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Chemistry and spectroscopy of aromatic diradicals in cryogenic matrices

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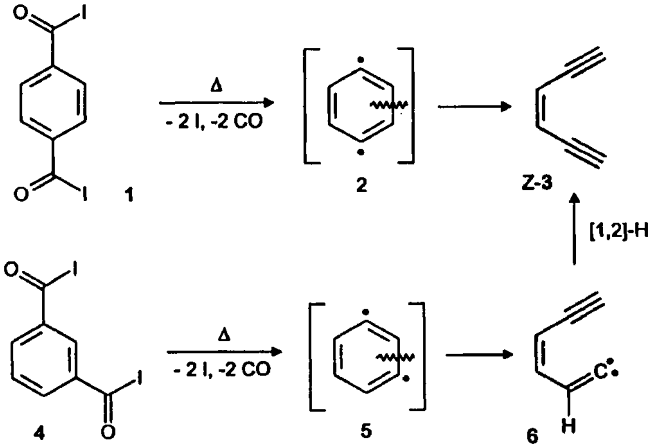
Abstract: The matrix isolation of a variety of aromatic diradicals is described in this report. Flash vacuum pyrolysis of terephthaloyl and isophthaloyl diiodide produces E/Z mixtures of hexa-1,5-diyne-3-ene but no dehydrobenzene. [2.2]Paracyclophanes are highly strained molecules and are shown to be 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 C_6H_4 (m/z = 76), I (m/z = 127), and I_2 (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 (ΔH_R = -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.

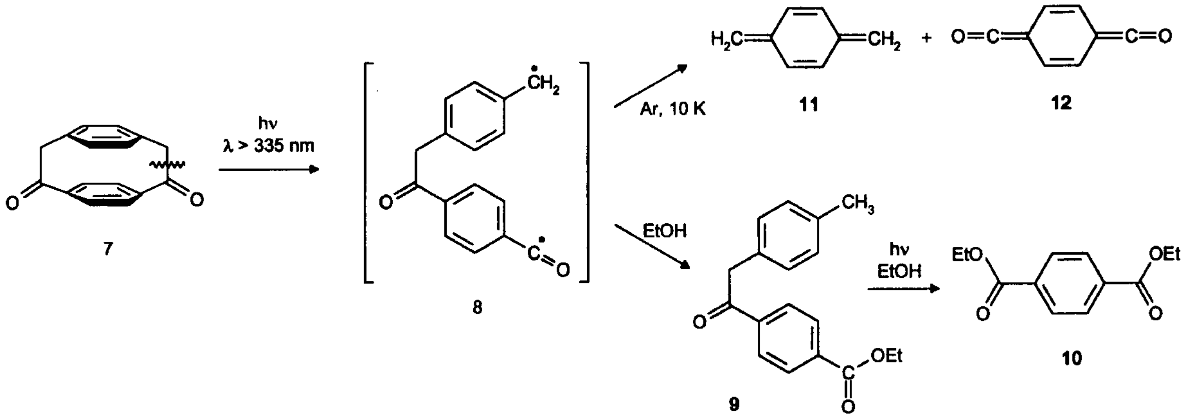


FVP of isophthaloyl diiodide **4** results in a similar mixture of products than FVP of **1** with E/Z mixtures of enediyne **3** as the only C_6H_4 isomers. The formation of **3** from **4** requires a hydrogen migration in one of the intermediate radicals or in **5** (5). A plausible mechanism is the 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.

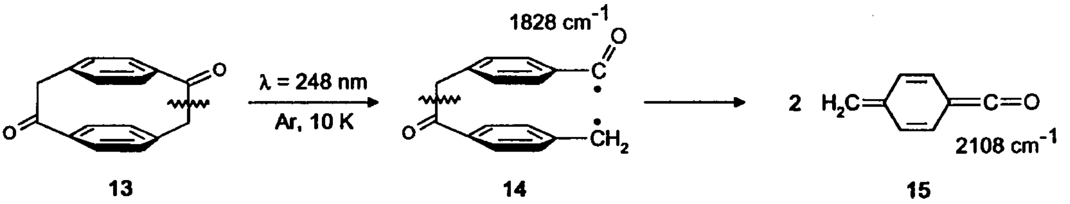
Photolysis of [2.2]Paracyclophanes

[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**.



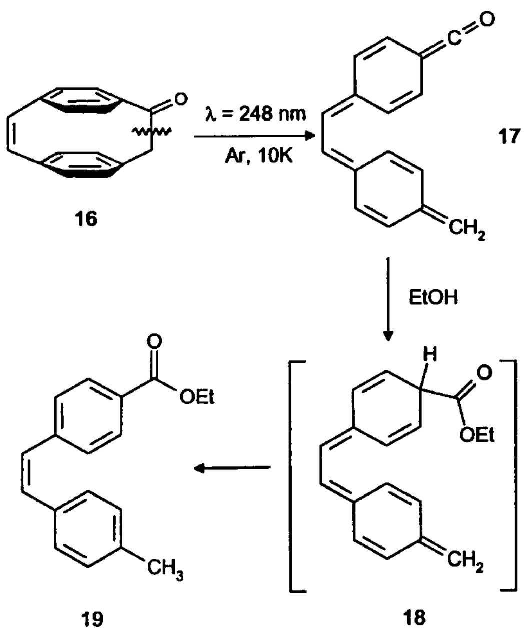
Irradiation of cyclophane **7** in argon at 10 K yields *p*-xylylene **11** and bisketene **12** as the only products. Obviously diradical **8** is not stable under these conditions and readily cleaves to **11** and **12**. Bisketene **12** was identified by comparison of the IR spectrum with the *ab-initio* (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.



Photolysis (λ = 248 nm, KrF Excimer-Laser) of [2.2]paracyclophane-1,9-dione **13**, matrix isolated in argon at 10 K, leads to the formation of an intense ketene IR absorption at 2108 cm^{-1}, assigned to ketene **15**, and a medium intensity absorption at 1828 cm^{-1}. The latter was tentatively assigned to the carbonyl absorption of diradical **14**. Prolonged irradiation results in the decrease of the 1828 cm^{-1} absorption and exclusively formation of **15**.

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*-xylylene 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 I 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.



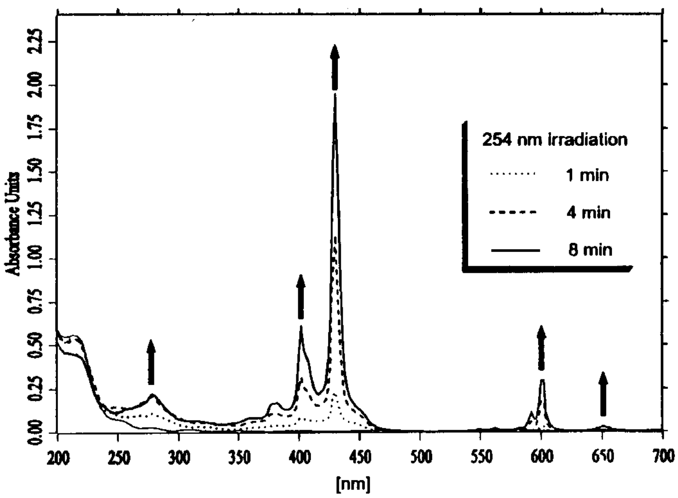
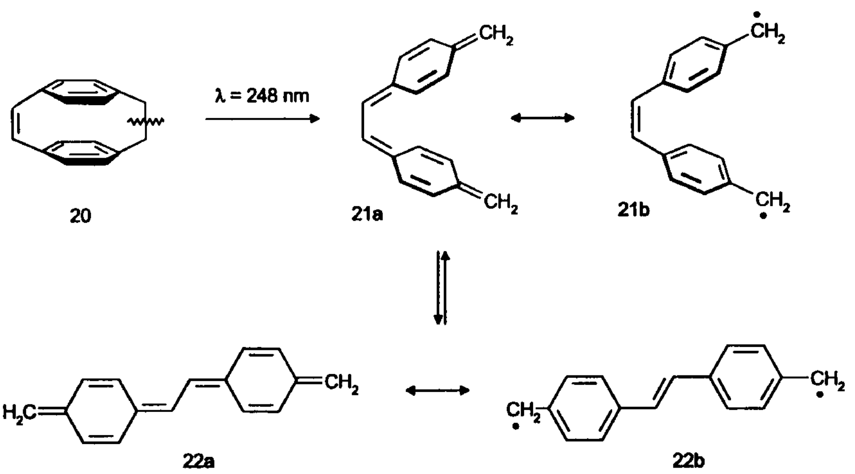


Figure 1. UV/Vis spectra showing the photochemistry of cyclophane **20**, matrix-isolated in argon at 10 K. The spectra were taken after 1 min, 4 min, and 8 min irradiation with a low-pressure mercury arc lamp (λ = 254 nm).



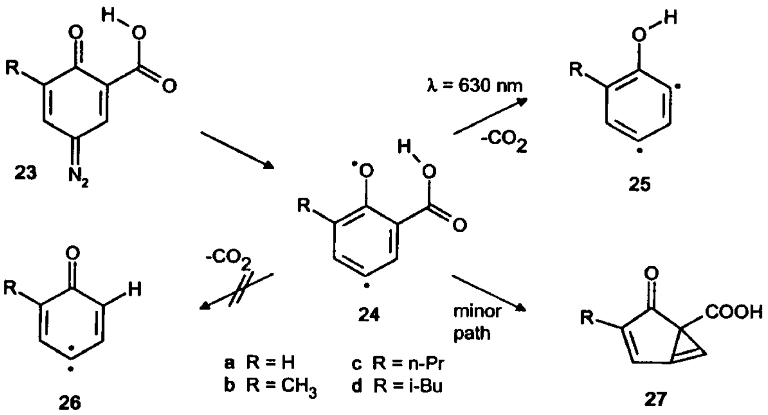
A strong and sharp absorption is observed at 440 nm, close to the longest-wavelength absorption of the benzyl radical in solid argon at 449.6 nm (7). The absorption maximum of *p*-Xylylene is found at much shorter wavelength, 320 nm (8), which indicates an open-shell structure **21b** - two benzyl radicals 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 cis/trans 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

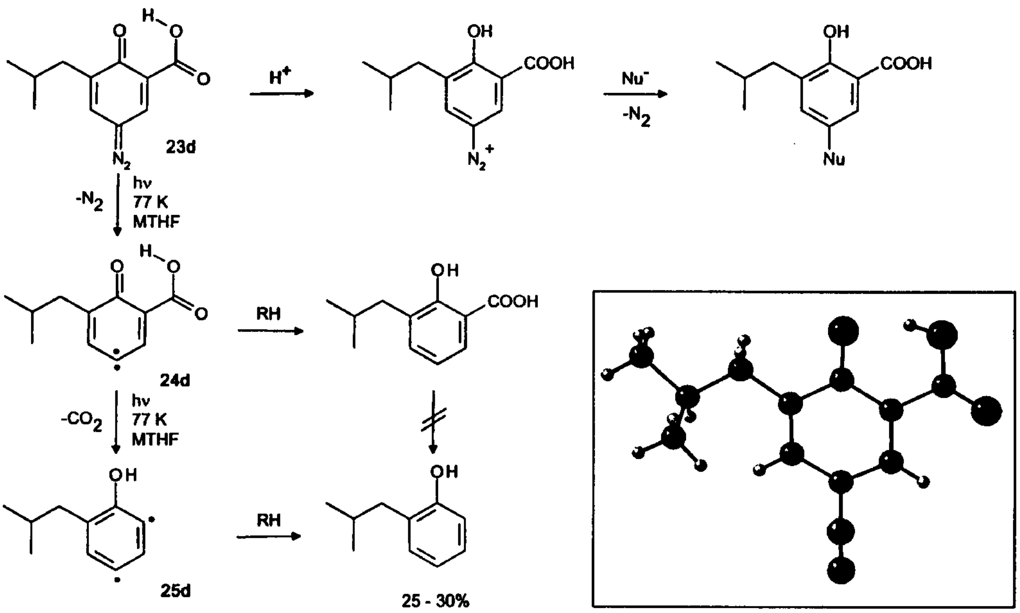
An approach to *m*-dehydrophenols is the photolysis of quinone diazides **23**, which on photolysis (432 nm) yield cyclohexadienylidenes **24** (10). Subsequent irradiation with red light (575 nm) results in the decarboxylation of **24** to give *m*-dehydrophenol **25**. The parent *m*-dehydrophenol **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, 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 N_2 to produce a phenyl cation. Diazonium salts could be observed by UV/Vis or ^{13}C-NMR spectroscopy.



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

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