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Stable Free Radicals. 8. Photochemical Decomposition of 1,8-Biphenylenediyl Bismethyl and *o*-Xylenyl Pyridinyl Diradicals

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Abstract: The photosensitivity of 1-benzyl-4-carbomethoxypyridinyl radicals has been found also in the pyridinyl diradicals, 1,8-biphenylenediyl bismethyl and *o*-xylenyl, and their magnesium complexes. In neither series is the quantum yield of decomposition especially high. Irradiation in the visible absorption band does not cause photodecomposition, but does apparently favor the formation of the most highly absorbing magnesium complexes. Irradiation in the first strong absorption band of the radical (near 400 nm) is more effective than irradiation in the short wavelength absorption band (260 nm) for causing photodecomposition. A specific synthesis for 1,8-dimethylbiphenylene has been developed.

In the course of investigations designed to study the properties of pyridinyl diradicals with specified distances separating the pyridinyl radical moieties, we experienced difficulty in generating and retaining a 1,8-biphenylenediyl bismethyl pyridinyl (**1**). A possible reason for this unexpected result became apparent only after we learned of the discovery of Ikegami and Watanabe[2a,b] that 1-benzyl-4-carbomethoxypyridinyl (**2**) was rather photosensitive, decomposing to methyl isonicotinate and the benzyl radical (eq 1). With proper precautions against exposure to light, we then successfully prepared diradical **1**. In order to establish conditions for the use of diradicals like **1** in other experiments, and to obtain further information on the novel process of photodecomposition of stable free radicals, we have made a study of the photolysis of two pyridinyl diradicals and their magnesium complexes. We here report the results, together with a synthesis developed for the specific preparation of 1,8-biphenylene.
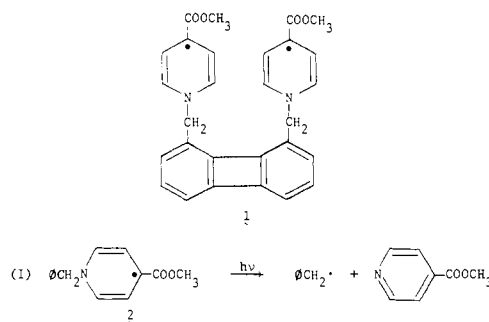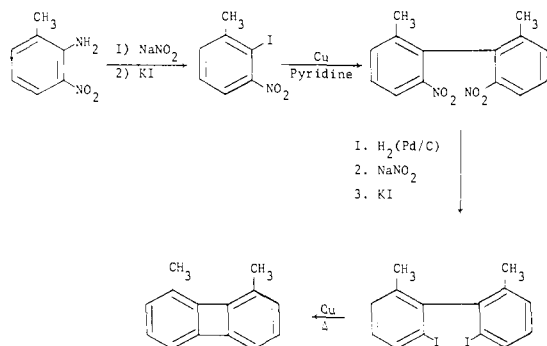

Results

Synthesis of 1,8-Dimethylbiphenylene. The usual synthesis of biphenylene derivatives via benzyne intermediates leads to

a mixture of 1,5-dimethyl- and 1,8-dimethylbiphenylenes.[3] Separation in high purity was difficult to achieve on a reasonable scale, although reported as "easy",[4] and we therefore chose to prepare 1,8-dimethylbiphenylene by an unambiguous route according to the classical method of Lothrop.[5] Scheme I shows the synthesis. The yield for the Ullmann reaction uti-

Scheme I

lized in the last step was particularly sensitive to the nature of the copper used as reagent, one sample resulting in an 80% yield of 1,8-dimethylbiphenylene while another sample of the same copper gave only traces of product.

Synthesis of Diradicals and Their Magnesium Complexes. The bisbromomethyl or the bisiodo derivatives of the dimethylarenes were prepared by free-radical bromination,[4] followed when appropriate by treatment with sodium iodide/acetone. Bispyridinium salts were prepared by heating with methyl isonicotinate in acetone. Diradicals were produced from the salts by reduction with sodium amalgam in acetonitrile, vacuum line techniques being necessary to exclude oxygen[6-8] (eq 2).

$$X^-Py^+CH_2ArCH_2Py^+X^- \xrightarrow[CH_3CN]{Na(Hg)} Py \cdot CH_2ArCH_2Py \cdot$$

(2)
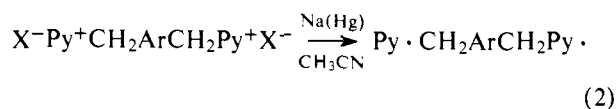
The magnesium complexes of the diradicals were generated by using magnesium metal as the reducing agent, intramolecular π-mer complexes being formed from both the 1,8-biphenylene and o-xylene precursors (eq 3).[7,9]

$$X^-Py^+CH_2ArCH_2Py^+X^- \xrightarrow[CH_3CN]{Mg} Ar(CH_2Py \cdot)_2MgX_2$$

(3)
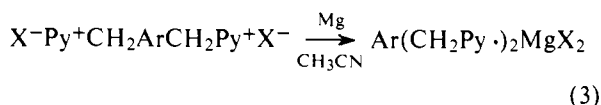
The only unusual precaution to be taken in the reductions is the exclusion of visible light, especially in the case of the 1,8-biphenylene derivative.

Properties of the Diradicals and Their Complexes. From our previous work on pyridinyl diradicals connected on the nitrogen through a chain of methylene groups,[7] we knew that intramolecular interaction (π-mer formation) was reflected in (a) the appearance of a visible charge-transfer band comparable in strength to the first strong ultraviolet absorption band of pyridinyl monoradicals and (b) a reduction of EPR signal intensity. The 1,8-biphenylenediyl diradical 1 had a light absorption very similar to that of a pyridinyl monoradical, in which are superimposed the well-known absorption bands of biphenylene (λ_{max} 620 nm (ϵ_{max} 116), 392 (8530), 362 (15 100), 345 (12 800), 305 (15 500)). The most significant feature of the spectrum is the high ratio of radical ultraviolet and visible absorption intensities, which are established firmly through titration (Figure 1).

In contrast, the magnesium iodide complex of the 1,8-biphenylenediyl diradical has a spectrum characteristic of diradical π-mer complexes, with a ratio of 3.9 between the near-ultraviolet and visible absorption intensities: λ_{max} 640 nm
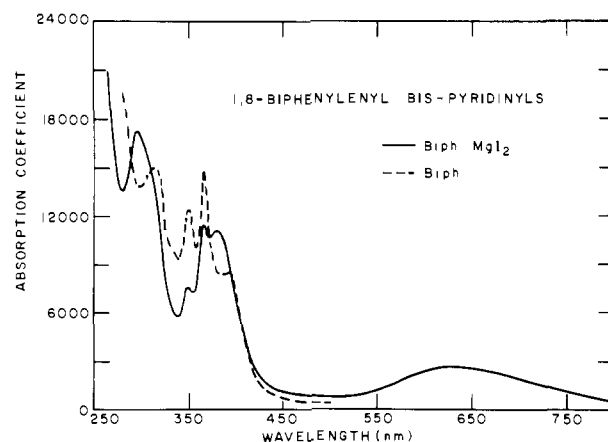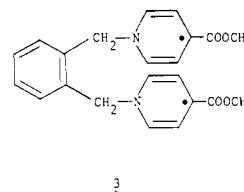
Figure 1. A comparison of the spectra of the biphenylenediyl bismethyl (4-carbomethoxypyridinyl) diradical (1:) and the corresponding magnesium iodide complex (1:MgI$_2$), both in CH$_3$CN solution.

(ϵ_{max} 3000), 380 (11 250), 366 (11 650), 348 (8000), 290 (17 450) (Figure 1).

Both the o-xylenyl pyridinyl diradical (3) and its magnesium

3

complex had an absorption spectrum in acetonitrile with a low ratio between the intensities of the near-ultraviolet and visible absorption bands. Diradical: λ_{max} 690 nm (ϵ_{max} 2200), 382 (2700). Diradical magnesium iodide complex:[7a] 605 (7900), 380 (16 200).

The o-xylenyl diradical could be stored at 0 °C for periods of more than 1 year. Although we did not have the opportunity to observe the 1,8-biphenylenediyl diradical 1 over a long time, the magnesium complex decomposed at an appreciable rate even at 0 °C, and was completely gone after a few days.

The EPR spectra of the 1,8-biphenylene diradical and its magnesium complex were very similar, both being exchange narrowed (width ca. 13 G) to the same extent, with very little structure apparent.

EPR measurements for the o-xylene diradical and its magnesium complex did not reveal any measurable spin.

Photolysis of the Diradicals. Irradiation of the diradicals in the visible (620 nm for the 1,8-biphenylene derivative, 690 nm for the o-xylene diradical) led to no apparent change.

Irradiation of the diradicals at 400 nm led to substantial loss of diradical, with a quantum yield of photodecomposition of 7×10^{-4} for the 1,8-biphenylene derivative and 6×10^{-3} for the o-xylene compound.

Irradiation in the visible absorption band of the diradical magnesium complexes led to a 10% increase in light absorption in the visible region without much change in spectrum shape; a greater increase (ca. 15%) in the near-ultraviolet and a substantial increase (ca. 33%) in the ultraviolet band unique to the complex at 280 nm could be observed for the o-xylene case. Similar changes apparently occurred for visible irradiation of the 1,8-biphenylene complex but were difficult to quantitate because of the extremely strong absorption of biphenylene. Visible irradiation of 3:MgBr$_2$ in CH$_3$CN led to substantial (25–50%) increases in intensity with no change in shape. However, 3:MgBr$_2$ was stable to irradiation at shorter wavelengths, except for further increases in intensity like those resulting from visible irradiation.
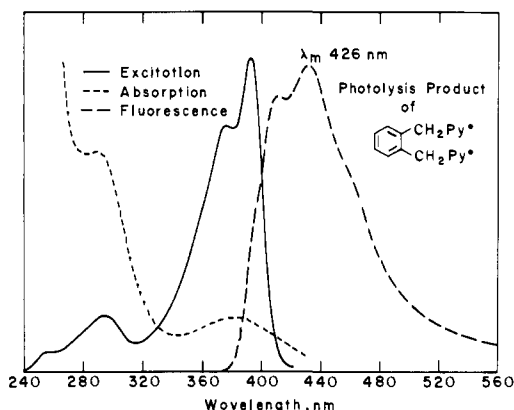
Figure 2. Absorption, corrected excitation, and corrected fluorescence spectra of solutions obtained after photolysis of the *o*-xylenyl bis(4-carbomethoxypyridinyl) diradical.

Irradiation of the magnesium complexes of the diradicals at 400 nm led to loss of the complexes, the quantum yields of photodecomposition (biphenylene derivative) being 5×10^{-4} and (*o*-xylene derivative) 3×10^{-3}.

Irradiation of either the biphenylene diradical or the biphenylene diradical magnesium complex produced methyl isonicotinate and 1,8-dimethylbiphenylene, identified by TLC and UV spectroscopy after chromatography. Irradiation of either the *o*-xylene diradical or its magnesium complex yielded methyl isonicotinate and a material with an absorption maximum at 376 nm. In the case of the complex, 0.9 mol of methyl isonicotinate formed per mol of starting complex and the 376-nm absorbing product was found to be fluorescent. Very little *o*-xylene was detected in the photolyses of *o*-xylene derivatives.

The fluorescent product has an emission maximum at 426 nm. The absorption spectrum of the final photolysate, the excitation for the fluorescence, and the fluorescence spectrum are shown in Figure 2. The product is tentatively identified as a mixture of an adduct of acetonitrile and an azaanthracene and an azaanthracene derivative (see below). There are strong peaks in the photolysate mass spectrum at *m/e* 239, 279, and
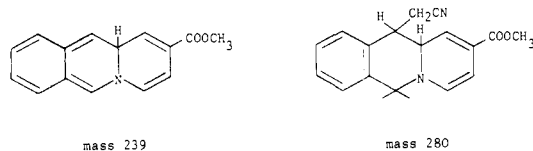
280, but insufficient material was available to completely characterize the product(s).

In contrast to the foregoing, neither the diradical magnesium bromide complex, **3**:MgBr$_2$ (**3** = 1,1′-trimethylenebis(4-carbomethoxypyridinyl)) nor the monoradical, 1-*tert*-butyl-4-carbomethoxypyridinyl, was changed by prolonged irradiation in the near-ultraviolet absorption band (380 nm for **3**:MgBr$_2$, 390 nm for the *tert*-butyl radical).

Discussion

The distance between the pyridinyl radical moieties in diradicals like **1** and **3** can be defined for an arrangement in which the plane of the pyridinyl radicals is perpendicular to the plane of the arene ring. Thus, in the *o*-xylene diradical, the distance is 2.9 Å, while in the 1,8-biphenylene diradical, the distance is 3.8 Å. A significant result of the present research is the finding that the *o*-xylene diradical forms an intramolecular π-mer, while the 1,8-biphenylene diradical does not. Given 3.3–3.4 Å as a typical distance for a π–π complex between two planar systems, the failure to form a π-mer shows how important the distance for close approach is.
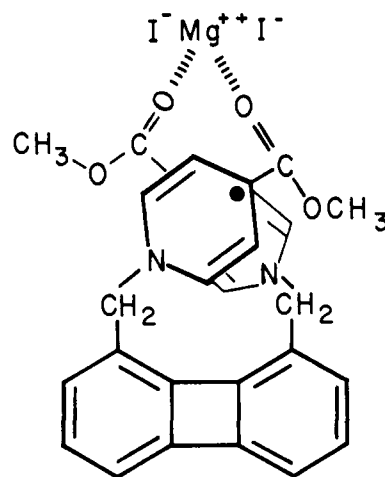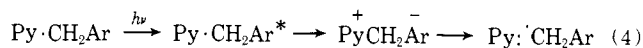

Figure 3. A representation of the magnesium iodide complex of the diradical derived from **1**:. The pyridinyl radical rings have been twisted 90° for visibility.

Nevertheless, the 1,8-biphenylene diradical does form a π-meric magnesium halide complex, suggesting the structure shown in Figure 3. The strain present in this structure (**1**: MgX$_2$) is reflected in its instability on storage, unusual for a simple magnesium complex. (We utilize the magnesium complex of 1,1′-trimethylenebis(4-carbomethoxypyridinyl) as a final purification for oxygen-free acetonitrile and normally store the solution at room temperature on the vacuum line.)

The simplest explanation for the photolysis is that excitation of the pyridinyl radical leads to the formation of an exciplex via electron transfer to the aryl ring, followed by dissociation of the excited state exciplex ion pair to a reactive free radical and a very stable molecule, methyl isonicotinate (eq 4). It is

$$\text{Py}\cdot\text{CH}_2\text{Ar} \xrightarrow{h\nu} \text{Py}\cdot\text{CH}_2\text{Ar}^* \longrightarrow \overset{+}{\text{Py}}\text{CH}_2\overset{-}{\text{Ar}} \longrightarrow \text{Py}: \text{CH}_2\text{Ar} \quad (4)$$

not excluded that direct excitation to the exciplex could occur, but such a process should be more important for monoradicals and diradicals in which π-mer formation does not preempt possible overlap between the arene ring and the pyridinyl ring.

Diradicals disappear on irradiation without sign of monoradical intermediates. Either the latter are much more sensitive to photolysis or the intermediate diradical (·CH$_2$ArCH$_2$Py·) yields a covalent cyclic product quite rapidly (e.g., **4**).

4
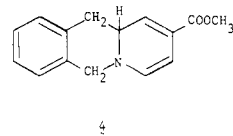
The effect of visible irradiation in producing a substantial change in the visible and ultraviolet absorption especially characteristic of the magnesium complex (and therefore presumed to be directly related to some interaction of the magnesium ion with the ester group in an excited state) is ascribed to some change in ligand binding around the magnesium. A rearrangement to the most highly absorbing complex apparently occurs (cf. Ikegami and co-workers on isomeric triplets of pyridinyl radical dimers[11,12]).

The interesting new radical photochemistry described by Ikegami and Watanabe[1] and ourselves appears worthy of further investigation into scope and mechanism.

Experimental Section

1,8-Dimethylbiphenylene. (General procedures are based on ref 13 and 14.) 2-Iodo-3-nitrotoluene, mp 65–66 °C from EtOH, was made from the corresponding amino compound via diazotization and po-

tassium iodide treatment in 80% yield. 2,2'-Dimethyl-6,6'-dinitrobiphenyl, mp 108-109 °C from EtOH, was prepared by refluxing the pure iodo compound (20 g, 0.075 mol) and Cu bronze (20 g, 0.33 g-atom) under N_2 for 24 h, cooling, extraction with benzene-ether, drying of extract, removal of solvent, and crystallization. Hydrogenation of 2.72 g (0.01 mol) over Pd/C (10%) in methanol (100 mL) gave 1.55 g (73%) of 2,2'-diamino-6,6'-dimethylbiphenyl, mp 135-136 °C from EtOH. This was converted to the corresponding diiodo derivative via diazotization and treatment with warm (50-60 °C) potassium iodide. Chromatography on alumina yielded 70% of pure material, mp 84-86 °C. The diiodo compound (6.3 g, 0.0145 mol) was melted in a small flask under N_2 and electrolytic copper (Fisher) (6.0 g, 0.092 g-atom) was added in small portions. The temperature was raised to 220-230 °C and the mixture stirred for 24 h. After cooling, the solid was extracted three times with ether, the solvent evaporated, and the residue chromatographed on neutral alumina. Elution with petroleum ether (bp 60-80 °C) gave 1.94 g (75%) of 1,8-dimethylbiphenylene: mp 80-81 °C (reported[3] 74-78 °C); NMR (CDCl$_3$) δ 2.13 (s, 6 H, CH$_3$), 6.5 (m, 6 H, aromatic H).

1,8-Biphenylenediyl Bismethyl(4-carbomethoxypyridinium) Bromide and Iodide. The 1,8-bis(bromomethyl)biphenylene was made according to Wilcox et al.[4] and converted to the bis(iodomethyl)biphenylene with sodium iodide in acetone. The somewhat photosensitive diiodo derivative was reacted with methyl isonicotinate in hot acetone (14 h reflux) to yield red crystals of the bispyridinium iodide, mp 192 °C dec. The bispyridinium bromide was prepared in a similar fashion, mp 170 °C dec. Both salts had the expected equivalent weight: iodide, calcd 353, found 355.4; bromide, calcd 306, found 305.4. NMR (Me$_2$SO): δ 4.01 (s, 6 H, COOCH$_3$), 5.93 (s, 4 H, CH$_2$N$^+$), 6.4-6.9 (m, 6 H, aromatic H), 8.50 (d, 4 H, 3,5-H$_2$(Py)), 9.31 (d, 4 H, 2,6-H$_2$(py)). The pyridinium salts derived from o-xylene were prepared from the dibromo compound (Fluka) and methyl isonicotinate. Dibromide: equiv wt calcd 269, found 267; mp 145 °C dec; NMR (Me$_2$SO) δ 4.1 (s, 6 H, COOCH$_3$), 6.35 (s, 4 H, CH$_2$N$^+$), 7.36 (m, 4 H, aromatic H), 8.55 (d, 4 H, 3,5-H$_2$(py)), 9.40 (d, 4 H, 2,6-H$_2$(py)).

The following preparations were carried out in red light in apparatus covered with aluminum foil.

Diradicals. The bispyridinium salt is placed together with 3% sodium amalgam (20-fold excess) in a flask which is then sealed.[8] Acetonitrile is distilled in from a reservoir on the vacuum line, and, after the solvent is carefully melted (ca. 20 mL/g sodium amalgam), the whole is stirred at about 0 °C until the color change appears to be complete (30-60 min). The solution is usually filtered and extracted with benzene, the benzene evaporated, and the solid extracted with isopentane and filtered. Isopentane is removed and acetonitrile distilled in to yield a solution of the diradical. The solution is divided into portions and stored at 0 °C in sealed tubes bearing break-seals.

Diradical Magnesium Halide Complexes. The bispyridinium salt is stirred together with magnesium turnings (20-fold excess) in acetonitrile at temperatures near 0 °C until the color change is complete (30-60 min)[9]. The solution is filtered and utilized by dividing among tubes bearing break-seals.

Photolysis Procedure. Monochromatic light (20-nm slit width) from the 150-W xenon source of an MPF-4 spectrofluorimeter for which the light flux had been measured by actinometry[15] was utilized to irradiate the diradical or diradical magnesium complex solutions for specified periods of time, first at 600 nm and then at 380-400 nm. The changes in the solution were followed by ultraviolet and visible spectrophotometry using a Cary Model 17 spectrophotometer. After the radical absorptions had disappeared, the cells were opened, shaken with air, and reexamined to see if any air-sensitive compounds had been present in the solution. The solutions were also analyzed by chromatography (TLC, GLC, Hewlett-Packard HP5830A and a 10% SE-30 column).

References and Notes

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