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# Flash Photolysis of 1,3-Dichloro-1,3-diphenylpropane in Polar Solvents: Generation of a Stabilized $\gamma$-Chloropropyl Cation, Subsequent Formation of a Propenyl Cation, and Nucleophilic Trapping of Both Cations

**Miguel Angel Miranda,*[†] Julia Pérez-Prieto,*[‡] Enrique Font-Sanchis,[†] Klára Kónya,[§] and J. C. Scaiano*[§]**

*Instituto de Tecnología Química, Universidad Politécnica de Valencia, Camino de Vera s/n, Valencia, 46071 Spain, Departamento de Química Orgánica, Facultad de Farmacia, Universidad de Valencia, Vicént Andrés Estelles s/n, Burjasot, 46100 Valencia, Spain, and Department of Chemistry, University of Ottawa, Ottawa, Canada K1N 6N5*

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Photolysis of 1,3-dichloro-1,3-diphenylpropane (**1**) in 2,2,2-trifluoroethanol at 266 nm leads to a $\gamma$-chloropropyl cation (**2a**) following loss of chloride ion. Kinetic evidence has been obtained for the interconversion between the open chain cation and the corresponding cyclic chloronium ion (**2b**); thermal loss of hydrogen chloride gives the 1,3-diphenyl-2-propenyl cation (**3**). The formation of this species occurs through a monophotonic process; the involvement of a two-photon process in the photoheterolysis of dihalide **1** has been ruled out by studying the formation of cation **3** from **1** at different laser intensities. The lack of power dependence implies that 3-chloro-1,3-diphenylpropene (**4**) is not an intermediate in the photoheterolysis of dihalide **1**. The reaction of both cationic intermediates (**2** and **3**) with different nucleophiles has also been examined. Finally, two-laser two-photon experiments have allowed the study of the photoisomerization of *E,E*-**3** into *Z,E*-**3**.

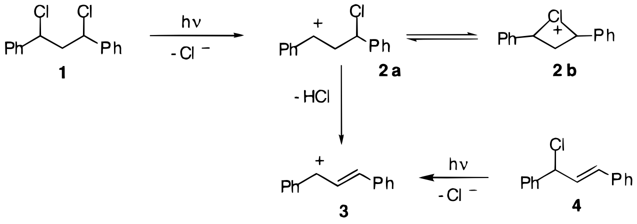
## Introduction

Photoheterolysis of benzylic chlorides in low-nucleophilicity polar solvents, such as 2,2,2-trifluoroethanol (TFE) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), has been extensively studied.[1−3] These experiments have established that simple benzyl cations, such as cumyl and 1-phenylethyl cations, can exist in solution as free ions; the radicals arising from a competing photohomolysis are also observed frequently.

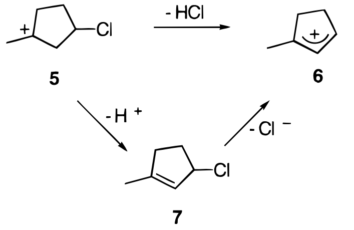
To our knowledge no studies on the photobehavior of bichromophoric dichlorides in polar solvents have been reported so far. However, laser flash photolysis in such media would be expected to generate the benzylic cations and allow the study of the influence of a neighboring chlorine atom. Haloalkylcarbocations ($\beta$-, $\delta$-, and $\epsilon$-) have been generated by heterolysis of the corresponding dihalide in superacid media.[4−6] $^{13}$CMR chemical shifts experiments have been interpreted as evidence for an interaction between the vacant orbital of the cationic center of the haloalkylcarbocations with a lone electron pair of the halogen atom.[4−6] Therefore, both the open halocarbocation and the cyclic halonium ion are in equilibrium. However, the existence of four-membered chloronium ions (formed from $\gamma$-chloropropyl cations) has not been established.

Photoheterolysis of 1,3-dichloro-1,3-diphenylpropane (**1**) in TFE should generate a benzylic cation (**2a**) with a chlorine atom in the $\gamma$-position. In this case, time-resolved techniques could allow the examination of the influence of a $\gamma$-halogen on the reactivity and lifetime of the cationic intermediate (Scheme 1). On the other hand, it is known that 3-chloro-1-methylcyclopentyl cation (**5**), formed from several precursors in superacid media, thermally eliminates hydrogen chloride and yields 1-methyl-2-cyclopentenyl cation (**6**) (Scheme 2). Other $\gamma$-chloroalkylcarbocations exhibit a similar behavior.[7] There is some controversy concerning the mechanism of formation of these alkenyl cations. Either direct hydrogen chloride elimination or proton loss followed by heterolysis of the resulting 3-chloroalkenes (i.e., **7**) could explain formation of the observed intermediates.

**SCHEME 1**



**SCHEME 2**



We have previously reported that adsorption of dihalide **1** within acid zeolites[8,9] generates *E,E*-1,3-diphenyl-2-propenyl cation (**3**) as persistent species. It was therefore anticipated that photoheterolysis of **1** would give rise to cation **2a**, which, in analogy to cation **5**, could dehydrohalogenate thermally to cation **3**. Accordingly, it could be possible to study the (photo)reactivity of both cations in solution.

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[†] Universidad Politécnica de Valencia.

[‡] Universidad de Valencia.

[§] University of Ottawa.

We report here that photolysis of 1,3-dichloro-1,3-diphenylpropane in TFE at 266 nm leads to the formation of the propenyl cation **3** through a monophotonic process. Evidence has been obtained for the interconversion between a benzylic cation (**2a**) and a cyclic chloronium ion (**2b**) accompanied by loss of hydrogen chloride to give the propenyl cation **3**. The involvement of a two-photon process in the photoheterolysis of dihalide **1** has been ruled out by studying the formation of cation **3** at different laser intensities. The lack of a power dependence implies that 3-chloro-1,3-diphenylpropene (**4**) is not a required intermediate in the conversion of **2** to **3**. The reaction of both intermediates (benzylic and propenyl cation) with different nucleophiles has also been examined. Finally, two-laser two-photon experiments have allowed the study of the photoisomerization of *E*,*E*-**3** into *Z*,*E*-**3**.

## Experimental Section

**Synthesis of Products**. 1,3-Dichloro-1,3-diphenylpropane (**1**)[10] and 3-chloro-1,3-diphenylpropene (**4**)[11] were synthesized from the corresponding alcohols, 1,3-diphenyl-1,3-propanediol[12] and 1,3-diphenyl-2-propen-1-ol,[13] respectively, by treatment with a concentrated HCl aqueous solution as previously described.[10,11] Briefly, the alcohol was added to concentrated hydrochloric acid. The mixture was stirred at room temperature. The solution was then neutralized with NaOH, extracted with ether, and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure.

**Laser Flash Photolysis**. These experiments were carried out using a Nd:YAG laser using the fourth harmonic (266 nm, $<10$ ns, $\leq 20$ mJ/pulse) or a dye laser pumped with an excimer laser operated with HCl/Xe/Ne gas mixtures (308 nm, ca. 6 ns, $\sim 50$ mJ/pulse). Transient signals were captured with a Tektronix model 2440 digital oscilloscope that was interfaced to a computer, which also controlled the experiment. The system was operated with software written in the LabVIEW 3.1.1 environment from National Instruments. Other aspects of this instrument are similar to those described earlier.[14,15] The two-laser two-color experiments were performed by sending a trigger pulse to a Stanford Research Systems model DG 535 delay generator, which then sent TTL pulses that fired the lasers at the desired sequence. All experiments were carried out using flow cells constructed from 7 × 7 mm Suprasil quartz tubing. Samples were contained in a 100 mL reservoir tank, which was purged with a slow stream of either nitrogen or oxygen, as required.

## Results

Laser flash photolysis at 266 nm of deaerated solutions containing 1 mM **1** in TFE produces a broad transient absorption centered around 490 nm. The formation of this intermediate follows biphasic kinetics, as shown in Figure 1. A significant fraction of this signal is formed "instantaneously" on the nanosecond time scale, while the rest forms with a lifetime of $\sim 13$ $\mu$s (see inset in Figure 1). Both components (i.e., the instantaneous and the time-resolved growth) lead to the same transient spectrum, suggesting that both processes lead to the same transient species. No other band was observed in the region between 280 and 700 nm. The implication of this observation is clearly that the same reaction intermediate is produced in two different kinetic regimes. Such behavior may reflect the involvement of two different precursors leading to a common species. This absorption decayed with the same kinetics over the entire spectrum, thus supporting that only one reaction intermediate is responsible for the transient spectrum with $\lambda_{max}$ 490 nm. The decay followed first-order kinetics with a lifetime of $\sim 125$ $\mu$s under our experimental conditions. This strong signal was not quenched by molecular oxygen and agreed well with that obtained for *E*,*E*-**3** under different conditions, such as ionization of 1,3-diphenyl-2-propenol in $FSO_3H/SO_2$ solution at low temperature,[16] absorption of dichloride **1** in the cavities of an acid zeolite,[8,9] or photoprotonation of 1,3-diphenylpropa-1,2-diene in TFE.[17]

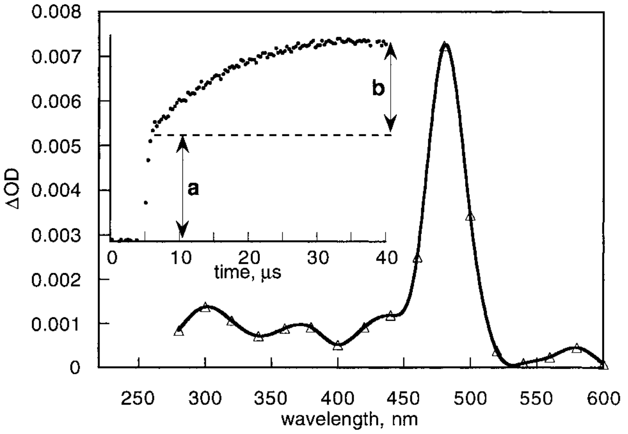


**Figure 1.** Transient absorption spectra obtained upon 266 nm laser flash photolysis of **1** in TFE 1630 ns after the laser pulse. The inset shows the growth as monitored at 490 nm.

The result is surprising since we expected that photoinduced heterolytic cleavage of the C−Cl bond in **1** would lead to the 3-chloro-1,3-diphenylpropyl cation (**2a**), which should absorb in the 320 nm region[1] and be much shorter lived that the intermediate of Figure 1, or the associated growth of $\sim 13$ $\mu$s detected. Even more stabilized cations such as 1-(4-methoxyphenyl)ethyl and 2(4-methylphenyl)propyl have significantly shorter lifetimes.[1]

We considered the possibility that the near-instantaneous rise in the inset of Figure 1, which we attribute to the formation of **3**, could be due to the occurrence of a biphotonic process under conditions of laser excitation. In other words the two-photon excitation could lead to the dehydrochlorination of **2** during the short laser pulse. However, the ratio between the "jump" and growth contributions (i.e., a/b in the inset in Figure 1) was insensitive to the laser power, for a change of a factor of 7 in the laser dose. The absence of power dependence of this ratio and the fact that the total signal intensity showed a linear dependence with the laser power indicate that both components of the 490 nm transient have a monophotonic origin. These experiments further confirm that while there are two sources of the alkyl cation **3**, both are monophotonic.

The photolysis of **1** in TFE was a clean heterolysis reaction, with no evidence for photohomolysis. In contrast, in acetonitrile two different signals were observed (Figure 2). The band at 360 nm was readily quenched by oxygen, while that centered at $\sim 490$ nm was not quenched by oxygen. The signal at 360 nm is consistent with the formation of the 1,3-diphenyl-2-propenyl radical (**9**, $\lambda_{max}$ 360 nm) produced from the 3-chloro-1,3-diphenylpropyl radical (**8**, $\lambda_{max}$ 320 nm), according to the mechanism of Scheme 3, which we have already established in the case of cyclohexane as solvent.[10,18] Thus, photolysis of **1** in acetonitrile produced both the propenyl radical **9** and the propenyl cation **3**. Clearly, the homolytic cleavage can involve two-photon processes under conditions where the heterolytic cleavage does not; this is consistent with the strong absorption of the benzylic radicals at the laser wavelength, as already noted in the case of nonpolar solvents.[18]

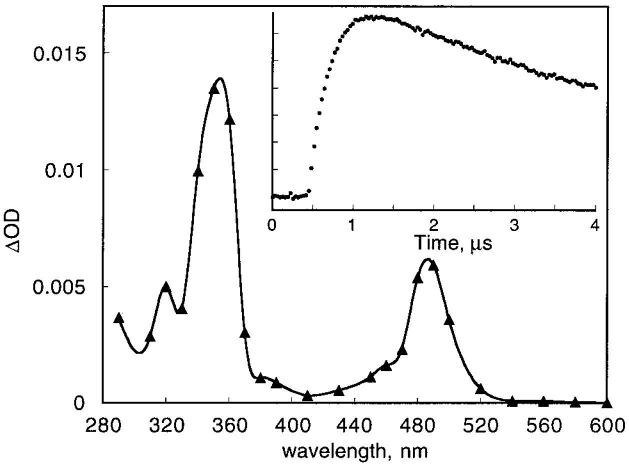


**Figure 2.** Transient absorption spectrum obtained upon 266 nm laser flash photolysis of **1** in acetonitrile 1.74 μs after laser pulse. The inset shows the kinetic trace at 490 nm.

While **2** may not be directly detectable under our experimental conditions, it is still possible to study its reactions with a variety of scavengers by examining the effect of the quencher on the growth kinetics associated with the formation of **3** (i.e., at 490 nm). The bimolecular rate constant can be determined from the slope of plots of the experimental pseudo-first-order rate constants for the growth of **3** as a fraction of the quencher concentration, i.e.,

$$k_{\text{expt}} = k_0 + k_{\text{q2}}[\text{Q}] \tag{1}$$

In this equation $k_0$ is the growth rate in the absence of quencher, and $k_{\text{q2}}$ is the rate constant for the reaction of the nucleophilic quencher with the transient. In this case analysis of the 490 nm growth signals for **3** yields rate constants for its precursor, **2**. As expected,[19] large rate constants were obtained for the reaction of **2** with azide ion, alcohols, sulfur compounds, and amines (see Table 1). Azide ion, which is a well-known cation scavenger, reacted at close to the diffusion-controlled rate limit. Halide quenching of **2**, while efficient, proved complex, perhaps due to accompanying ionic strength effects.

For the purpose of comparison, we have also determined rate constants for the reaction of **3** with the nucleophiles used as quenchers for **2**. Naturally, as the quencher concentration increases and **2** is trapped, the yield of **3** decreases. This can interfere with the determination of rate constants for **3**, as deteriorating signal-to-noise limits the accuracy of quenching experiments. While changes in the lifetime of **3** upon addition of nucleophiles were readily observed, the method of choice for the determination of rate constants for **3** involved irradiation of 3-chloro-1,3-diphenylpropene (**4**) at 266 nm in TFE. This precursor provides an essentially instantaneous and clean source of the carbocation **3**. Its reactivity ($k_{\text{q3}}$) with different nucleophilic quenchers was studied by measuring the effect of addition of increasing amounts of quencher on the lifetime of the signal at 490 nm. Again, as expected for a cationic species, an increase in the decay rate constants ($k_{\text{expt}}$) was observed. These rate constants have also been included in Table 1.

**TABLE 1: Rate Constants in TFE (20 °C) for Reaction of Cations 2, 3, and $Ph_2CH^+$ with Solvent ($s^{-1}$) and Nucleophiles ($M^{-1}\ s^{-1}$)**

| nucleophile[a] | $k_{\text{q2}}$(**2**) | $k_{\text{q3}}$(**3**) | $k(\text{Ph}_2\text{CH}^+)$[b] |
|---|---|---|---|
| $CH_3CN$ | $(5.0 \times 10^{6})$[c] | $(1.8 \times 10^{5})$[c] | $(2.5 \times 10^{6})$[c] |
| TFE | $(1.0 \times 10^{5})$[c] | $(8.0 \times 10^{3})$[c] | $(3.0 \times 10^{6})$[c] |
| $N_3^-$ | $4.8 \times 10^{9}$ | $6.4 \times 10^{9}$ | $5.3 \times 10^{9}$ |
| $Cl^-$ | see text | $2.2 \times 10^{8}$ | $1.9 \times 10^{9}$ |
| $I^-$ | see text | $6.7 \times 10^{9}$ | $7.5 \times 10^{9}$ |
| MeOH | $6.6 \times 10^{5}$ | $1.3 \times 10^{5}$ | $1.0 \times 10^{7}$ |
| EtOH | $1.7 \times 10^{5}$ |  | $1.3 \times 10^{7}$ |
| $^{i}$PrOH |  | $1.0 \times 10^{5}$ | $7.8 \times 10^{6}$ |
| $^{t}$BuOH |  | $0.3 \times 10^{5}$ | $3.2 \times 10^{6}$ |
| $^{i}Pr_2S$ | $5.6 \times 10^{9}$ | $5.5 \times 10^{8}$ |  |
| $(c{-}C_6H_{12})SH$ | $5.6 \times 10^{9}$ | $6.8 \times 10^{7}$ |  |
| $(c{-}C_6H_{12})NH_2$ | $9.7 \times 10^{7}$ | $6.8 \times 10^{7}$ |  |
| piperidine |  | $7.8 \times 10^{7}$ |  |
| $(n\text{-}C_6H_{13})_3N$ | $3.4 \times 10^{8}$ | $1.2 \times 10^{8}$ |  |

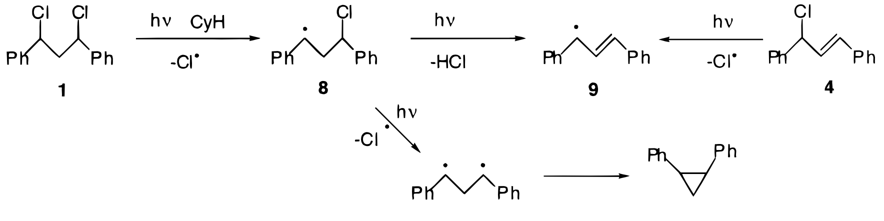
[a] For $Cl^-$ and $I^-$ the counterion is $(n\text{-Bu})_4N^+$. [b] For a compilation see ref 21. [c] First-order rate constant.

The cation **3** is expected to show *Z*−*E* isomerism. To examine the possible photoisomerization of **3**, we examined these processes using two-laser two-color laser flash photolysis techniques. This technique allows direct examination of the effect of laser excitation on the behavior of reaction intermediates. A first laser pulse (*synthesis laser*) produces the intermediate of interest (e.g., the 1,3-diphenyl-2-propenyl cation, **3**), while the second laser pulse from the *photolysis laser* excites this intermediate.[20] The wavelength of the photolysis laser is usually selected so as to match the optical absorption of the intermediate of interest. Thus, a 1 mM solution of 3-chloro-1,3-diphenyl-1-propene (**4**) in TFE was excited using a 266 nm pulse to produce the transient **3**, which was then (typically 10−20 μs later) photolyzed using a second laser with 480 nm pulse (dye laser pumped with a 308 nm excimer laser HC1/Xe/Ne); both lasers were incident from the front face. Photolysis of transient **3** led to partial bleaching of the signal at 490 nm, concomitant with the rise of a new signal at 520 nm (Figure 3). The newly generated species is identified as cation *Z,E*-**3** by comparison with the spectrum of this cation in zeolite media.[8,9] The *Z,E*-**3** cation decays with a lifetime of ∼3.5 μs. Judging from the excellent return to the pre-excitation level, this decay must involve thermal back-isomerization. In a related system, a signal at 520 nm was previously observed as a shoulder of the 490 nm band of *D,E,*-2,4-diphenyl-3-buten-2-yl cation obtained by protonation of 1,3-diphenylbuta-1,2-diene and was assigned to the *Z*−*E*-isomer.[17]

## Discussion

The shape of the trace in the inset in Figure 1 provides a fundamental piece of evidence to understand the photochemistry of **1** in polar solvents. Thus, we believe that photolysis of **1** yields **2a**, the open or carbocation form of **2**. The carbocation **2a** then partitions between two pathways: dehydrochlorination

**SCHEME 3**



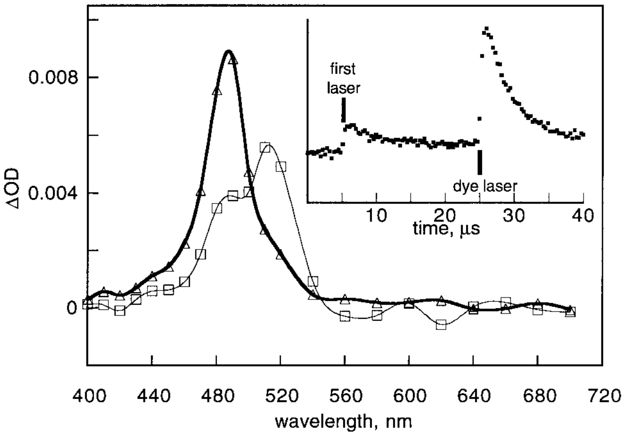


**Figure 3.** Transient absorption spectrum of *E,E*-**3** obtained upon laser flash photolysis of **4** in TFE 0.72 $\mu$s (△) after laser pulse. Two-laser two-color experiment showing the transient absorption spectra obtained upon excitation at 480 nm with the dye laser 21.5 $\mu$s (□) after the first laser pulse (i.e., these two spectra correspond to before and after the second laser pulse). The inset shows the kinetic trace at 520 nm; the jump after the second (dye) laser pulse corresponds to the formation of *Z,E*-**3**.

leads to **3**, with its characteristic maximum at 490 nm. While our data do not provide an absolute rate constant for this process, it is clear that it must compete with both the expected rapid decay of benzylic carbocations,[1] as well as the equilibration with **2b** (vide infra); we conservatively estimate that the rate constant for dehydrochlorination must be $\gg 10^6$ $s^{-1}$. The other pathway for **2a** is its interconversion/equilibration with the chloronium ion, **2b**. That this is an equilibrium, rather than an irreversible process, is supported by the slow component in the formation of **3**. The growth component in the inset in Figure 1 (part b of the trace) has a rate constant of $8.7 \times 10^4$ $s^{-1}$. If we assume that every time **2a** is produced it partitions about equally between **2b** and **3** (note that the growth and jump have about the same magnitude), then the rate constant for the **2b** → **2a** interconversion must be about twice the value measured, or $\sim 1.7 \times 10^5$ $s^{-1}$. Clearly we would expect **2b** to be detectable if it was not for the interference from the signals from **2a**. Unfortunately, under our experimental conditions attempts to detect **2b** directly were unsuccessful. We note that our experiments rule out the possibility of a multiphoton process or that the signals of Figure 1 are due to more than one intermediate.

The rate constants of Table 1 were determined in an attempt to establish the effect of carbocation cyclization to a chloronium ion on the dynamics of reactions with nucleophiles. For the purposes of comparison we have included literature values for the diphenylmethyl carbocation. The reaction with azide ion is interesting in that the values are sufficiently close to diffusion control to argue that reaction of **2** must occur from the chloronium ion form and thus that **2b** is more than a mere reservoir for **2a**. Other than in the extreme case of azide, both **2** and **3** are somewhat less reactive than the diphenylmethyl cation. In the case of **2** our results with moderate quenchers (e.g., alcohols) could be interpreted in terms of either a reduced reactivity of **2b** or a low relative concentration of **2a**, with **2b** acting as a reservoir. For **3** decreased reactivity relative to $Ph_2CH^+$ is not surprising given its increased stability.

Despite the well-established characterization of a few chloronium ions under superacid conditions,[4-6] we believe this is the first report on these intermediates under reactive conditions. Our results are consistent with the small barriers for interconversion estimated in related systems.[5,6]

In conclusion, the equilibrium between **2a** and **2b** provides a rationale for the long lifetime of **2** in comparison with typical benzylic cations. Thus, **2a** partitions between efficient dehydrochlorination and reversible cyclization to **2b**. While in TFE the photochemistry of **1** involves exclusive heterolysis, in acetonitrile both homolytic and heterolytic cleavage take place. We also report for the first time on the photoisomerization of cation *E,E*-**3** to its stereoisomer *Z,E*-**3** in solution, a process that undergoes thermal reversion with a lifetime of 3.5 $\mu$s at room temperature.

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