products. All of the species mentioned above have been postulated as intermediates in many thermal and photochemical transformations. Modern time-resolved techniques (laser flash photolysis, two-laser two-color flash photolysis, etc.) allow their direct detection and characterization by spectroscopic methods.

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