Photolysis of Chloride Precursors as a Method to Prepare and Characterize the Triplet State of Fluorenyl-substituted m-Xylylene Diradicals

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Abstract: Fluorenyl substituted m-xylylene triplet diradicals are conveniently generated from the corresponding dichloride precursors upon photolysis at <100 K in 2-MeTHF glass. Under similar conditions tert-butyl substituted Schlenk type m-xylylene could not be generated from the dichloride precursor 6. Compound 6, however could be dehalogenated with zinc dust in both toluene and 2-MeTHF to produce the triplet diradical. © 1997 Elsevier Science Ltd. All rights reserved.

m-Xylylene has been the focus of studies of molecular magnetism because its triplet state is more stable than its singlet state[1] Further, the presence of an aromatic ring could, in principle, provide more thermodynamic stability than aliphatic triplet states. Finally, it appears to be ideal as a ferromagnetic coupling unit between high spin fragments because bond formation between the units cannot be achieved through the m-xylene system.[2]

m-Xylylene itself has been generated by photolysis of various precursors and gives a triplet esr signal which reveals modest interaction between the unpaired electrons ($|D|/hc = 0.011$ cm^{-1}).[3] The photoelectron (PE) spectrum of the m-xylylene radical anion reveals a 9.6 kcal/mol singlet-triplet gap[4] which is consistent with the theoretical estimate for planar species,[5] and the PE spectrum does not suggest large geometry changes between the radical ion, the singlet, and the triplet.
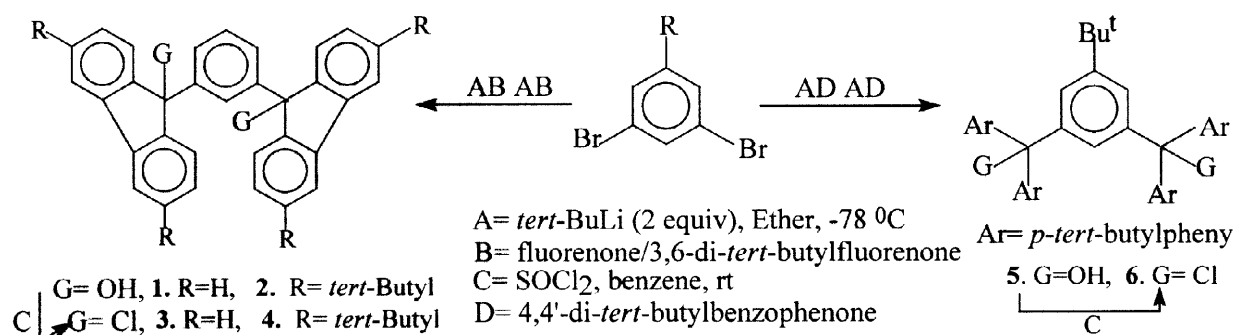
m-Xylylene itself, however, is very unstable with respect to dimerization and reaction with oxygen so substituted derivatives have been studied. The most famous of these is Schlenk's hydrocarbon, tetraphenyl-m-xylylene, which can be generated from the corresponding chloride by treatment with silver or zinc metal.[6] It too is unstable upon warming and to oxygen. In order to prevent radical coupling, Rajca prepared Schlenk-type triplets with tert-butyl substituents on the para positions of the rings attached to the central m-xylene unit.[7] By reducing the corresponding bis methyl ethers and oxidizing the resulting dianions he could not only determine the zero-field splitting parameters, but could characterize the extent of interaction of the electrons as a function of geometry. Larger D values result with larger substituents on the central ring. Apparently the substituents force the other phenyls to twist out of conjugation decreasing the delocalization of each electron onto the phenyl groups attached so that greater electron- electron interaction occurs within the central ring.

Finally, no introduction to this subject should ignore the work of Veciana *et. al.*[8] who not only prepared perchloro Schlenk's hydrocarbon, but chromatographically separated the *meso* and C_2 diastereomers because they are stable in oxygen, and determined the zero field splitting parameters of each.

We report here our efforts to prepare and characterize the triplet state of fluorenyl substituted *m*-xylylenes by photolysis of the dichlorides in the hope that this substitution might provide more stable species for elaboration in the form of higher spin systems.

Because photolysis of alpha, alpha'-dichloro-*m*-xylene provided the parent *m*-xylylene triplet, it seemed appropriate to synthesize dichloroprecursors by a route not unlike that utilized by Rajca.[7a] *m*-Dibromobenzene was lithiated and added to fluorenone twice or to 3,6-di-*tert*-butyl fluorenone twice to give the corresponding diols which were converted to the chlorides by reaction with thionyl choride (Scheme 1).[9] The precursors to the parent diradical and that to the *tert*-butyl- substituted diradical, **3** and **4**, respectively,

Scheme I

A= *tert*-BuLi (2 equiv), Ether, -78 °C
B= fluorenone/3,6-di-*tert*-butylfluorenone
C= SOCl₂, benzene, rt
D= 4,4'-di-*tert*-butylbenzophenone

G= OH, **1.** R=H, **2.** R= *tert*-Butyl
G= Cl, **3.** R=H, **4.** R= *tert*-Butyl

Ar= *p*-*tert*-butylpheny
5. G=OH, **6.** G= Cl

were photolyzed directly in an esr cavity in 2-methyltetrahydrofuran (MTHF) glass at temperatures at or below 100 K using pyrex filtered radiation from a xenon-mercury arc (at 100 K monoradical signal at the center dominates the spectrum). The precursors absorb weakly above 300 nm so irradiation required 10-20 minutes before a reasonable esr spectrum appeared. The spectrum from **4** is given in fig 1a. Further, a $\Delta m_s = 2$ transition (fig 1b) was observed giving further evidence that this is the spectrum of a triplet state. The D and E values are: $|D|/hv=0.0061$ cm^{-1} and $|E|/hv <0.00037$ cm^{-1}. The triplet esr derived from **3** was similar to that from **4** except that the two outer lines were not well separated from the inner lines. The $\Delta m_s = 2$ transition was also observed as well from photolysis of **3**. This spectrum could not be generated by photolysis in ethanol solution at or below 100 K; instead the spectrum of fig 1c was formed. However, use of 2,2,2-trideuterioethanol gave the spectrum of fig 1d indicating that the spectrum is primarily that derived from solvent. The triplet spectrum could not be generated by zinc dehalogenation in toluene solution at 0 °C (15 min) followed by usual decantation and freezing (77 K), a reaction that provided triplet esr spectra of similarly substituted Schlenk hydrocarbons.[6] Upon treatment with zinc, **4** gave a red color suggesting the possibility of overreduction to give a fluorenyl anion.

The precursor to the *p-tert*-butyl substituted Schlenk hydrocarbon with an additional *tert*-butyl group at the *meta* position on the central ring, **6**, was prepared (Scheme 1).[9] Treatment of **6** with zinc dust in either MTHF or in toluene at 0 °C as described above gave text book like triplet esr spectra at 100 K consisting of six lines in the $\Delta m_s = 1$ with identical zero-field splitting parameters: $|D|/hv=0.007$ cm^{-1} and $|E|/hv = 0.0007$ cm^{-1}, fig 2. However, in our hands **6** could not be photolyzed to provide the triplet spectrum.[10] It is also true that the uv spectrum of **6** showed less absorbance above 300 nm than the precursors **3** and **4**; however photolysis of these samples with 250 – 260 nm light also gave the same result as it was with >300 nm light.
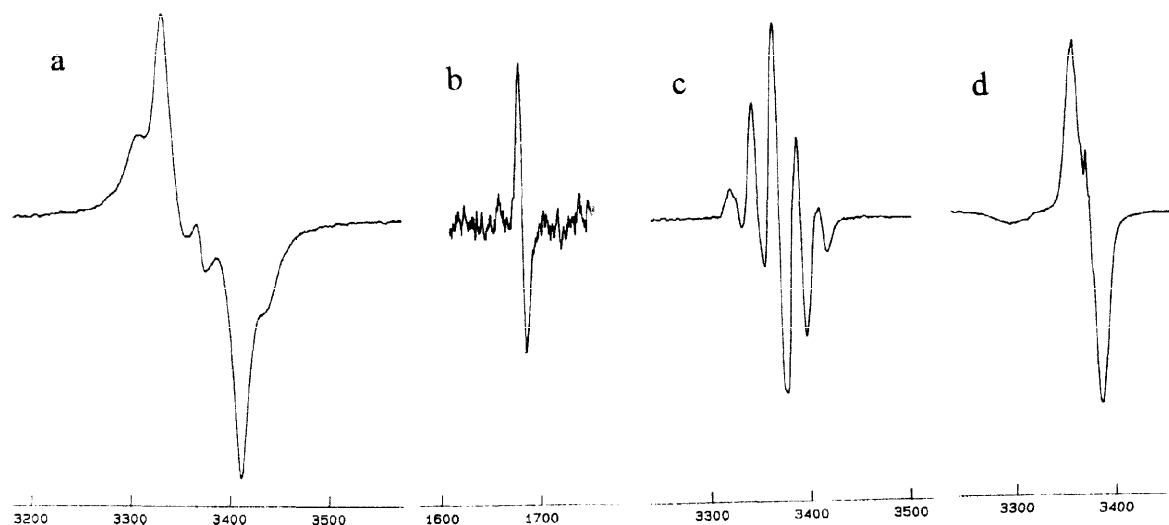
Fig. 1. ESR spectra from the photolysis of **4** in the esr cavity: (a) $\Delta m_s = 1$ transition in MTHF at 50 K (b) $\Delta m_s = 2$ transition in MTHF at 50 K; $\Delta m_s = 1$ transition at 99 K: (c) in CH_3CH_2OH (d) in CD_3CH_2OH.

While extensive studies of the stabilities of Schlenk-type and fluorenyl substituted *m*-xylylenes were not conducted, the triplet spectrum generated by zinc dehalogenation of **6** could be recovered by cooling a sample which had previously been warmed to room temperature; however, the triplet spectrum from photolysis of **3** or **4** could not be regenerated once the sample was warmed to 140-145 K; only radical impurity peak could be observed.

The dichloro precursors to Schlenk type and bis fluorenyl-substituted *m*- xylylenes provide an interesting contrast in behavior. The Schlenk precursors can be reduced with zinc dust to produce the triplet diradical, but they cannot be photolyzed to give these species. On the other hand, the fluorenyl substituted precursors can be photolyzed in order to give the corresponding triplet species, but treatment with zinc probably results in over reduction as might be expected for fluorenyl species. It is not clear why the Schlenk species cannot be photolyzed to

Fig. 2. ESR spectrum from **6** in MTHF at 100 K.

give the triplet species.

Despite the fact that fluorenyl triplet species can be produced by photolysis of bischloride precursors, note must be taken of the fact that this occurs only in MTHF solvent. Ethanol solvent, which has been used to generate the parent m-xylylene triplet,[3] gave a spectrum which appears to be that from the solvent since deuterated solvent provided a different spectrum. Nonetheless, the ability to photolyze the chlorides provides an important route to these diradicals.

Comparison of the D values of the fluorenyl triplet species generated here to those of the Schlenk-type diradical studied by Rajca that have no substituent on the central ring($|D/hc|=0.0066$ cm^{-1})[7] and to the Schlenk diradical itself ($|D/hc|=0.0079$ cm^{-1}) reveals smaller values suggesting greater delocalization in the fluorenyl case. This may be the result of the planarity of these substituents relative to the phenyl substituents which are probably twisted out of plane in propeller arrangements.

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9. All compounds were characterized by NMR (^{1}H and ^{13}C) and HRMS.

10. Photolysis of **6** in 2-MeTHF at or below 100 K gave a different esr spectrum consisting of six lines indicative of hyperfine interactions of a monoradical and also having narrower width (117 G as opposed to 146 G). No half- field transition could be observed under photolysis condition. We are currently studying the origin of this spectrum.