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Five-Membered-Ring 9-I-2 Radicals: Direct Detection and Comparison with Other Hypervalent Iodine Radicals

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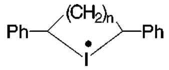
ABSTRACT



6a (n = 1) λ_{max} 320, τ = 9.5 µs
6b (n = 2) λ_{max} 330, τ = 14 µs
6c (n = 3) λ_{max} 350, τ = 4.4 µs

Photolysis of 1,4-diiodo-1,4-diphenylbutane leads to a five-membered-ring 9-I-2 radical (6b), whose absorption spectrum and stability are compared with those of other hypervalent iodine radicals of different ring size.

Cyclic hypervalent radicals 9-X-*n* (*n* = number of substituents joined to X heteroatoms with nine electrons in the valence shell)[1] have been proposed as transient reaction intermediates in many radical reactions.[2] Thus, several research groups have found evidence for the intermediacy of hypervalent trivalent sulfuranyl (9-S-3) and selenuranyl (9-Se-3) or tetravalent phosphoranyl (9-P-4) radicals in homolytic substitutions.[2,3] There is also evidence of the generation of iodine radicals (9-I-2) via homolytic cleavage of a hypervalent iodine(III)−peroxy or −halide bond.[4] In these cases formation of the iodine radical could be facilitated by conjugative overlap of the breaking bond with π-orbitals of the aromatic nucleus connected to the iodine atom.

Theoretical calculations predict that reactions involving intramolecular homolytic substitution at the tellurium atom should proceed via 9-Te-3 hypervalent intermediates; conversely, the analogous reactions involving sulfur and selenium should take place without the involvement of intermediates, except for the 1,6-translocation of selenyl.[5] Calculations on 1,5-, 1,6-, and 1,7-intramolecular homolytic translocation of halogen atoms between carbon centers appear to be in ageement with halogen transfer proceeding via transition states rather than through 9-X-2 intermediates.[6] The energy barriers in excess of 120 kJ mol^{-1} found for this process have been rationalized as a consequence of significant deviations from the expected collinear arrangement of attacking and leaving radicals at the halogen atom.

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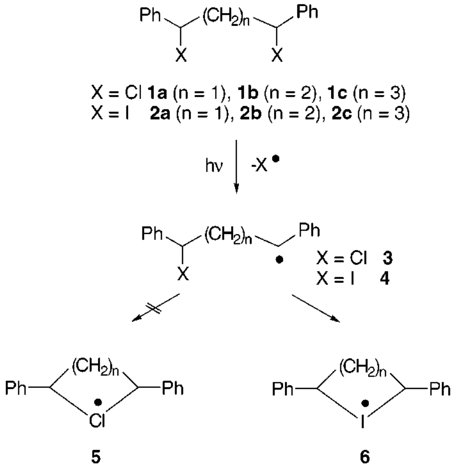
We have previously reported that photolysis of dichlorodiphenylalkanes **1** (n = 1−3) in cyclohexane produces homolysis of one carbon−halogen bond (Scheme 1).[7] Laser flash photolysis experiments have demonstrated the formation of chloroalkyl radicals **3**, which have the characteristic narrow absorption at 320 nm and are readily quenched by oxygen at close to the diffusion-controlled limit; these are common features of benzylic radicals.[8] Thus, no cyclic hypervalent chlorine radicals 9-Cl-2 (**5**) have been detected. By contrast, in the laser photolysis of the 1,3- and 1,5-diiodo analogues **2a** and **2c**, formation of the cyclic hypervalent iodine radical intermediates **6a** and **6c** was observed.[9] These intermediates are characterized by broader UV-absorption bands, longer lifetimes, lower reactivity with oxygen, and typical photochemical reactivity to give 1,2-diphenylcycloalkanes.[10]

Scheme 1



In this context, we now wish to report on the detection of the first five-membered-ring hypervalent iodine radical (**6b**); its properties are compared with those of analogous cyclic intermediates of different ring sizes.

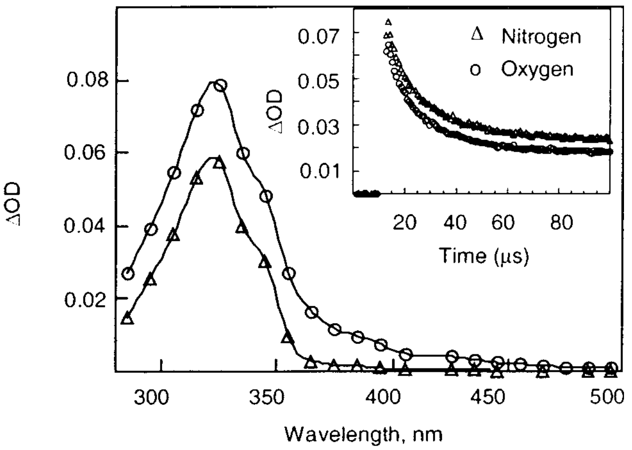


Figure 1. Transient absorption spectra recorded following laser excitation of **2b** in cyclohexane under nitrogen 2 μs (○) and 30 μs (△) after the laser (266 nm) pulse. The inset shows the effect of oxygen on the decay of the transient formed as monitored at 325 nm.

Laser flash photolysis of 1,4-diiodo-1,4-diphenylbutane (**2b**)[11] (deaerated cyclohexane solutions), using either a Nd:YAG laser (fourth harmonic, 266 nm) or a XeCl excimer laser (308 nm), yielded a transient with broad absorption at λ_{max} 330 nm and a tail extending to about 450 nm. This tail disappeared faster than the rest of the spectrum. In oxygen-saturated solutions the lifetimes of both transients were only slightly shorter than those observed upon nitrogen bubbling (inset, Figure 1). Hence, the spectroscopic data support the formation of two transients with low reactivity toward oxygen. On the basis of the literature, the tail of the absorption band between 370 and 450 nm could be ascribed to a complex of iodine atoms with the starting iodo compound.[9,12] The transient with a maximum at 330 nm had a lifetime around 14 μs under our experimental conditions and was assigned to the cyclic 9-I-2 radical **6b**. As in the case of the homologues **2a** and **2c**, no benzylic radical **4b** was detected after photolysis of the first C−I bond of **2b**.

When the size of the signal assigned to **6b** was plotted against the laser power, a slight downward curvature was obtained (see Figure 2). This type of curvature is common when the initial transient undergoes further photolysis during the laser pulse. To study the photobehavior of **6b**, two-laser−

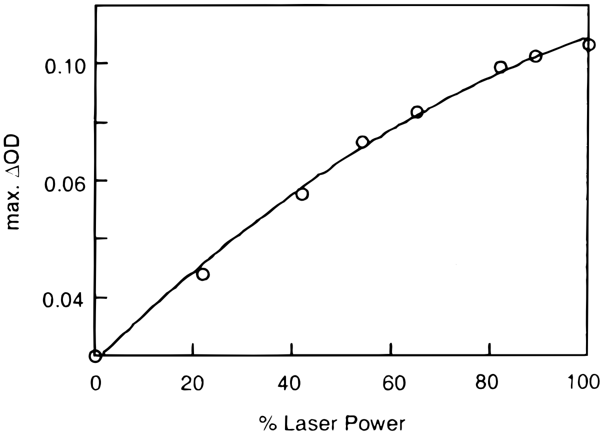


Figure 2. Effect of laser power on signal intensity following 266 nm laser flash photolysis of **2b** (monitored at 325 nm). 100% laser power corresponds to 10 mJ/pulse.

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(10) These features are similar to those of related hypervalent selenuranyl radicals: Ouchi, A.; Koga, Y.; Ham, M. M.; Ito, O. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1705−1709.

two-color flash photolysis[13] was performed using 266 nm pulses to produce the transient and a second nitrogen laser pulse (337 nm) to irradiate it. A permanent and irreversible bleaching of the signal monitored at 330 nm was concomitant with formation of more IR−I• complex absorbing at 380 nm (Figure 3). These data agree well with extrusion of the iodine atom upon irradiation of hypervalent radical **6b**. Analysis of the laser photolysate by GC/MS showed the formation of products such as styrene, 1,2-diphenylcyclobutane, and 1-phenyl-1,2,3,4-tetrahydronaphthalene, fingerprints for the intermediacy of the 1,4-diphenyl-1,4-butanediyl biradical.[14]

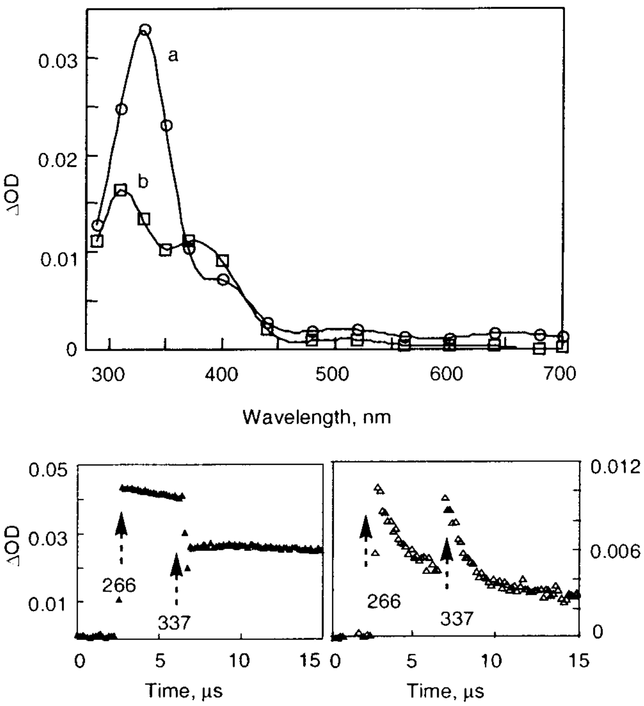
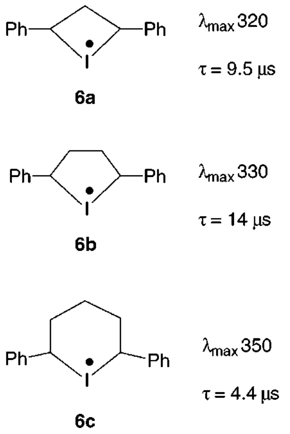


Figure 3. Top: (a) transient absorption spectra recorded following laser excitation (266 nm) of **2b** under nitrogen 0.2 μs (○) after laser pulse. (b) Transient absorption spectrum obtained upon two-laser−two-color excitation of **2b** (□). The intermediate generated by means of a 266 nm laser pulse is photolyzed after 2.1 μs by a second laser at 337 nm. Botton: kinetic trace at 330 nm (left) and 380 nm (right); the bleaching at 330 nm corresponds to the disappearance of **6b** and the new decay at 380 nm corresponds to formation of more IR−I•complex.

Scheme 2 shows the comparative data obtained for the three cyclic 9-I-2 radicals **6a**−**c**. The absorption maxima are shifted to higher values with increasing ring size. On the other hand, the five-membered radical is more stable than the six-membered homologue; this is in agreement with ab initio calculations on the energy barrier for cyclization of ω-tellurium alkyl radicals.[5] Interestingly, even the four-membered iodine radical is more stable than the six-membered homologue. Theoretical calculations on hypervalent radicals of this type face some difficulties;[3a,5] however, simple molecular modeling suggests that delocalization of the unpaired electron on the halogen on both aromatic rings may be easier to achieve in the four- and five-membered ring systems than in the six-membered one, where the chair ring conformation tends to place the second aromatic ring in an unfavorable orientation for interaction.

Scheme 2



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[11] Compound **2b** was prepared from the corresponding diol by treatment with iodotrimethylsilane[9] (solid, mp 95 °C, 90% yield). Data for **2b** (diasteromeric mixture): ^{1}H NMR (250 MHz, CDCl$_3$) δ = 2.0−2.1(m, 1H), 2.3 (t, J = 3.5 Hz, 2H), 2.45−2.55 (m, 1H), 5.05−5.15 (m, 2H), 7.25−7.4 (m, 10H); ^{13}C NMR (75.46 MHz, CDCl$_3$) δ = 143.4(s), 128.8 (d), 128.2 (d), 127.0 (d), 41.5 (t), 41.3 (t), 31.7 (d), 31.5 (d)Anal. Calcd for $C_{16}H_{16}I_2$: C, 41.59; H, 3.49. Found: C, 41.76; H, 3.61.

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