Chemistry and spectroscopy of aromatic diradicals in cryogenic matrices

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Abstract: The matrix isolation of a variety of aromatic diradicals is described in this report. Flash vacuum pyrolysis of terephthaloyl and isophthaloyl diiodide produces E/Z mixtures of hexa-1,5-diyne-3-ene but no dehydrobenzene. [2.2]Paracyclophanes are highly strained molecules and are shown to be precursors of a variety of interesting diradicals, novel ketenes, and unusual quinoid compounds. Photolysis of substituted quinone diazides provides access to m-dehydrophenols, and thus allows for the direct spectroscopic observation of a derivative of m-dehydrobenzene.

Introduction

p-Didehydrobenzene and related diradicals are key intermediates in the Bergman cyclization and other thermal aromatization reactions and have attracted much attention during the last years. Despite this interest, only little unequivocal spectroscopic evidence has been reported for these elusive species. In our laboratory a variety of precursors of m- and p-dehydrobenzene and other aromatic diradicals have been investigated under the condition of matrix isolation. Three classes of precursors of aromatic diradicals are described in this report: phthaloyl diiodides as thermal, and [2.2]paracyclophanes and quinone diazides as photochemical precursors. The products were characterized by trapping experiments as well as by isolation in rare gas matrices with IR and UV/Vis spectroscopic detection. Comparison of the IR spectra with ab initio calculations allowed for an assignment of vibrational modes.

Flash Vacuum Pyrolysis of Terephthaloyl Diiodide and Isophthaloyl Diiodide

The flash vacuum pyrolysis (FVP) of terephthaloyl diiodide 1 was investigated by on-line mass spectroscopic detection or by subsequent trapping of the products in solid argon at 10 K (1, 2). At temperatures above 500°C the formation of C₆H₄ (m/z = 76), I (m/z = 127), and I₂ (m/z = 254) concurrent with the decrease of mass peaks assigned to 1 is observed. Matrix isolation of the pyrolysis products reveals the formation of an E/Z mixture of hexa-1,5-diyne-3-ene 3 but no evidence for the formation of p-dehydrobenzene 2. This is in accord with recent experimental (3) and theoretical (4) thermochemical data for the Bergman rearrangement, which come to the conclusion that 2 lies in an energy well of around 19.8 kcal/mol. Thus, under FVP conditions, the exothermic ring-opening (ΔHR = -8.5 kcal/mol) to Z-3 is expected to be the major process. Other products of the FVP are benzene and iodobenzene, presumably formed by reactions of the radical intermediates with surface contaminations.
FVP of isophthaloyl diiodide 4 results in a similar mixture of products than FVP of 1 with E/Z mixtures of enediyne 3 as the only C₆H₄ isomers. The formation of 3 from 4 requires a hydrogen migration in one of the intermediate radicals or in 5 (5). A plausible mechanism is the ring-opening of 5 to produce vinylidene 6, which undergoes a rapid [1,2]-H shift to Z-3 (6). These results clearly demonstrate that FVP is not suitable for the generation of p- and m-dehydrobenzene.

**Photolysis of [2.2]Paracyclophanes**

[2.2]Paracyclophanes are strained molecules and thus should be useful precursors of high energy molecules. We therefore investigated the photochemistry of a series of [2.2]cyclophanes. In all cases the primary photochemical reaction was cleavage of the aliphatic C-C bond to produce a diradical. The photochemistry of [2.2]paracyclophane-1,10-dione 7 was followed in ethanol at room temperature and at 77 K, in 2-methyl-tetrahydrofuran (MTHF) at 77 K and in argon at 10 K. After short irradiation times (1 - 5 min, λ > 335 nm) ester 9, the trapping product of diradical 8, is the major product. Prolonged irradiation (> 20 min) transforms ester 9 to diethyl terephthalate 10. These experiments reveal that 10 is exclusively formed by photolysis of 9 and not by trapping of bisketene 12.

Irradiation of cyclophane 7 in argon at 10 K yields p-xylene 11 and bisketene 12 as the only products. Obviously diradical 8 is not stable under these conditions and readily cleaves to 11 and 12. Bisketene 12 was identified by comparison of the IR spectrum with the ab-initio (RHF/6-31G(d)) calculated spectrum. The ketene stretching mode is assigned to a very intense absorption at 2082 cm⁻¹. Short wavelength UV irradiation (λ > 230 nm) results in the slow degradation of 12 and formation of CO. However, no further photoproduct, and in particular no p-dehydrobenzene, could be identified.

Irradiation of matrix-isolated [2.2]Paracyclophane-9-en-1-one 16 with the intense light of an KrF Excimer-Laser results in a yellow-green coloring of the matrix which is caused by the broad absorption at 440 nm of ketene 17. The IR spectrum of 17 exhibits both elements of p-xylene and ketene 16. Photolysis of cyclophane 16 in ethanol results in the formation of ester 19. The formation of 19 can be rationalized by ethanol trapping of ketene 17 to give the labile ester 18, which rapidly tautomerizes to 19.

The cyclophanes described so far contain one or two carbonyl groups, and the primary photochemical step in all cases was Norrish Type 1 cleavage. To extend the usage of cyclophane photochemistry for the generation of diradicals we also investigated [2.2]paracyclophane-9-ene 20. Irradiation (λ = 248 nm) of 20 leads to a new compound with the UV/Vis spectrum shown in Fig. 1.
Chemistry of aromatic diradicals in cryogenic matrices

A strong and sharp absorption is observed at 440 nm, close to the longest-wavelength absorption of the benzyl radical in solid argon at 449.6 nm (7). The absorption maximum of p-Xylylene is found at much shorter wavelength, 320 nm (8), which indicates an open-shell structure 21b - two benzyl radicals linked to an ethylene subunit - for the photoproduct rather than a closed-shell quinoid structure 21a. There are two additional weak absorptions in the red, at 600 nm and 650 nm, which provide additional evidence for a diradicaloid structure.

The UV/Vis as well as the IR spectrum remains unchanged after warming the matrix from 10 to 40 K. No evidence for the cisltrans isomerization to give 22 was obtained from these experiments. This is in accordance with thermochemical data for the rearrangement 20 → 21 → 22 from oxygen trapping experiments and MMEVBH calculations by Roth et al. (9).

Photochemistry of Quinone Diazides

An approach to m-dehydrophenols is the photolysis of quinone diazides 23, which on photolysis (432 nm) yield cyclohexadienylidenes 24 (10). Subsequent irradiation with red light (575 nm) results in the decarboxylation of 24 to give m-dehydrophenol 25. The parent m-dehydrophenol 25a has been characterized by comparison of the experimental with ab initio (GVB/6-31G) calculated IR spectra. Since 23a shows a very low solubility in most solvents, the solution photochemistry could not be determined. Quinone diazides bearing alkyl side chains are more soluble in polar solvents. Irradiation (λ = 308 nm) with a low-pressure mercury arc lamp (λ = 254 nm) produces strong absorption的特点.
nm, XeCl Excimer-Laser) of 23d in MTHF glasses at 77 K produces 3-isobutyl salicylic acid, the trapping product of carbene 24d, and 2-isobutyl phenol, the trapping product of dehydrophenol 25d (Scheme 1).

In acidic solvents, such as trifluoroethanol, the addition of nucleophiles is observed. This can be rationalized if the formation of a diazonium salt is postulated, which photochemically looses N₂ to produce a phenyl cation. Diazonium salts could be observed by UV/Vis or ¹³C-NMR spectroscopy.

Scheme 1. Photochemistry of quinone diazide 23d. The insert shows the X-ray structure of 23d.

References
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6. The formation of vinylidenes in the thermal ring-opening of m-dehydrobenzene was proposed by R. F. C. Brown at the ISNA 8.