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A Four-Member Ring Hypervalent Iodine Radical

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A four-member ring hypervalent iodine radical has been detected in the laser flash photolysis of 1,3-diiodo-1,3-diphenylpropane. This species absorbs at 320 nm, has a lifetime of ∼9.5 μs in cyclohexane, and is not quenchable by oxygen. Excitation of this radical by means of laser-drop photolysis results the formation of *trans*-1,2-diphenylcyclopropane through concerted iodine extrusion.

Introduction

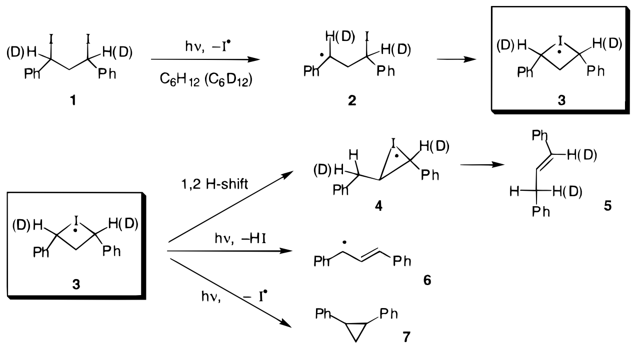
Photolysis of benzylic halides in nonpolar solvents is known to produce homolysis of the carbon−halogen bond.[1] In the case of benzylic 1,2-dihalides, light-induced cleavage of the first C−X bond gives rise to haloalkyl radicals.[2] The formation of three-membered ring bromine radicals has been proposed to explain the unexpected stability of 1-naphthyl-2-bromoethyl radical, which has a lifetime of 6.47 μs and is not oxygen-quenchable.[3] Moreover, photolysis of 1,5-diiodo-1,5-diphenylpentane in cyclohexane leads to a 5-iodopentyl radical, which cyclizes to a six-membered hypervalent iodine radical. This species also has a relatively long lifetime (4.4 μs) and is unreactive toward oxygen.[4] Likewise, the stability of thio- and seleno-alkyl radicals has been related to the participation of the corresponding heteroatom through bridged structures.[5] We now report the detection of **3** (see Scheme 1), which is the first four-membered ring hypervalent halogen radical described. Its lifetime (∼9.5 μs) is even longer than that of the six-membered ring analogue (probably reflecting the less-favorable steric interactions in the six-member ring, where the phenyl rings, probably equatorial, may interact with other atoms).

Experimental Section

Compounds **1**, **1**-1,3-d_2, and 1-iodo-1,3-diphenylpropane were prepared from the corresponding diol or alcohol by treatment with iodotrimethylsilane.[4] Data for **1** (diasteromeric mixture): ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 2.7$ (dt, ^2J(H,H) = 15 Hz, ^3J(H,H) = 8 Hz, 1H; CH$_2$), 3.0 (t, ^3J(H,H) = 8 Hz, 2H; CH$_2$), 3.25 (dt, ^2J(H,H) = 15 Hz, ^3J(H,H) = 8 Hz, 1H; CH$_2$), 5.0 (t, ^3J(H,H) = 8 Hz, 2H; CH), 5.1 (t, ^3J(H,H) = 8 Hz, 2H; CH), 7.1−7.3 (m, 20H; arom). ^{13}C NMR (75.46 MHz, CDCl$_3$): $\delta = 142.2$ (s), 141.1 (s), 128.9 (d), 128.3 (d), 127.3 (d), 127.1 (d), 51.6 (d), 51.3 (d), 31.2 (t), 30.9 (t). Elemental analysis for $C_{15}H_{14}I_2$: calcd C 40.21, H 3.15; found C 40.50, H 3.20. MS (70 eV): m/z (%): 194 (100)[M$^+$ − 2I].

Compound **1**-1,3-d$_2$: ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 2.7$ (d, ^2J(H,H) = 15 Hz, 1H; CH$_2$), 3.0 (s, 2H; CH$_2$), 3.2 (d, ^2J(H,H) = 15 Hz, 1H; CH$_2$), 7.1−7.3 (m, 20H; arom).

SCHEME 1



Compound 1-iodo-1,3-diphenylpropane: ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 2.3−2.9$ (m, 4H; CH$_2$), 5.0 (t, ^3J(H,H) = 7 Hz, 1H; CH), 7.1−7.4 (m, 10H; arom). ^{13}C NMR (75.46 MHz, CDCl$_3$): $\delta = 143.8$ (s), 140.2 (s), 128.7 (d), 128.5 (d), 127.9 (d), 127.1 (d), 126.2 (d), 42.7 (d), 35.6 (t), 33.2 (t). Elemental analysis for $C_{15}H_{15}I$: calcd C 55.92, H 4.69; found C 55.83, H 4.65. MS (70 eV): m/z (%): 194 (100)[M$^+$ − IH].

Laser flash photolysis experiments were carried out with a Nd:YAG laser using the fourth harmonic (266 nm, <10 ns, ≤20 mJ/pulse) or with a dye laser pumped with an excimer laser operated with HCl/Xe/Ne gas mixtures (308 nm, ∼6 ns, ≤50 mJ/pulse). Transient signals were captured with a Tektronix model 2440 digital oscilloscope, which was interfaced to a computer that 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.[6,7] All experiments were carried out with flow cells constructed from 7 × 7 mm Suprasil quartz tubing. Samples were contained in a 100-mL reservoir tank that was purged with a slow stream of either nitrogen or oxygen, as required. The absorbance of the samples at the laser wavelength was adjusted to ∼0.3 for a 7-mm optical path.

For laser-drop photolysis,[4,8] the beam from a Nd:YAG laser using the fourth harmonic (266 nm, <10 ns, ≤20 mJ/pulse) was focused by means of a quartz lens into a drop of the

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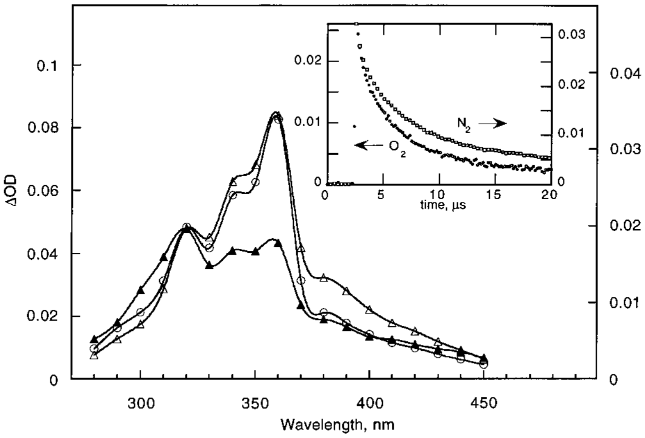

Figure 1. Transient absorption spectra recorded following laser excitation (266 nm) of **1** under nitrogen at 112 ns (Δ) or 1380 ns (o), left scale, and under oxygen at 1400 ns (▲; right scale) after the laser pulse. The inset illustrates the limited sensitivity of the signal at 380 nm to the saturation of the solution by nitrogen or oxygen.

photolysis solution suspended from a 2-in. syringe needle (20 gauge). Further details for this experiment have been described earlier.[8]

Results and Discussion

The experiments reported here involved steady-state irradiations and studies using laser flash photolysis[6,7] and the laser-drop technique.[8]

Lamp irradiation (medium-pressure mercury, Pyrex filter, 1 h) of a 10 mM deaerated solution of 1,3-diiodo-1,3-diphenylpropane (**1**) in cyclohexane led to complete consumption of the starting material and formation of *trans*-1,3-diphenylpropene (*trans*-**5**) as the main product (90% yield). Only 10% of the product was detected as the cis-isomer.[9] The photodecomposition was accompanied by coloration of the solution, clearly indicative of the formation of molecular iodine. Formation of the olefin can be explained through homolytic cleavage of a carbon−iodine bond to give the benzylic radical **2**. Ring closure to the four-membered hypervalent iodine radical **3**, followed by hydrogen migration from C2 to C1, would lead to **4**. Final loss of an iodine atom would give rise to **5**.[10] Clear evidence supporting this mechanistic proposal was obtained by irradiating the deuterium-labeled diiodo compound **1**-*1,3*-d_2 in C_6D_{12}. Hydrogen atom migration from C2 in **3** to the terminal carbon generated the hydrogen migration product *trans*-**5**-*1,3*-d_2 (Scheme 1).

Upon laser flash photolysis of **1** (deaerated 1 mM cyclohexane solutions) with use of either a Nd:YAG laser (fourth harmonic, 266 nm) or a XeCl excimer laser (308 nm), a broad transient absorption band was observed with maxima at 320, 340, and 360 nm (Figure 1) and extending to ~450 nm. The disappearance of the absorption tail at 370−450 nm was relatively rapid. By contrast, the rest of the spectrum seemed to decay with uniform kinetics. When oxygen-saturated solutions of **1** were irradiated**,** the shape of the spectrum was different: It showed a well-resolved band centered at 320 nm and diminished maxima at 340 and 360 nm (Figure 1). The use of a double-*y* axis in Figure 1 allows us to compare the spectral shape under nitrogen or oxygen and in the latter case, shows a marked decrease in the relative importance of transient absorptions at 360 nm.

Therefore, the spectroscopic data and their time- and oxygen-dependence show that three different transients are formed in the photolysis of **1**. According to the literature, the tail of the absorption band between 370 and 450 nm, which showed little sensitivity to oxygen (see inset in Figure 1), can be predominantly ascribed to a complex of iodine atoms, including the starting iodo compound (**1**).[11,12] The transient peaks at 340 and 360 nm, which have a lifetime of ~10 µs and are quenched by oxygen, must be from the well-characterized 1,3-diphenylpropen-1-yl radical (**6**) formed through a two-photon process.[13] Accordingly, the formation of transient **6** was reduced when we used attenuated homogeneous laser pulses (Figure 2). Finally, the absorption at 320 nm followed first-order (or pseudo-first order) kinetics, had a lifetime of ~9.5 µs under our experimental conditions, and was not quenched by oxygen (see insert A in Figure 2). Therefore, this transient could not be a benzylic radical, which should have a lifetime of 2−3 µs and be quenched by oxygen at close to the diffusion-controlled limit.[14] Hence, we assigned the structure of a hypervalent iodine radical (**3**) to this transient.

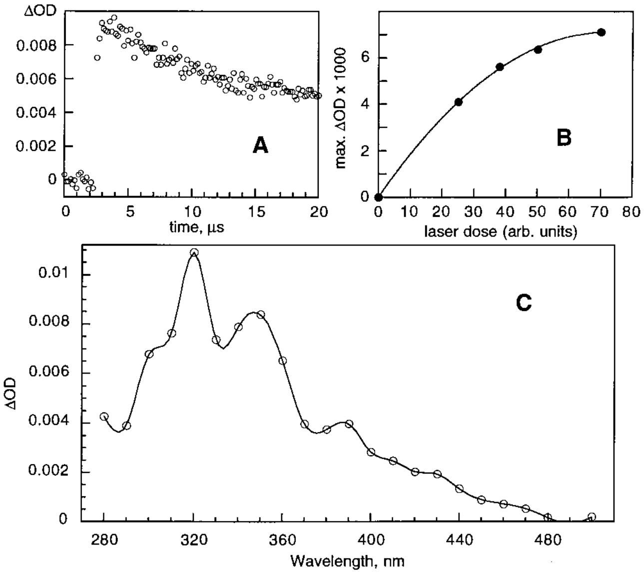

Figure 2. Transient absorption spectrum (C) recorded 1.2 µs after laser excitation of **1** at 266 nm by use of attenuated homogeneous laser pulses. (A) Kinetic trace monitored at 320 nm. (B) Effect of the laser power on signal intensity monitored at 320 nm.

Furthermore, a downward curvature was obtained when the size of the signal at 320 nm was plotted against the laser power (see insert B, Figure 2). This type of curvature is common when the initial transient undergoes further photolysis during the laser pulse. Therefore, to ascertain the primary photoproducts that resulted from photolysis of this four-membered ring hypervalent iodine radical, we used the laser-drop technique, which technique provides a way of performing high-intensity photolysis with conversions suitable for product studies,[8,15] while minimizing the amounts of secondary products. When drops of deaerated 2 mM solution of compound **1** in cyclohexane were irradiated by the focused output from a 266 nm laser, 60% conversion of the diiodo compound was achieved (1 cycle), mainly, *cis*- and *trans*-1,2-diphenylcyclopropane (**7**) (90%, 0.1/0.9 ratio) and *trans*-1,2-diphenylpropene (10%) were formed.

In principle, two different mechanisms could explain the formation of 1,2-diphenylcyclopropane in the photolysis of **3**: intermediacy of the 1,3-diphenylpropanediyl biradical or concerted iodine atom extrusion with formation of a carbon−carbon bond. We can rule out the first mechanism because photolysis of the biradical would be expected to lead to a nearly equimolar mixture of *cis*- and *trans*-1,2-diphenylcyclopropane.[16] The strong predominance of the trans-isomer agrees with the outcome expected for the concerted process and provides chemical evidence on the stereochemistry of the hypervalent radical **3**.

In summary, laser flash photolysis of 1,3-diiodo-1,3-diphenylpropane (**1**) leads to a species that absorbs at 320 nm, has a lifetime of ~9.5 μs in cyclohexane, and is not quenchable by oxygen. This species is neither an iodine atom complex nor a typical benzylic-type radical; it has been assigned to the hypervalent iodine radical **3**. Consistent with this, photolysis of **3** leads predominantly to *trans*-1,2-diphenylcyclopropane and, as a minor product, allylic radical **6**. Hypervalent radical **3** is the first example of a four-member hypervalent iodine radical.

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(9) Under similar conditions, 1,3-diphenyl-1-iodopropane was converted into a mixture of *trans*-1,3-diphenylpropene (53%) and 1,3-diphenylpropane (47%), through disproportionation of the 1,3-diphenyl-1-propyl radical intermediate. Thus, the intermediacy of the monoiodo compound in the photolysis of **1** can be safely ruled out since 1,3-diphenylpropane was not observed in its photolysate.

(10) Irradiation of *trans*-**5** under similar conditions led to its isomerization to the cis-isomer (67%). By contrast, when iodine was added to the solution before the irradiation, no transformation was detected. This suggests quenching of the excited olefin by the iodine.

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