

# Detection of Phenyl-Substituted Radical Cations Derived from Cyclopentyl- and Urazole-Type Azoalkanes by Pulse Radiolysis: Influence of Heteroatom Substitution on the Radical Cation Reactivities

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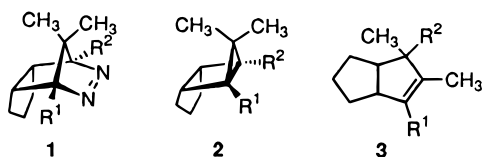
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**Abstract:** The radical cations of cyclopentane- and urazole-annulated azoalkanes and housanes were generated by pulse radiolysis and the transients characterized spectrally and kinetically by time-resolved optical monitoring. For the bridgehead-substituted diphenyl derivatives of the cyclopentane-annulated azoalkane **1** and housane **2** only the corresponding proximate 1,2 radical cation species were observed, generated from the initially formed and too short-lived ( $< 1 \mu\text{s}$ ) distonic 1,3 radical cation by 1,2-methyl migration. In contrast, for the corresponding urazole-annulated azoalkanes **4**, the initial distonic 1,3 radical cations **5**<sup>•+</sup> were detected, and of these the methyl-substituted **5b**<sup>•+</sup> deprotonates to the radical **5b**<sup>•</sup>.

## Introduction

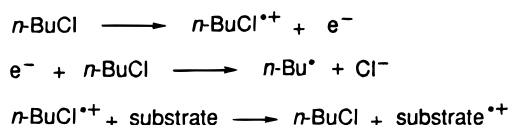
The photochemically (PET) and chemically (CET) induced electron-transfer chemistry of cyclopentane-annulated azoalkanes **1** and housanes **2** has recently been thoroughly investigated from the point of view of product studies.<sup>3</sup> We have found that the azoalkanes **1** and their corresponding housanes **2** rearrange on



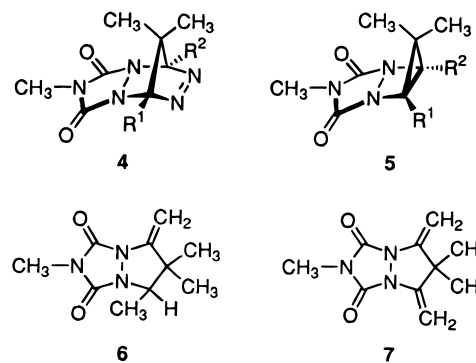
electron-transfer oxidation to the corresponding cyclopentenes **3**.<sup>3</sup> In previous studies<sup>4</sup> we have established by means of stereolabeled housanes that the rearrangement upon electron transfer to the corresponding cyclopentenes takes place diastereo-<sup>4a</sup> and regioselectively.<sup>4b</sup> In addition, EPR spectroscopy under matrix isolation conditions of the intervening radical cations derived from azoalkanes **1** and their corresponding housanes **2** proved helpful in detecting and characterizing such transients and thereby gaining valuable mechanistic insight.<sup>4</sup>

In contrast, the urazole-annulated housanes **5**, generated from the corresponding azoalkanes **4** by photodenitrogenation, do not rearrange upon electron transfer to analogous cyclopentenes. Instead, upon oxidation the urazole-annulated housane **5** ( $R^1 = R^2 = \text{CH}_3$ ) afforded the olefins **6** and **7** with exocyclic double bonds. Thus, the adjacent urazole ring alters significantly the chemical fate of the intermediary 1,3 radical cation.<sup>5</sup> Consequently, it was of interest to generate the authentic radical

## Scheme 1. Radiolytic Generation of Radical Cations in *n*-BuCl



cations of the carbocyclic azoalkanes **1** and housanes **2** and the corresponding urazole-annulated analogs **4** and **5** by pulse



radiolysis to assess their optical properties and kinetic behaviour with time-resolved UV spectroscopy. For this purpose we employed the non-nucleophilic *n*-butyl chloride as the solvent of choice for the radiolytic generation of the radical cations (Scheme 1) due to its ability to scavenge irreversibly electrons produced by the ionizing radiation. Presently we report the results of this study, in which we demonstrate that pulse radiolysis is a valuable method for characterizing such transient radical cations.

## Results and Discussion

### Cyclopentane-Annulated Azoalkanes **1** and Housanes **2**.

Upon pulse radiolysis in *n*-butyl chloride, the substrate azoalkane

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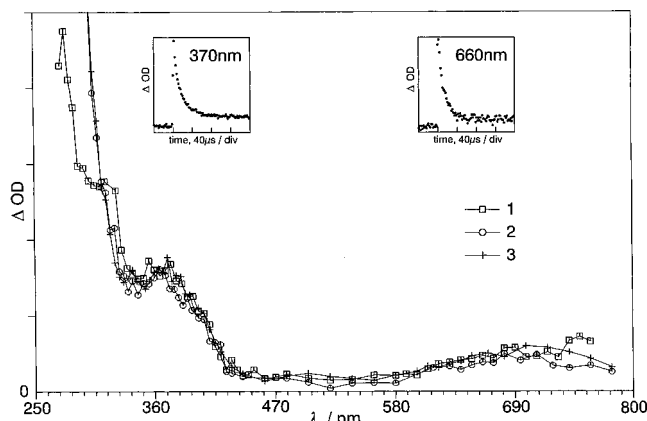
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(3) (a) Adam, W.; Heidenfelder, T.; Sahin, C. *Synthesis* **1995**, 1163. (b) Sahin, C. Ph.D. Thesis, 1995, Würzburg.

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**Figure 1.** Absorption spectra of transients on radiolysis in deoxygenated *n*-BuCl of 1 mM azoalkane **1** (squares) recorded at 1.9  $\mu$ s, 1 mM (solution saturated with O<sub>2</sub>) housane **2** (circles) recorded at 1.6  $\mu$ s, and 1 mM cyclopentane **3** (crosses) recorded at 1.5  $\mu$ s after the pulse; the insets show the decay of the transient derived from **2**.

**Table 1.** Spectral Characteristics and Kinetics of the Transients Obtained in the Pulse Radiolysis under Deoxygenated Conditions

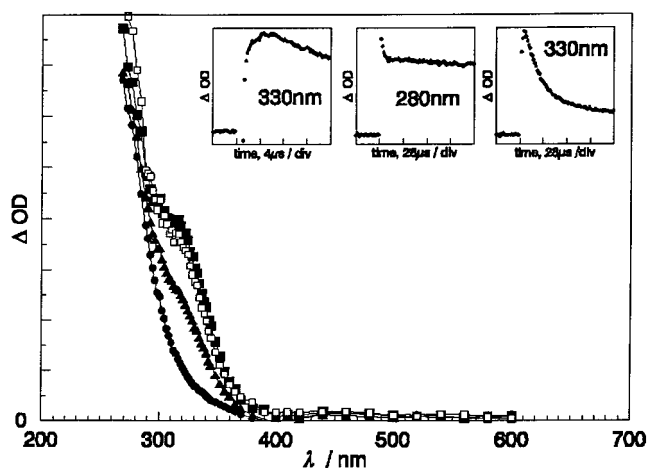
substrate <sup>a</sup>	radical	$\lambda_{\text{max}}/\text{nm}^b$	first half-life/ $\mu\text{s}^c$
<b>1</b>	<b>3<sup>+</sup></b>	365–385	6.3 $\pm$ 0.4
<b>1</b>	<b>3<sup>+</sup></b>	630–670	8.2 $\pm$ 1.9
<b>2</b>	<b>3<sup>+</sup></b>	362–382	12.0 $\pm$ 0.6
<b>2</b>	<b>3<sup>+</sup></b>	650–700	13.3 $\pm$ 1.8
<b>4a</b>	<b>5a<sup>+</sup></b>	325	75 $\pm$ 16
<b>4b</b>	<b>5b<sup>+</sup></b>	325	<i>d</i>

<sup>a</sup> 1 mM solutions of **1**, **2**, or **4** in *n*-butyl chloride; the solutions were deoxygenated by purging with argon gas. <sup>b</sup> Wavelengths of the most intense transient absorptions. <sup>c</sup> Predominantly second-order decays. <sup>d</sup> First-order decay with  $k = 3.7 \times 10^{-5} \text{ s}^{-1}$ , see text.

**1** (1 mM) and its housane **2** (1 mM) gave similar absorption spectra (Figure 1). Two main absorption bands at 370 and 700 nm, and a shoulder at 400 nm, were observed, and their identical decay rate (Table 1) implies that the same transient species is involved. The presence of molecular oxygen did not have a significant influence on the spectra of the transients, especially in the case of the housane **2**. For the azoalkane **1**, however, an additional absorption at  $<300 \text{ nm}$  was detected, which was scavenged by molecular oxygen. This may be attributed to the formation of unknown additional radical intermediates. As a consequence, the transient obtained by pulse radiolysis of azoalkane **1** disappeared faster than that of the housane **2** (Table 1) under argon atmosphere. In the presence of molecular oxygen, these transients were scavenged and the spectra of both substrates looked more similar.

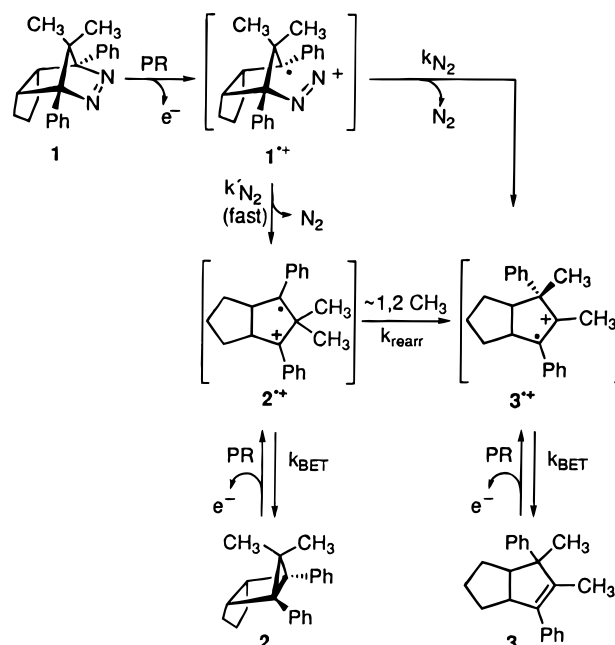
On the basis of the similarity of the absorption spectra of the azoalkane **1** and the housane **2** with those<sup>3</sup> of the styrene radical cation,<sup>6</sup> and our previous product studies, we assign the styrene-type proximate (delocalized) 1,2 radical cation **3<sup>+</sup>** structure to this transient (Scheme 2). In support of this mechanism, we have irradiated a 1 mM solution of cyclopentene **3** in *n*-BuCl and found the same absorption spectrum as in the case of the azoalkane **1** or housane **2** (see Figure 1). The corresponding distonic 1,3 radical cation **2<sup>+</sup>** is apparently too short-lived<sup>4</sup> to be detected at the available time resolution (ca. 1  $\mu$ s) of the pulse-radiolysis apparatus.

In the proposed mechanism, the oxidation of the substrate by the solvent radical cation leads to the azoalkane radical cation **1<sup>+</sup>**, which either rearranges concomitantly with dinitrogen loss



**Figure 2.** Absorption spectra on pulse radiolysis of an oxygenated 1 mM solution of **4b** in *n*-BuCl, recorded at 2.5 (open squares), 3.7 (full circles), 20 (solid triangles), and 100  $\mu$ s (open triangles) after the pulse; the insets display the presence of a fast transformation followed by the decay (in O<sub>2</sub>-saturated solution) of the resulting species (see text).

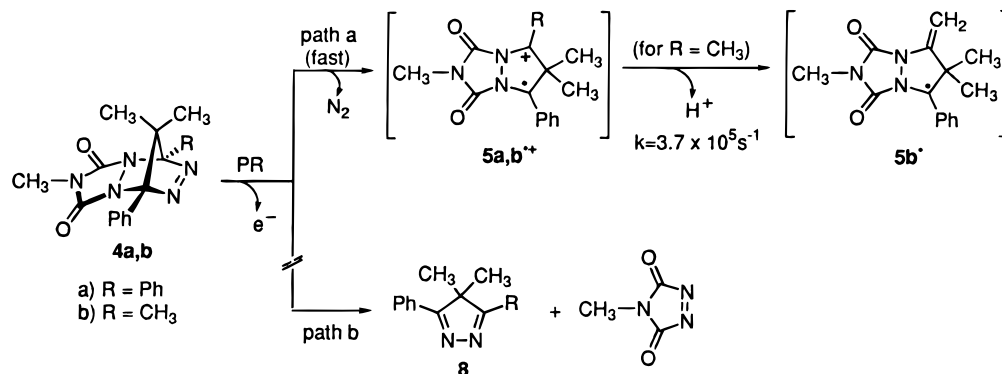
**Scheme 2.** Radical Cation Formation on Pulse Radiolysis (PR) of the Cyclopentane-Annulated Azoalkane **1** and Housane **2**



(step  $k_{\text{N}_2}$  in Scheme 2) directly to the 1,2 radical cation **3<sup>+</sup>**, or first eliminates N<sub>2</sub> (step  $k'_{\text{N}_2}$ ) to give the distonic 1,3 radical cation **2<sup>+</sup>**, which subsequently rearranges ( $k_{\text{rearr}}$ ) by 1,2-methyl migration to the delocalized **3<sup>+</sup>**. In support, we cite our previous results on related azoalkanes and their housanes.<sup>4</sup> Upon radiolysis of the azoalkanes under matrix isolation even at a temperature as low as 77 K, only the corresponding olefin 1,2 radical cation was observed by EPR spectroscopy. In the case of the housanes, sufficiently persistent 1,3 radical cations could be detected by EPR spectroscopy at 77 K, which rearranged to the corresponding 1,2 radical cations. Thus, it is reasonable to assume that the 1,2 radical cation **3<sup>+</sup>** is the most likely detectable transient under the present conditions of the radiolysis of azoalkane **1** and also its housane **2**. Such 1,2 radical cations are known to be relatively unreactive toward molecular oxygen, in agreement with our experimental observations.

**Urazole-Annulated Azoalkanes.** The time-resolved pulse-radiolysis spectra observed in the case of the symmetrical

(6) Brede, O.; David, F.; Steenken, S. *J. Chem. Soc., Perkin Trans. 2* **1995**, 23.

**Scheme 3.** Transients from the Urazole-Annulated Azoalkanes **4a** and **4b** on Pulse Radiolysis (PR) in *n*-BuCl

diphenyl-substituted azoalkane **4a** and the unsymmetrical phenyl methyl derivative **4b** (Figure 2) both show absorption at ca. 320–330 nm. In the case of **4b**, the spectrum recorded immediately after the pulse (2.5  $\mu$ s) has a peak at  $\leq 275$  nm with a shoulder at ca. 320 nm. This spectrum undergoes a rapid change (decrease at 280 nm and a concomitant increase at 330 nm, see insets in Figure 2) with a first-order rate constant of ca.  $3.7 \times 10^5 \text{ s}^{-1}$ , which is not changed in the presence of  $\text{O}_2$ . The resulting species (**5b\***, see later) slowly decays by second-order kinetics (first half-life 1.9 ms). This decay is accelerated by  $\text{O}_2$  (see inset at the right in Figure 2), from which a rate constant of ca.  $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  was extracted for the reaction of  $\text{O}_2$  with radical **5b\***.

The initial transient may tentatively be assigned to the 1,3 radical cation **5b<sup>+</sup>** (Scheme 3). The followup reaction for the unsymmetrical methyl-substituted derivative **4b** is interpreted in terms of deprotonation of the 1,3 radical cation **5b<sup>+</sup>** (path a, Scheme 3), as observed also for the chemical electron-transfer (CET) reaction of the housane **5b**.<sup>5</sup> This stabilization process leads to the monoradical **5b\***, which has a high reactivity with  $\text{O}_2$  (a characteristic feature of *neutral* radicals). For the symmetrical diphenyl-substituted azoalkane **4a**, only the first transient was observed, since deprotonation is not possible.

The possibility that the observed transients derive from the corresponding isopyrazoles **8**, produced by retrocleavage of the azoalkanes **4a,b** (path b, Scheme 3), was excluded by pulse radiolysis experiments on the authentic isopyrazoles **8**. Distinctly different transient spectra were observed for the latter, with broad absorption between 400 and 800 nm.

For further control, time-resolved laser flash photolysis of the azoalkanes **4a,b** was performed in acetonitrile under either an argon or oxygen atmosphere. For both derivatives **4a** and **4b**, the observed transients differed completely from the ones obtained under the pulse-radiolysis conditions. Excitation either with 408-nm light, which selectively excites the azo chromophore, or with 248-nm light led to transients which are assigned to the triplet diradical precursors of the housanes **5a,b**.<sup>5b</sup>

**Comparison of the Cyclopentane- and Urazole-Annulated Radical Cations.** Our present kinetic and spectral studies (Table 1) of the transients observed in the pulse radiolysis of the azoalkanes **1** and **4** and housane **2** demonstrate distinctly different behavior between the cyclopentane- and urazole-annulated radical cation structures **2<sup>+</sup>** and **5<sup>+</sup>**, in agreement with the previously described chemistry.<sup>3,5</sup> Thus, in the time domain of the pulse radiolysis (ca. 1  $\mu$ s to 1 ms), the first detectable transient from the cyclopentane-annulated azoalkane **1** and housane **2** is the 1,2 radical cation **3<sup>+</sup>**. It is produced from the initial short-lived (<1  $\mu$ s) distonic 1,3 radical cation **2<sup>+</sup>** by 1,2-methyl migration (Scheme 2). In contrast, for the urazole-annulated systems, in the case of azoalkane **4b**, the

corresponding 1,3 radical cation **5b<sup>+</sup>** could be observed optically and its lifetime estimated (Figure 2,  $\tau$  ca. 2.7  $\mu$ s). Usually, proximate 1,2 radical cations are more persistent than the corresponding distonic ones.<sup>4,7</sup> Thus, the substantially lower reactivity of the urazole- (**5a<sup>+</sup>**) *versus* the cyclopentane-annulated (**2<sup>+</sup>**) 1,3 radical cation derives apparently from the stabilization by the urazole moiety since all other structural features are identical. Presumably, the charge and possibly also the spin are delocalized onto the adjacent nitrogen atoms of the urazole moiety.

Of mechanistic interest is the fact that when one of the phenyl groups is replaced by a methyl group, as in the case of the 1,3 radical cation **5b<sup>+</sup>** derived from azoalkane **4b**, the lifetime is greatly reduced as compared to **5a<sup>+</sup>**; however, this more reactive species is still sufficiently persistent to be detected optically as the initially generated authentic 1,3 radical cation **5b<sup>+</sup>**. Due to the methyl group at the bridgehead site, deprotonation to the radical **5b\*** takes place, as supported by previous product studies.<sup>5a</sup>

## Conclusion

Time-resolved optical absorption spectroscopy makes possible the detection and characterization of transient radical cations generated from phenyl-substituted azoalkanes or their corresponding bicyclo[2.1.0]pentanes (housanes) by pulse radiolysis. This method is especially valuable when EPR spectroscopy is inconclusive as for the substrates **1**, **2**, and **4a** because of unresolved hyperfine structure or insufficient lifetime. Such spectral and kinetic analysis nicely complement the product studies of the CET and PET chemistry and, thus, permit mechanistic information to be obtained.

## Experimental Section

**Synthesis of Starting Materials.** The two [4H]pyrazoles were prepared according to the literature<sup>8</sup> from the corresponding diketones. The azoalkanes **1** and **4** were obtained from the [4H]pyrazoles **8a,b** by reaction with either cyclopentadiene<sup>9</sup> or 4-methyl-1,2,4-triazoline-3,5-dione (MTAD)<sup>10</sup> and purified according to the known procedures. The housane **2** was generated by direct photolysis of azoalkane **1** (364 nm, argon-ion laser) in methylene chloride.<sup>9</sup>

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**Pulse Radiolyses.** For the pulse-radiolysis experiments, ca. 1 mM solutions in *n*-butyl chloride were used. The solutions were deoxygenated by purging with pure (99.998%) Ar gas before radiolysis. A 3-MeV van de Graaf accelerator was used, which delivered 100-ns pulses with doses in the range of 10–20 Gy. The optical absorption signals of the transients were digitized simultaneously by Tektronix 7612 and 7912 transient recorders interfaced with a DEC LSIII/73<sup>+</sup> computer. The latter was also used for process control of the apparatus and for on-line (pre)analysis of the experimental data. Final data analysis was performed on a Microvax II connected with the LSI by Ethernet.

**Laser Photolyses.** After deoxygenation by purging with argon gas, solutions of the azoalkanes **4a,b** (OD/cm ca. 1 at the excitation wavelength) in acetonitrile were allowed to flow through a 2-mm (in

the direction of the laser beam) by 4-mm (in the direction of the analysis light) Suprasil quartz cell (flow rates ca. 1–2 mL/min) and photolyzed with 20-ns pulses of 248-nm light (ca. 5–40 mJ/pulse) from a Lambda-Physik EMG103MSC excimer laser or 20-ns pulses of 408-nm light (ca. 2–10 mJ/pulse) from a Lambda-Physik dye laser. The photolytically induced optical transmission changes, which typically corresponded to peak optical density changes ( $\Delta OD$ ) of 0.01–0.1 (depending on substrate concentration, quantum yield, and pulse power), were digitized with a Tektronix 7912 or 7612 digitizer and a computer system similar to that employed for the pulse-radiolysis experiments.

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