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Room Temperature Observation of *p*-Xylylenes by ^{1}H NMR and Evidence for Diradical Intermediates in Their Oligomerization

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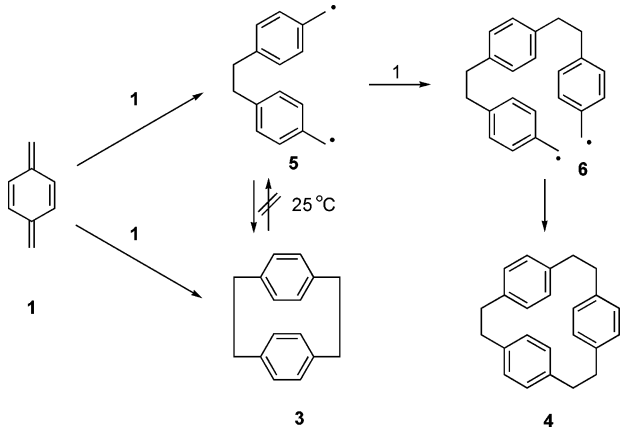
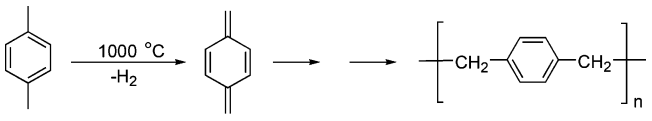
Received August 3, 2005



p-Quinodimethanes (*p*-QDMs) are reactive molecules that have been invoked as transient intermediates in a number of reactions. Dilute solutions of benzene-based *p*-QDMs, *p*-xylylene (**1**), α-methyl-*p*-xylylene (**10**), and 2,5-dimethyl-*p*-xylylene (**11**) can be prepared by fluoride-induced elimination of trimethylsilyl acetate from the appropriate precursor. It has been found that these solutions are stable enough to allow these reactive *p*-QDMs to be observed by ^{1}H NMR spectroscopy at room temperature. For the first time, the ^{13}C NMR spectrum of *p*-QDM **1** was observed. After several hours at room temperature, these *p*-QDMs form dimers, trimers, and insoluble oligomers. Formation of trimers provides evidence that *p*-QDMs **1**, **10**, and **11** dimerize by a stepwise mechanism involving dimeric diradicals as intermediates.

Introduction

p-Quinodimethanes (*p*-QDMs), a class of compounds also known as Chichibabin hydrocarbons,[1] are reactive molecules that have been invoked as transient intermediates in a number of reactions. *p*-Xylylene (**1**), the parent benzene-based *p*-QDM, was first proposed by Szwarc as an intermediate in the pyrolysis of *p*-xylene that yielded poly-*p*-xylylene (**2**),[2] a commercially important polymer.[3]



In addition to poly-*p*-xylylene (**2**), [2.2]paracyclophane, dimer **3**,[4−6] and [2.2.2]paracyclophane, trimer **4**,[5,6] were also isolated from the pyrolysis of *p*-xylene.

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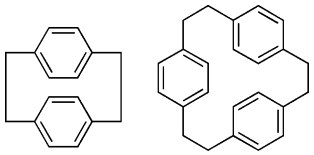
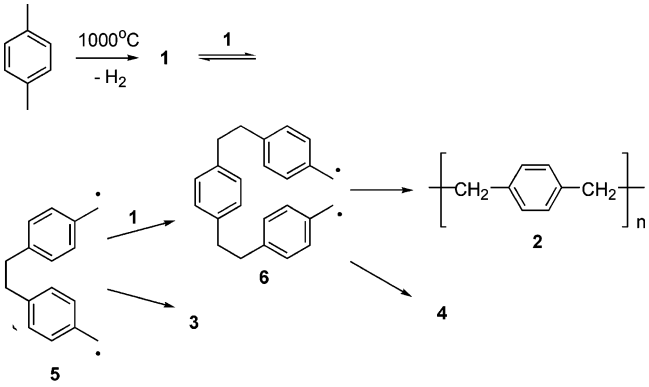
(1) Errede, L. A.; Szwarc, M. *Q. Rev., Chem. Soc.* **1958**, *12*, 301.
(2) (a) Szwarc, M. *Discuss. Faraday Soc.* **1947**, *2*, 46. (b) Szwarc, M. *J. Chem. Phys.* **1948**, *16*, 128. (c) Szwarc, M. *J. Polym. Sci.* **1951**, *6*, 319.
(3) (a) Gorham, W. F. In *Encyclopedia of Polymer Science and Technology*; Gaylord, N. G., Bikales, N., Eds.; Wiley-Interscience: New York, 1971; Vol. 15, pp 98−113. (b) Niegish, W. D. In *Encyclopedia of Polymer Science and Technology*; Gaylord, N. G., Bikales, N., Eds.; Wiley-Interscience: New York, 1971; Vol. 15, pp 113−124. (c) Lee, S. M. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed.; Wiley: New York, 1983; Vol. 24, pp 744−771. (d) Beach W. F.; Lee, C.; Bassett, D. R.; Austin, T. M.; Olson, R. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley: New York, 1989; Vol. 17, p 990.
(4) (a) Brown, C. J.; Farthing, A. C. *Nature* **1949**, *164*, 915. (b) Farthing, A. C. *J. Chem. Soc.* **1953**, 3261.
(5) Auspos, L. A.; Burnam, C. W.; Hall, L. A. R.; Hubbard, J. K.; Kirk, Wm., Jr.; Schaefgen, J. R.; Speck, S. B. *J. Polym. Sci.* **1955**, *15*, 19.
(6) Schaefgen, J. R. *J. Polym. Sci.* **1955**, *15*, 203.

10.1021/jo0516279 CCC: $33.50
Published on Web 02/03/2006



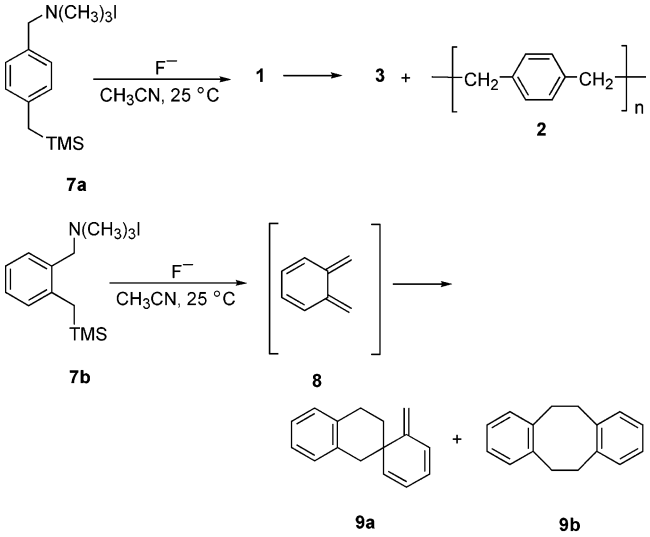
3 **4**

Errede and co-workers were able to prepare solutions of *p*-QDM **1** at −78 °C by dissolving the *p*-xylene pyrolysate in a cold, well-stirred solvent,[1,7] and they observed that dimer **3**, trimer **4**, and a tetramer were produced if dilute solutions of *p*-QDM **1** were warmed from −78 °C to room temperature.[8] Gorham found that heating dimer **3** in the gas phase formed what he suspected to be *p*-QDM **1**, and when this vapor was allowed to condense on a cool surface, it formed a polymer.[9] It was proposed that dimer **3**, trimer **4**, and the polymer of *p*-QDM **1** (**2**) were formed via an initially formed dimeric diradical, **5**:[1,6,8,10] two molecules of **1** would combine to form diradical **5**, which could close to form dimer **3** or react with another molecule of **1** to form trimeric diradical **6**, which could close to form trimer **4** or go on to polymer **2**.

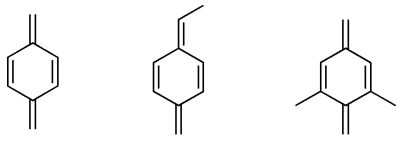


Over the past several years our group has studied the mechanism of oligomerization of other *o*- and *p*-QDMs, including ones based on furan or on thiophene. Studies of the dimerization[11] of furan-based *o*-QDMs, including ones substituted with deuterium atoms[12] and *tert*-butyl groups,[13] support a stepwise mechanism involving diradicals at the 2-methylene groups. α-Methyl furan-based *o*-QDM[14] and α-methyl thiophene-based *p*-QDM[15] were both found to form acyclic dimers. Their formation is reasonably explained by intramolecular disproportionation of dimeric diradicals. Upon standing, solutions of furan-based *p*-QDM and thiophene-based *p*-QDM form trimers, and this provides firm evidence for the existence of dimeric diradicals as intermediates.[15] Further evidence of dimeric diradicals is the formation of a mixed trimer when a solution of the furan-based and the thiophene-based *p*-QDMs was allowed to react.[15]

Ito et al. used a fluoride-induced 1,6-elimination of trimethylsilyl iodide and trimethylamine from [*p*-((trimethylsilyl)-methyl)benzyl]trimethylammonium iodide (**7a**) to yield dimer **3** and polymer **2**.[16] *o*-Xylylene (**8**) also can be generated by a fluoride-induced 1,4-elimination of trimethylsilyl iodide and trimethylamine from [*o*-((trimethylsilyl)methyl)benzyl]trimethylammonium iodide (**7b**).[17,18] *o*-QDM **8** rapidly dimerizes to [4 + 2] dimer **9a** and [4 + 4] dimer **9b** in a ratio of 11:1, and these dimers are thought to arise from a diradical intermediate.[17−19]



To more fully characterize benzene-based *p*-QDMs and to study their oligomerization in some detail, we developed a procedure that allows the preparation of dilute solutions of **1**, **10**, and **11** at room temperature. Under these conditions, these reactive molecules are long-lived enough that their ^{1}H NMR spectra can be observed and their oligomerization can be followed by ^{1}H NMR. The results of this study are presented in this article.



1 **10** **11**

Results

***p*-Xylylene (1) Oligomerization Studies.** *p*-Xylylene (**1**) was prepared as a dilute solution in CD_3CN (ca. 10^{-3} M) by the fluoride-induced elimination[17] of trimethylsilyl acetate from [*p*-((trimethylsilyl)methyl)phenyl]methyl acetate (**12**).

(7) (a) Errede, L. A.; Landrum, B. F. *J. Am. Chem. Soc.* **1957**, *79*, 4952. (b) Errede, L. A.; Hoyt, J. M. *J. Am. Chem. Soc.* **1960**, *82*, 436.

(8) (a) Errede, L. A.; Cassidy, J. P. *J. Am. Chem. Soc.* **1960**, *82*, 3653. (b) Errede, L. A.; Gregorian, R. S.; Hoyt, J. M. *J. Am. Chem. Soc.* **1960**, *82*, 5218.

(9) Gorham, W. F. *J. Polym. Sci., Part A: Polym. Chem.* **1966**, *4*, 3027.

(10) Reich, H. J.; Cram, D. J. *J. Am. Chem. Soc.* **1969**, *91*, 3517.

(11) Trahanovsky, W. S.; Cassady, T. J.; Woods, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 6691.

(12) Chou, C.-H.; Trahanovsky, W. S. *J. Am. Chem. Soc.* **1986**, *108*, 4138.

(13) Trahanovsky, W. S.; Huang, Y.-c. J.; Leung, M.-k. *J. Org. Chem.* **1994**, *59*, 2594.

(14) (a) Leung, M.-k.; Trahanovsky, W. S. *J. Am. Chem. Soc.* **1995**, *117*, 841. (b) Leung, M.-k. Ph.D. Dissertation, Iowa State University, Ames, IA, 1991.

(15) (a) Trahanovsky, W. S.; Miller, D. L.; Wang, L. *J. Org. Chem.* **1997**, *62*, 8980. (b) Wang, L. M.S. Thesis, Iowa State University, Ames, IA, 1994.

(16) Ito, Y.; Miyata, S.; Nakatsuka, M.; Saegusa, T. *J. Org. Chem.* **1981**, *46*, 1043.

(17) (a) Trahanovsky, W. S.; Macias, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 6820. (b) Trahanovsky, W. S.; Chou, C.-H.; Fischer, D. R.; Gerstein, B. C. *J. Am. Chem. Soc.* **1988**, *110*, 6579.

(18) Segura, J. L.; Martín, N. *Chem. Rev.* **1999**, *99*, 3199.

(19) Errede, L. A. *J. Am. Chem. Soc.* **1961**, *83*, 949.

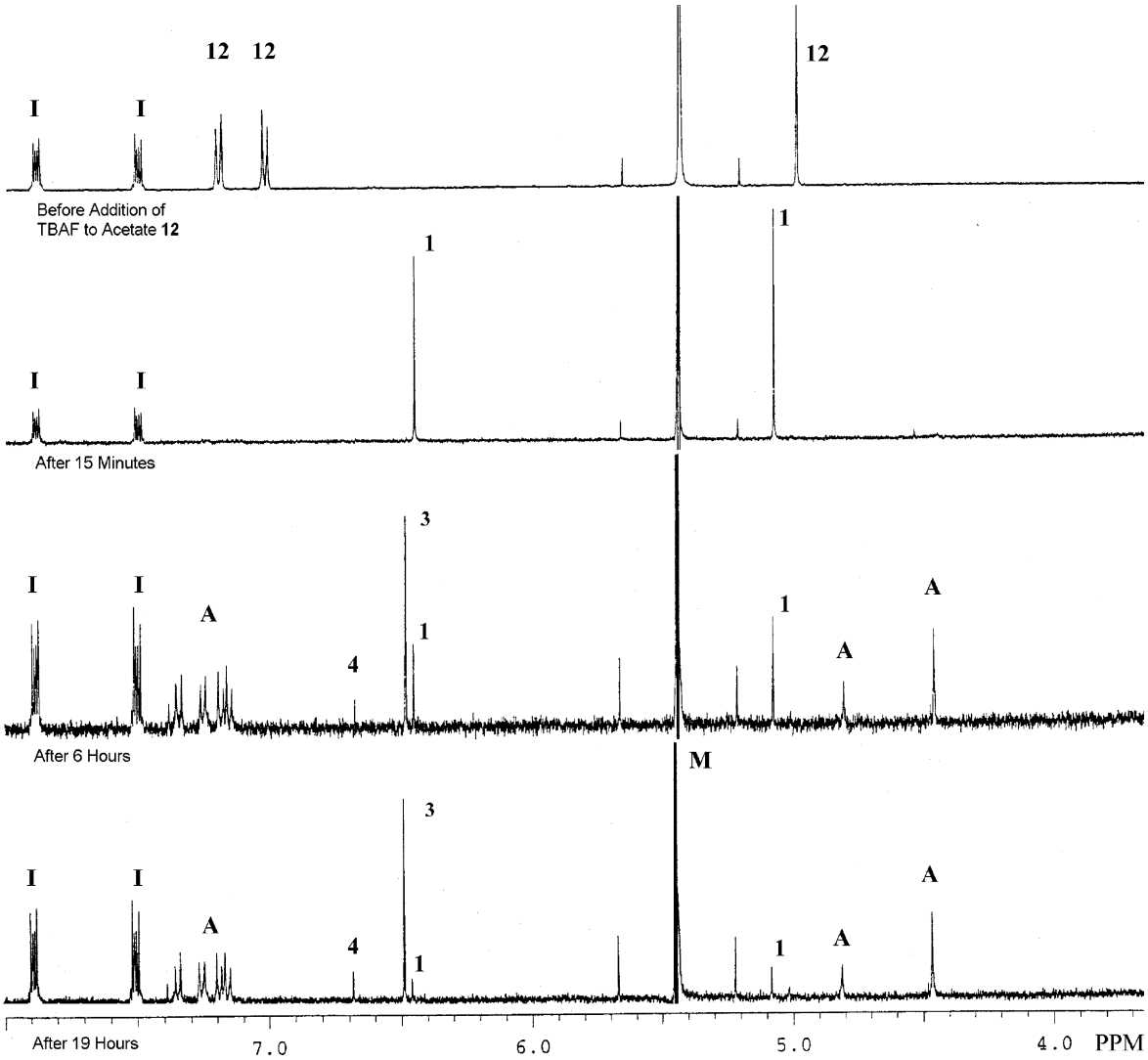
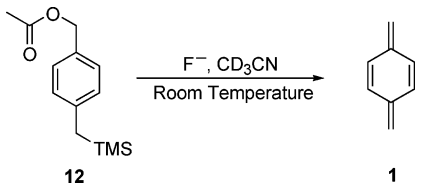


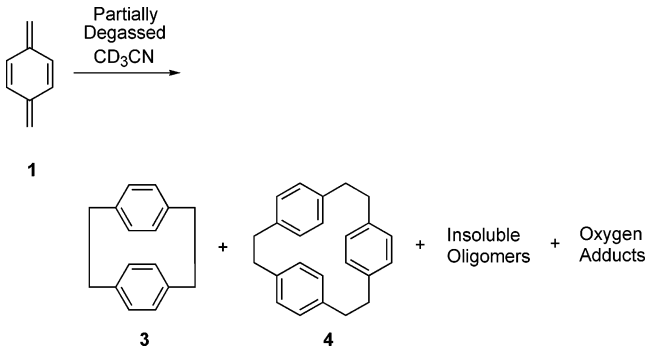
FIGURE 1. ^{1}H NMR spectrum (400 MHz, CD_3CN) of reaction progress of *p*-xylylene (**1**) in partially degassed CD_3CN. Upfield signals are masked by the TBAF. (**3**, **4**, and **12** are compound numbers given in the text. **I**: internal standard, naphthalene, **M**: methylene chloride, **A**: oxygen adducts.)



Naphthalene was used as an internal standard to determine the yield of products. Due to the stability of this dilute solution, we were able to obtain the ^{1}H NMR spectrum (Figure 1) at room temperature,[20] whereas the previously reported spectra were obtained at about −80 °C.[21] By studying the ^{1}H NMR spectrum over time, we were able to estimate the first half-life for the disappearance of *p*-QDM **1** to be approximately 4 h. With a more concentrated solution of *p*-QDM **1** ($\sim 10^{-2}$ M) and reduced temperature (−40 °C), a ^{13}C NMR spectrum (Figure 2) of *p*-QDM **1** (δ 140.3 [C], 129.9 [CH], and 115.5 [CH_2]) was obtained. The assignments of these peaks are based on their decrease of intensity with time and HMQC spectrum (see Figures S-17 to S-19 in the Supporting Information).

(20) Compound **1** was observed by UV spectroscopy at room temperature. See: Kaupp, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 442.

The product mixture that forms from the solution of *p*-QDM **1** varies based on the care taken to exclude oxygen (Table 1). Under standard freeze−pump−thaw degassing conditions, dimer **3** and trimer **4** were observed by ^{1}H NMR spectroscopy and confirmed after extraction by mass spectroscopy. Insoluble material formed in the reaction tube and is believed to be higher oligomers. The ^{1}H NMR spectrum showed signals near δ 4.5 that appear to be oxygen adducts which were compared to the ^{1}H NMR spectrum of the oxygen adducts prepared in an oxygenated solvent.



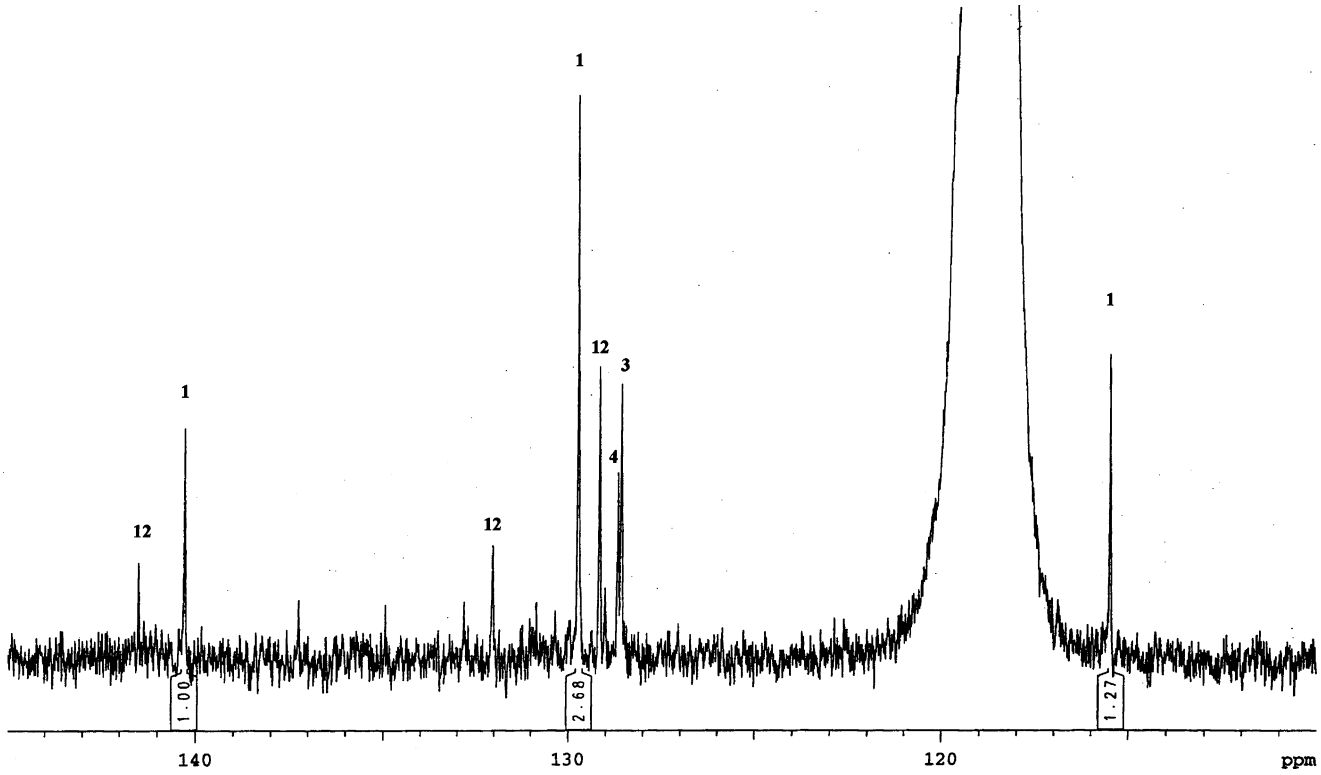


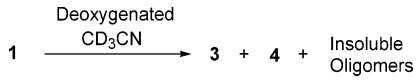
FIGURE 2. ^{13}C NMR spectrum (100 MHz, CD_3CN) of *p*-xylylene (**1**) with $Cr(acac)_3$. (**3**, **4**, and **12** are compound numbers given in the text, and the large signal is solvent.)

TABLE 1. Yields of [2.2]Paracyclophane (3) and [2.2.2]Paracyclophane (4) from *p*-Xylylene (1)

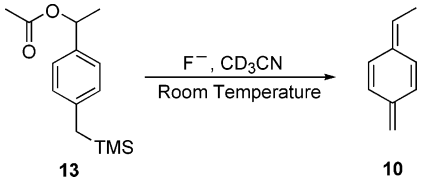
μmol **1**	μmol **3**	% yield	μmol **4**	% yield	oxygen adducts
1.1[a]	0.077	14	0.00015	0.04	present
1.5[a]	0.11	15	0.025	5	present
1.3[b]	0.23	35	0.031	7	trace

[a] Results of *p*-xylylene **1** in partially degassed CD_3CN. [b] Result of *p*-xylylene **1** in deoxygenated CD_3CN.

When *p*-QDM **1** was prepared in a solution that was rigorously freed of oxygen, its product mixture contained dimer **3**, trimer **4**, and what appear to be insoluble oligomers of *p*-QDM **1** (Table 1). The ^{1}H NMR spectrum of this mixture did not contain signals at δ 4.5 (see Figure S-26 in the Supporting Information).

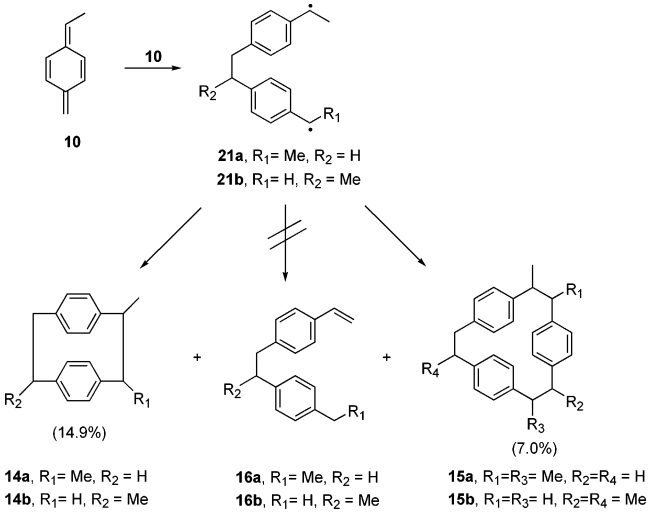


α-Methyl-*p*-xylylene (10) Oligomerization Studies. In an attempt to obtain additional evidence for dimeric diradical intermediates, the methyl derivative, α-methyl-*p*-xylylene (**10**) was studied. A dilute solution (10^{-3} M) of *p*-QDM **10** was prepared by a similar fluoride-induced elimination from 1-[*p*-((trimethylsilyl)methyl)phenyl]ethyl acetate (**13**).



13 **10**

SCHEME 1



The ^{1}H NMR spectrum of *p*-QDM **10** was also obtained at room temperature. As with the parent system, the presence of oxygen in the sample has a notable effect. When solutions of *p*-QDM **10** are prepared in the partially degassed CD_3CN and analyzed by ^{1}H NMR spectroscopy, oxygen-containing products are observed with trace amounts of cyclic dimers **14** and cyclic trimers **15**. When samples of *p*-QDM **10** were prepared with more care to exclude oxygen, the products are cyclic dimers **14** (14.9% yield), cyclic trimers **15** (7.0% yield), trace amounts of oxygen adducts, and insoluble oligomers (Scheme 1). Several of the signals in the ^{1}H NMR spectrum (Figure 3) of the product

(21) Williams, D. J.; Pearson, J. M.; Levy, M. *J. Am. Chem. Soc.* **1970**, *92*, 1436.

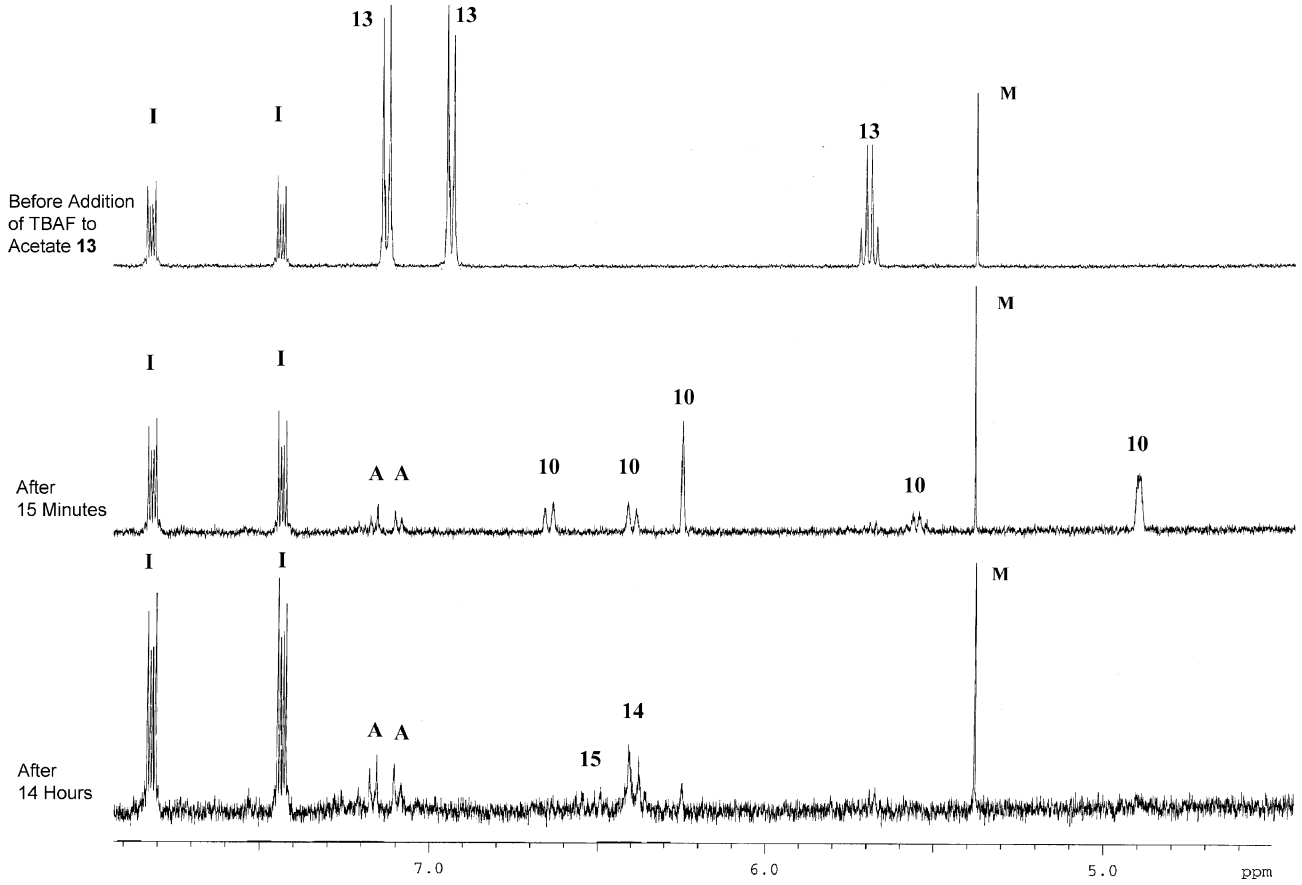
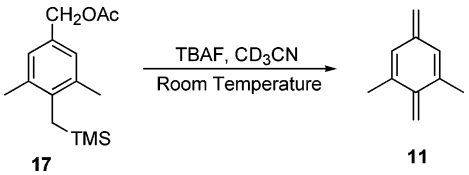


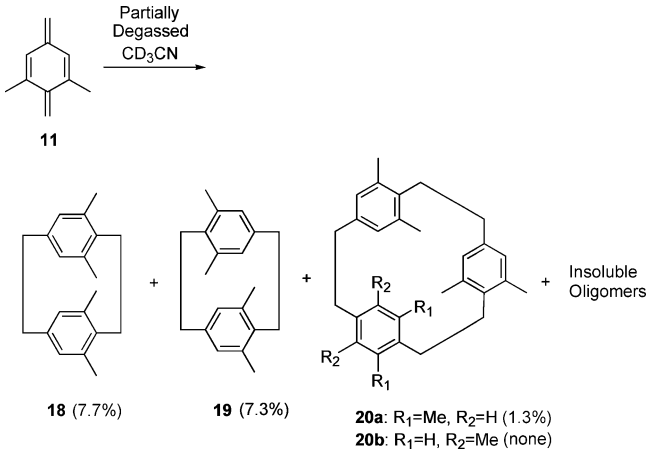
FIGURE 3. ^{1}H NMR spectrum (400 MHz, CD_3CN) of reaction progress of α-methyl-*p*-xylylene (**10**) in partially degassed CD_3CN. (**13** is a compound number given in the text. **A**: oxygen adducts, **I**: internal standard, naphthalene, **M**: methylene chloride.)

mixture can be assigned to dimers and trimers based on the similarity of these signals to those of the dimer and trimer of *p*-QDM **1**. Because the two regioisomeric dimers **14a** and **14b** each have two diastereoisomers and the two regioisomeric trimers **15a** and **15b** have four and two diastereoisomers, respectively, it is difficult to interpret if the reaction was regioselective. The reaction was repeated on a larger scale in CH_3CN. The product mixture was extracted with pentane, and the pentane extract was analyzed by GC/MS and by ^{1}H NMR spectroscopy. Three isomers of dimers **14** and four isomers of trimers **15** were identified in the extract by GC/MS (yields of each are given in the Experimental Section). We did not observe any evidence of acyclic dimers **16** by GC/MS or ^{1}H NMR spectroscopy (Figure 4).

2,6-Dimethyl-*p*-xylylene (11) Oligomerization Studies. A fluoride-induced elimination of trimethylsilyl acetate from [3,5-dimethyl-4-((trimethylsilyl)methyl)phenyl]methyl acetate (**17**) yielded 2,6-dimethyl-*p*-xylylene (**11**).



The ^{1}H NMR spectrum of *p*-QDM **8** was obtained in partially degassed CD_3CN at room temperature (Figure 5). Upon standing, a small amount of insoluble material (which we believe is higher oligomers) formed. Nearly equal amounts of head-to-head dimer **18** (7.7% yield) and head-to-tail dimer **19** (7.3% yield) along with a trace (1.3% yield) of trimer **20a** were identified by ^{1}H NMR spectroscopy (see Figure S-61 in the Supporting Information for expansion of **20a** signals) and GC/MS. The trimer was identified as the unsymmetrical trimer **20a** rather than the symmetrical trimer **20b** by its ^{1}H NMR spectrum, which shows three signals for aromatic hydrogens rather than just one, as expected for trimer **20b**. Only one trimer was found in the GC/MS of the product mixture.



***p*-Xylylene (1) and 2,6-Dimethyl-*p*-xylylene (11) Co-Oligomerization Studies.** A mixture of *p*-QDMs **1** and **11** was prepared by fluoride-induced eliminations from their respective

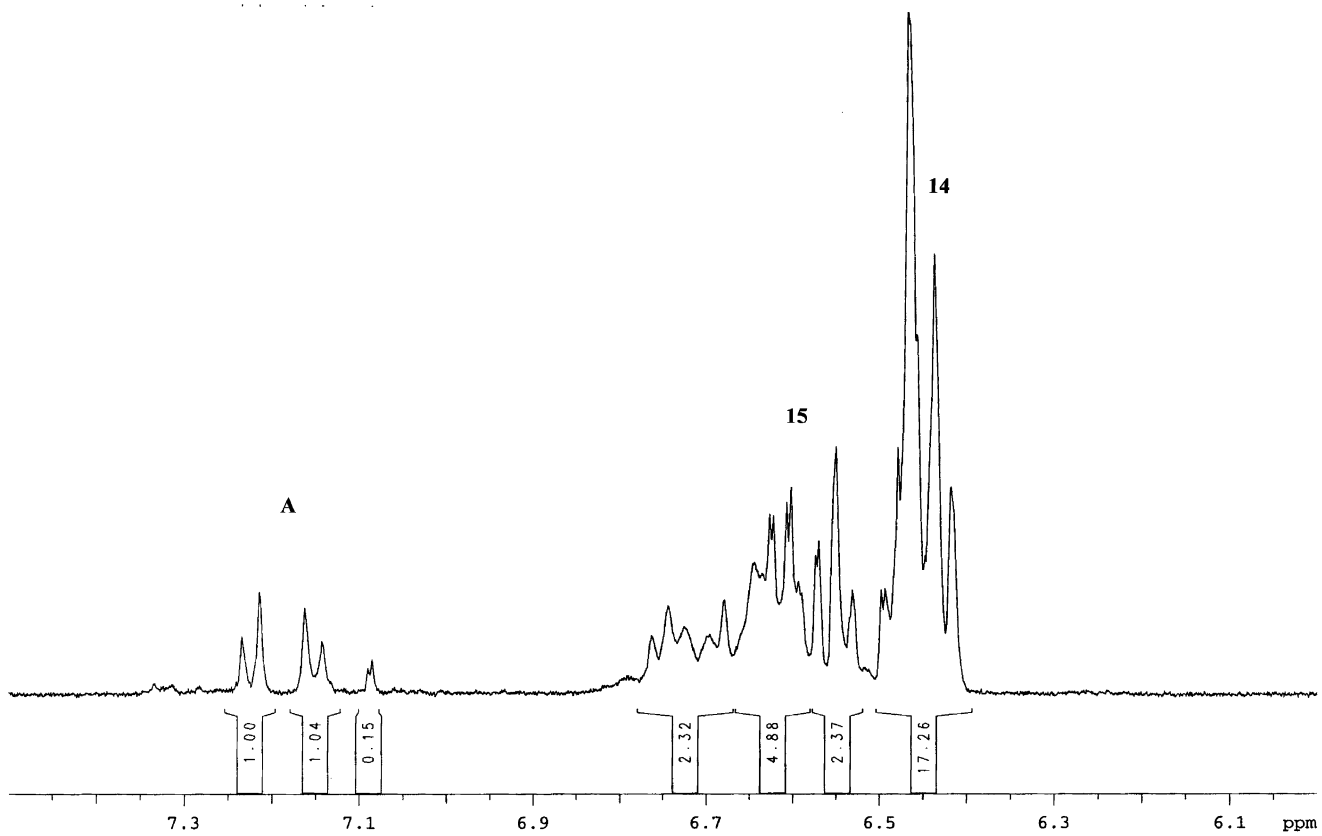
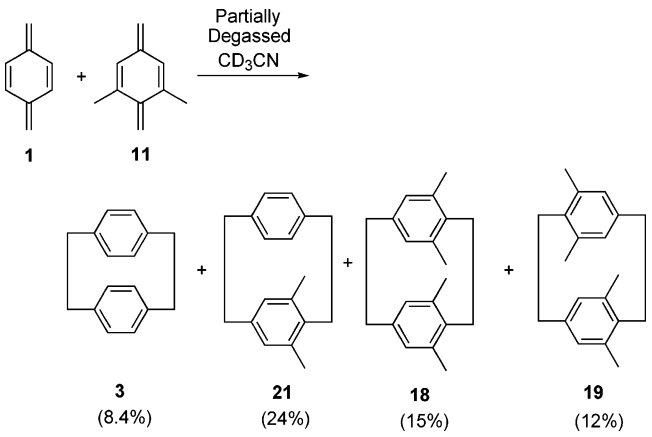


FIGURE 4. ^{1}H NMR spectrum (400 MHz, CD_3CN) of pentane extraction of product mixture of α-methyl-*p*-xylylene (**10**) in deoxygenated CH_3CN. (**14** and **15** [each are several steroisomers] are compound numbers given in the text. **A**: oxygen adducts.)

acetates **12** and **17**. The ^{1}H NMR spectrum (Figure 6) of the mixture clearly shows the ratio of *p*-QDMs **1** to **11** as being nearly 1 to 2. Upon standing, *p*-xylylene dimer **3** (8.4% yield), mixed dimer **21** (24% yield), head-to-head dimer **18** (15% yield), head-to-tail dimer **19** (12% yield), and insoluble oligomers were formed. We did not observe by ^{1}H NMR spectroscopy or GC/MS any evidence for significant amounts of trimers.



Discussion

***p*-Xylylene (1) Oligomerization Studies.** The fluoride-induced elimination of trimethylsilyl acetate has proven to be an effective and mild means of preparing *p*-QDMs. Under these mild conditions, *p*-xylylene (**1**) can be prepared as a dilute solution that persists for several hours at room temperature. Over a period of several hours, dimer **3**, trimer **4**, and insoluble materials are formed from **1**. In contrast to the pyrolysis preparations, reaction products are free of side products resulting from the pyrolysis of oligomers.

Two pathways could form dimer **3**: a concerted [6 + 6] cycloaddition of two molecules of *p*-QDM **1** or formation of an initial dimeric diradical **2** followed by closure of the diradical. It would be very difficult to bring together two molecules of *p*-QDM **1** in a supra−antara orientation because of the rigid six-membered rings, and the supra−supra concerted $6\pi + 6\pi$ cycloaddition would be expected to be forbidden by the Woodward−Hoffmann Rules.[22] Formation of trimer **4** at room temperature is consistent with the trapping of diradical **5** by a molecule of *p*-QDM **1**. Since dimer **3** does not open to diradical **5** at room temperature,[23] formation of dimer **3** must be stepwise, not concerted (Scheme 2).

Zwitterionic Intermediates. An alternative to the stepwise diradical mechanism is a stepwise mechanism involving zwitterionic intermediate **22**.[24] It is known that reactions involving zwitterionic intermediates are sensitive to changes in solvent polarity.[25] Although acetonitrile-d_3 was the only solvent used in this study, solutions of *p*-QDM **1** in hexane, prepared from the pyrolysis of *p*-xylene, are known to form a trace amount of dimer **3**.[8] There is no evidence of products resulting from the zwitterionic intermediates reacting with the solvent. The furan-

(22) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, 4th ed.; Kluwer Academic/Plenum Publishers: New York, 2000; pp 636−651.

(23) Reich and Cram[10] found that, at 200 °C, dimer **3** opens to diradical **2**, which could be in turn trapped with dimethyl maleate or dimethyl fumarate. The formation of diradical **2** was supported by the loss of the stereochemistry of the original diesters in their adducts.[10]

(24) Gompper, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 312.

(25) (a) DeCock, C.; Piettre, S.; Lahousse, F.; Janovsek, Z.; Meréngi, R.; Viehe, H. G. *Tetrahedron* **1985**, *41*, 4183. (b) Proskow, S.; Simmons, H. E.; Cairns, T. L. *J. Am. Chem. Soc.* **1966**, *88*, 5254.

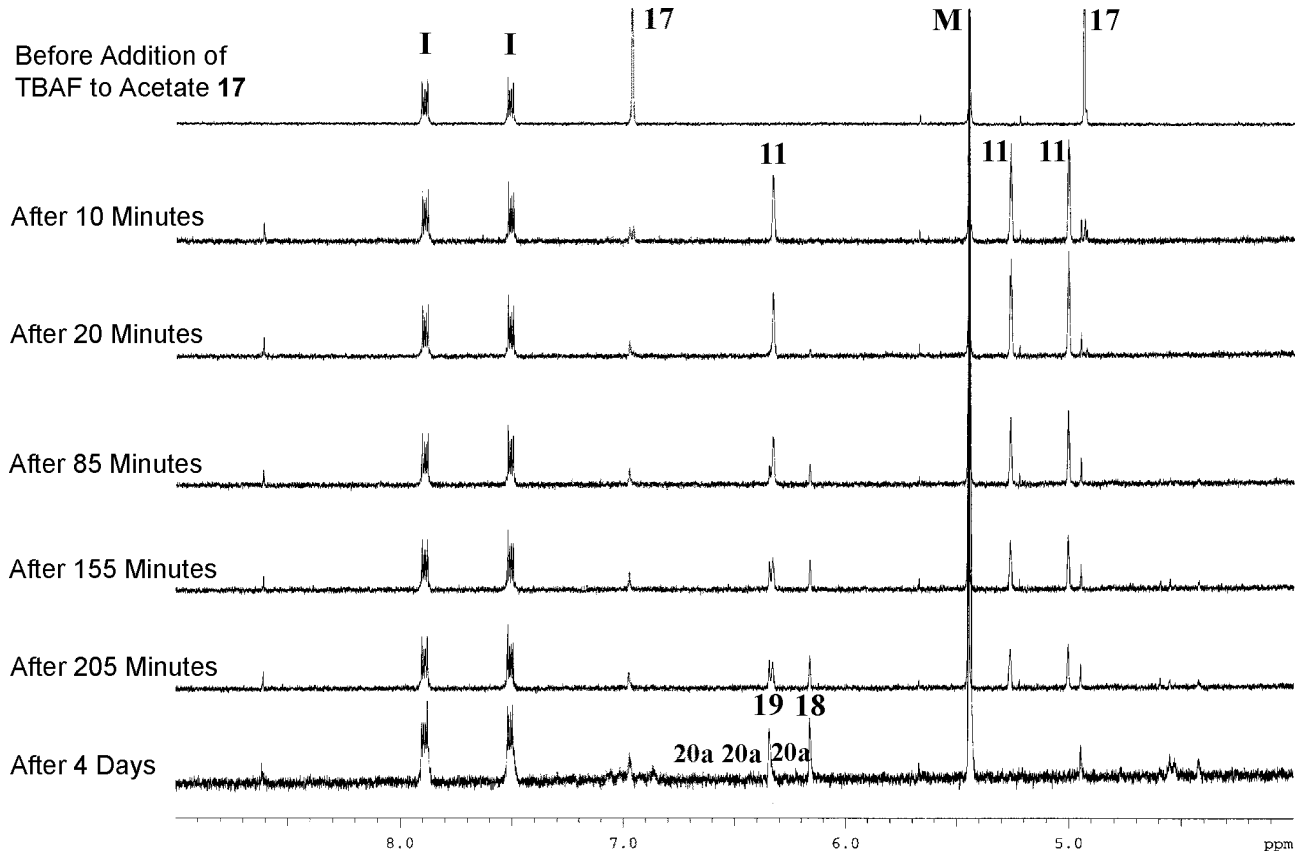
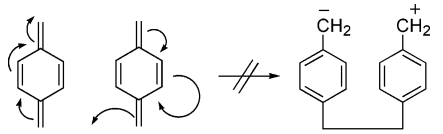


FIGURE 5. ^{1}H NMR spectrum (400 MHz, CD_3CN) of reaction progress of 2,6-dimethyl-*p*-xylylene (**11**) in partially degassed CD_3CN. (**17**, **18**, **19**, and **20a** are compound numbers given in the text. **I**: internal standard, naphthalene, **M**: methylene chloride.)

based *o*-QDM is thought to dimerize by a diradical intermediate rather than a zwitterionic intermediate because it exhibited no change in rate of dimerization when the polarity of solvent was changed.[12]



Further evidence against a zwitterionic intermediate is that unsymmetrical *p*-QDM **10** forms both head-to-head **14a** and head-to-tail **14b** dimers. Unsymmetrical molecules that dimerize by zwitterionic intermediates often form head-to-tail dimers. It has been proposed that this occurs because the positive end of one molecule would be expected to attack the negative end of the other.[25]

α-Methyl-*p*-xylylene (10) Oligomerization Studies. α-Methyl-*p*-xylylene (**10**) has a half-life slightly longer than that of *p*-xylylene (**1**) under comparable conditions. The slightly decreased reactivity of *p*-QDM **10** can be explained by the reduced reactivity caused by the steric hindrance of the α-methyl being nearly offset by the increased reactivity of the other α-position because the resulting diradical is more substituted and therefore more stable. ^{1}H NMR spectroscopy and GC/MS analysis confirmed the formation of three of the four possible cyclic dimers **14** and four of the six possible cyclic trimers **15**. Due to the large number of isomers, it is difficult to determine if the reaction is regioselective. Observation of trimers **15** again supports the existence of a dimeric diradical **23**. The formation of acyclic dimer **16**, the analogues of which were present in the α-methyl thiophene-based *p*-QDM and α-methyl furan-based *o*-QDM product mixtures, would have been strong evidence for a dimeric diradical **23**. A possible explanation for the lack of formation of acyclic dimer **16** is that it is too difficult to form the conformation needed for intramolecular disproportionation of dimeric diradicals with benzene-based *p*-QDMs.

2,6-Dimethyl-*p*-xylylene (11) Oligomerization Studies. 2,6-Dimethyl-*p*-xylylene (**11**) has a half-life similar to that of *p*-xylylene (**1**) under comparable conditions. The flanking methyl groups do not appear to reduce the reactivity of *p*-QDM **11**. Dimers **18** and **19** were formed in nearly equal amounts. Dimer **18** can arise from either dimeric diradical **24a** or **24b**, whereas dimer **19** can only be formed from dimeric diradical **24c** (Scheme 3). With its two flanking methyl groups, 2,6-dimethyl-*p*-xylylene (**11**) has one exocyclic methylene that is sterically hindered. This could have limited the possible dimeric diradicals that could form to the tail-to-tail diradical **24a** because head-to-head diradical **24b** and head-to-tail diradical **24c** would have too much steric hindrance to form. Since dimers **18** and **19** were formed in nearly equal amounts, the steric hindrance of the two methyl groups must be minimal. Trimer **20a** was observed by ^{1}H NMR spectroscopy and GC/MS, but evidence for trimer **20b** was not found. Trimer **20b** can only be formed from dimeric diradical **24c**, whereas trimer **20a** can form from either dimeric diradical **24a**, **24b**, or **24c** (Scheme 3). Lack of formation of trimer **20b** indicates that dimeric diradical **24c** must close to dimer **19** faster than being trapped to form trimer **20b**.

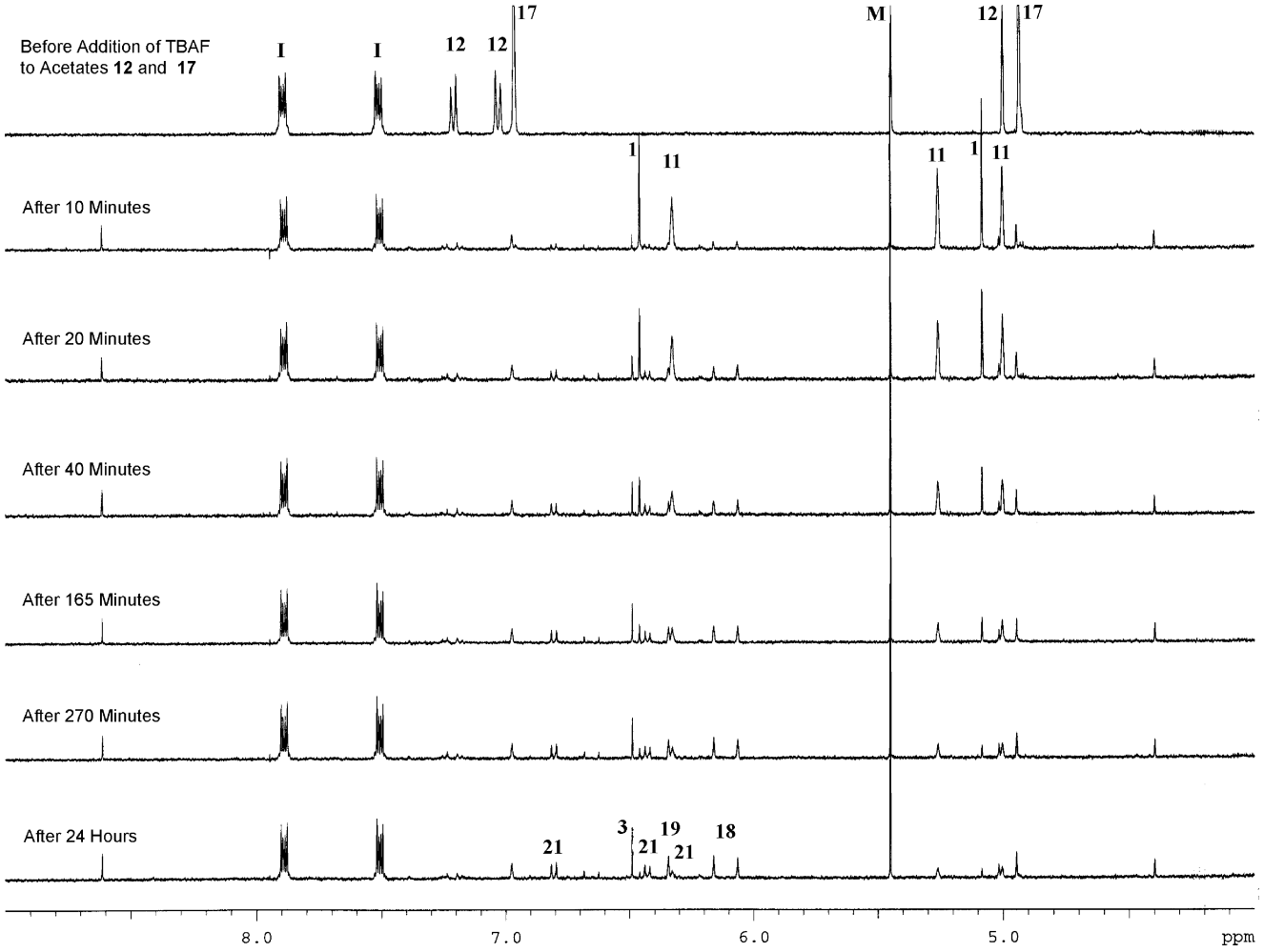
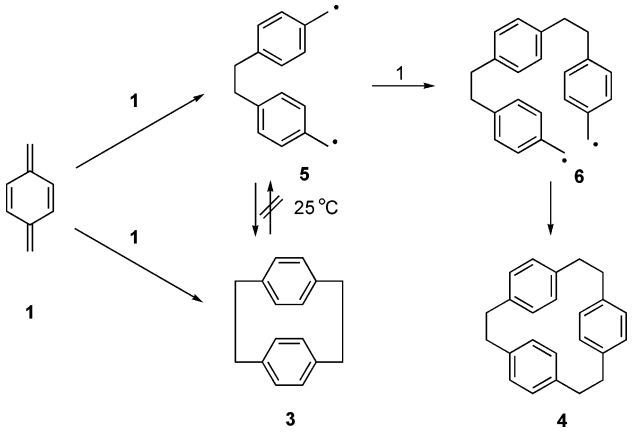


FIGURE 6. ^{1}H NMR spectrum (400 MHz, CD_3CN) of reaction progress of *p*-xylylene (**1**) and 2,6-dimethyl-*p*-xylylene (**11**) in partially degassed CD_3CN. (**3**, **12**, **17**, **18**, **19**, and **21** are compound numbers given in the text. **I**: internal standard, naphthalene, **M**: methylene chloride.)

SCHEME 2



***p*-Xylylene (1) and 2,6-Dimethyl-*p*-xylylene (11) Co-Oligomerization Studies.** Both *p*-QDMs **1** and **11** oligomerized at a similar rate and produced a mixed dimer **21**. This supports the theory that the flanking methyl groups of *p*-QDM **11** are having little effect on its reactivity. It is unclear why significant amounts of trimers were not observed from the mixed *p*-QDMs studies, whereas trimers were observed in both of the isolated studies of *p*-QDMs **1** and **11**. Possibly the formation of several different trimers resulted in low yields for all of them.

Conclusion

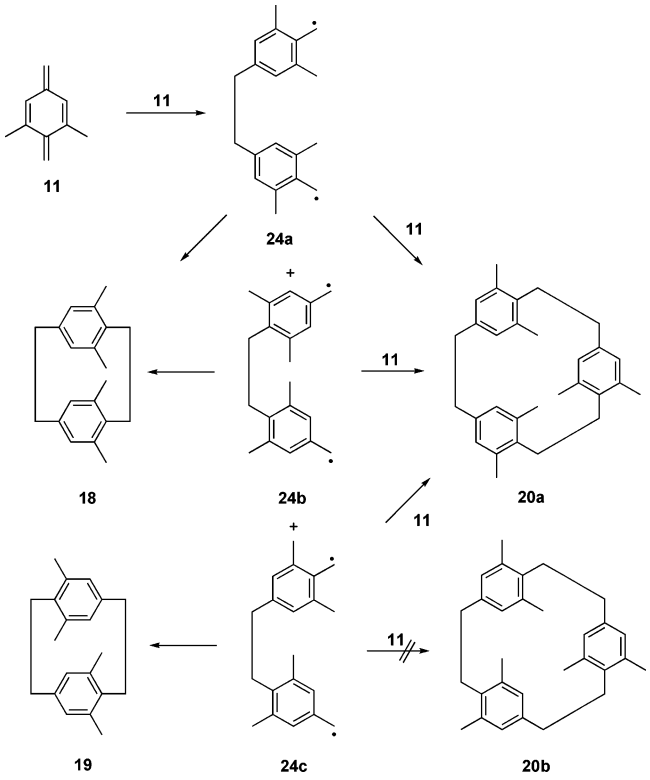
^{1}H NMR spectra of *p*-xylylene (**1**), α-methyl-*p*-xylylene (**10**), and 2,6-dimethyl-*p*-xylylene (**11**) have been observed at room temperature, and this allows a more detailed study of their chemistry. For the first time, the ^{13}C NMR spectrum of *p*-QDM **1** has been observed. Observation of trimers provides strong evidence that *p*-QDMs **1**, **10**, and **11** dimerize by a stepwise mechanism. The absence of acyclic dimer **16**, the analogues of which were present in the product mixtures of the α-methyl thiophene-based *p*-QDM and the α-methyl furan-based *o*-QDM, can be explained by conformational limitations of the dimeric diradicals of the benzene-based *p*-QDMs. Under comparable conditions, *p*-QDMs **1** and **11** were found to have similar reactivity but *p*-QDM **10** was found to be slightly less reactive.

Experimental Section

4-[(Trimethylsilyl)methyl]benzyl Alcohol. This alcohol was prepared in a 94% yield by lithium aluminum hydride (152 mg, 4 mmol) reduction of 4-[(trimethylsilyl)methyl]benzoic acid (375 mg, 1.8 mmol) using a procedure similar to the procedure outlined by Nystrom and Brown[26] for the reduction of phenylacetic acid to β-phenylethanol. ^{1}H NMR (400 MHz, CD_3CN) δ 7.191 and 7.009 (AA′BB′q, J = 7.6 Hz), 4.507 (s), 3.320 (br s), 2.107 (s), 0.001

(26) Nystrom, R. F.; Brown, W. G. *J. Am. Chem. Soc.* **1947**, *69*, 2548.

SCHEME 3



(s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 and 6.97 (AA′BB′q, J = 8 Hz, 4H), 4.61 (s, 2H), 2.06 (s, 2H), 1.56 (br s, 1H), −0.03 (s, 9H). [lit.[27] ^{1}H NMR ($CDCl_3$) δ 7.22 and 7.00 (ABq, J = 8.0 Hz, 4H, arom), 4.6 (s, 2H, CH_2), 2.12 (s, 2H, CH_2), 0.02 (s, 9H, $SiMe_3$)]; ^{13}C NMR (100 MHz, CD_3CN) δ 140.3, 138.4, 128.8, 127.8, 64.7, 26.9, −1.8. Anal. Calcd for $C_{11}H_{18}OSi$: C, 67.98; H, 9.34. Found: C, 68.14; H, 9.47.

[*p*-((Trimethylsilyl)methyl)phenyl]methyl Acetate (12). A solution of 109 mg of 4-[(trimethylsilyl)methyl]benzyl alcohol (0.56 mmol) and 0.3 mL of pyridine (3.7 mmol) in 2 mL of dry THF was prepared in a 10-mL flask. An argon atmosphere was placed over the solution. The solution was cooled to 0 °C and stirred. A solution of 0.125 mL of acetyl chloride (1.76 mmol) in 1 mL of dry THF was added dropwise to the alcohol solution by a syringe. The reaction mixture was allowed to warm to room temperature and was stirred for 2 h. The reaction mixture was added to 10 mL of ether. The ether solution was washed with brine twice and then with a saturated solution of $NaHCO_3$ and finally with brine again. The ether solution was dried with $MgSO_4$ and concentrated under reduced pressure to get 115 mg (87%) of viscous oil. ^{1}H NMR (400 MHz, CD_3CN) δ 7.193 and 7.012 (AA′BB′q, J = 8 Hz, 4H), 4.985 (s, 2H), 2.160 (s, 2H), 2.006 (s, 3H), −0.047 (s, 9H); ^{13}C NMR (100 MHz, CD_3CN) δ 171.6, 141.8, 132.9, 129.2, 129.1, 66.8, 22.4, 21.1, −2.0.

Drying and Initial Degassing of CD_3CN. Prior to use as a solvent in the preparation of *p*-QDMs, the CD_3CN was distilled from P_2O_5 under argon and then partially degassed by repeated freeze−pump−thaw cycles, except where indicated.[28]

***p*-Xylylene (1) in Partially Degassed CD_3CN.** To a tear-shaped flask was added 7.6 mg of TBAF (24 μmol). To a second tear-shaped flask was added 9.5 μL of a 5.0 × 10^{-2} M solution of naphthalene in CH_2Cl_2 (0.48 μmol) and 9 μL of an approximately 0.1 M solution of **12** in CH_2Cl_2 (∼1 μmol). The CH_2Cl_2 was removed at reduced pressures. The two flasks were placed into a nitrogen-filled glovebag. To the acetate flask was added about 0.8 mL of partially degassed CD_3CN. The acetate solution was transferred to an NMR tube, and the acetate was quantified by ^{1}H NMR. The NMR tube was returned to the glovebag. To the TBAF flask was added about 0.2 mL of partially degassed CD_3CN. The TBAF solution was added to the NMR tube. The sample was protected from light. The NMR tube was periodically removed from the glovebag for analysis by ^{1}H NMR spectroscopy. ^{1}H NMR (400 MHz, CD_3CN, 20 °C) δ 6.452 (s, 4H), 5.007 (s, 4H). [lit.[21] ^{1}H NMR (60 MHz, THF-d_8, −80 °C) δ 6.49, 5.10].

As the solution was allowed to stand, the *p*-xylylene (**1**) was consumed and [2.2] paracyclophane (**3**) (7% yield), [2.2.2]paracyclophane (**4**) (0.4% yield), oxygen adducts, and insoluble oligomers were formed. **3**: ^{1}H NMR (400 MHz, CD_3CN) δ 6.484 (s, 8H), 3.046 (s, 8H). [lit.[29] ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.48, 3.08]; GC/MS *m*/*z* (relative intensity) 209 (5), 208 (35), M^+, 105 (5), 104 (100), 78 (8), 77 (4). [lit.[30] GC/MS *m*/*z* (relative intensity) 208 (16), 104 (100), 103 (100)]. **4**: ^{1}H NMR (400 MHz, CD_3CN, 20 °C) δ 6.678 (s, 12H), 2.903 (s, 12H). [lit.[31] ^{1}H NMR (100 MHz, $CDCl_3$) δ 6.68 (Ar), 2.92 (CH_2), ^{1}H NMR (100 MHz, CD_3OD) δ 6.23 (Ar), 2.47 (CH_2)]; GC/MS *m*/*z* (relative intensity) 313 (15), 312 (77), 207 (14), 195 (12), 193 (31), 104 (100). [lit.[32] GC/MS *m*/*z* (relative intensity) 312 (44), 118 (32), 117 (100), 115 (59), 105 (90), 104 (83), 91 (54), 77(35)].

^{13}C NMR Spectrum of 1 at −40 °C. The sample was prepared in a manner similar to the one reported above for the partially degassed CD_3CN preparation of **1** except: (A) No naphthalene was added; (B) 7 mg of $Cr(acac)_3$ (a paramagnetic relaxation agent used to reduce the spin−lattice relaxation time) was added;[33] (C) 35 mg of TBAF (111 μmol) was used; (D) 100 μL of 0.1 M solution of **13** (∼10 μmol) was used; (E) 30 s after the TBAF solution was added, the NMR tube was placed into a CH_3CN/dry ice bath. ^{13}C NMR (100 MHz, CD_3CN, −40 °C) δ 140.3, 129.8, 115.5.

***p*-Xylylene (1) in Deoxygenated CD_3CN.** To a tear-shaped flask was added 7 mg of TBAF (22.2 μmol). To a second tear-shaped flask was added 10 μL of a 4.7 × 10^{-2} M solution of naphthalene in CH_2Cl_2 and 10 μL of an approximately 0.1 M solution of **12** in CH_2Cl_2. The CH_2Cl_2 was removed at reduced pressure. The two flasks were placed into a nitrogen-filled glovebag. To the acetate flask was added about 0.8 mL of partially degassed CD_3CN, and to the TBAF was added about 0.2 mL of partially degassed CD_3CN. The acetate solution was transferred to an NMR tube, and the acetate was quantified by NMR. The NMR tube was returned to the glovebag. The acetate solution was poured into one tube of a two-tube reaction cell.[34] The TBAF solution was added to the other tube of the cell. The cell was connected to a valved vacuum adapter. The two solutions were deoxygenated by two series of argon purging followed by three freeze−pump−thaw cycles. Once the cell had returned to room temperature, the cell was tipped to allow the TBAF solution to be added to the acetate solution. While still under a vacuum, the cell was wrapped in foil and placed into the glovebag. After 18 h, the reaction mixture, which contained some precipitate, was transferred to an NMR tube. The soluble products, **3** (35% yield) and **4** (7% yield), were quantified by NMR.

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(28) (a) Fischer, D. R. Ph.D. Dissertation, Iowa State University, Ames, IA, 1990; pp 91−121. (b) Trahanovsky, W. S.; Arvidson, K. B. *J. Org. Chem.* **1996**, *61*, 9528.

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(30) Hefelfinger, D. T.; Cram, D. J. *J. Am. Chem. Soc.* **1971**, *93*, 4754.

(31) Pierre, J.-L.; Baret, P.; Chautemps, P.; Armand, M. *J. Am. Chem. Soc.* **1981**, *103*, 2986.

(32) Tabushi, I.; Yamada, H.; Yoshida, Z.; Oda, R. *Tetrahedron* **1971**, *27*, 4845.

(33) Wehrli, F. W.; Marchand, A. P.; Wehrli, S. *Interpretation of Carbon-13 NMR Spectra*, 2nd ed.; Wiley & Sons: New York, 1988; pp 223−226.

(34) Reaction cell resembles a cow-type distillation receiver. For a complete description of the cell, see ref 12.

***p*-Xylylene (1) in Oxygenated CD_3CN.** The CD_3CN was distilled from P_2O_5 under dry air, and then oxygen was bubbled through the CD_3CN for 30 s. To a tear-shaped flask was added 7 mg of TBAF (22 μmol). To a second tear-shaped flask was added 10 μL of an approximately 0.1 M solution of **12** in CH_2Cl_2. The CH_2Cl_2 was removed at reduced pressure. The dried CD_3CN was added to the acetate flask and the TBAF flask, 0.8 and 0.2 mL, respectively. Both solutions were transferred to an NMR tube. The ^{1}H NMR spectrum showed that acetate **12** was consumed and signals consistent with oxygen adducts formed.

1-[*p*-((Trimethylsilyl)methyl)phenyl]ethanol. To a solution of 209 mg of 4-[(trimethylsilyl)methyl]benzaldehyde (1.09 mmol) in 3 mL of dry ether was added 0.4 mL of 3 M MeMgBr (1.2 mmol), dropwise. The reaction mixture was heated to reflux for 30 min. The reaction mixture was worked up in the normal manner to yield 197 mg (95%). ^{1}H NMR (400 MHz, CD_3CN) δ 7.186 and 6.975 (AA′BB′q, J = 8 Hz), 4.727 (q, J = 6.4 Hz), 2.073 (s), 1.353 (d, J = 6.4 Hz), −0.034 (s); ^{13}C NMR (100 MHz, CD_3CN) δ 143.3, 140.1, 128.7, 126.2, 69.9, 26.7, 25.9, −1.9. Anal. Calcd for $C_{12}H_{20}OSi$: C, 69.17; H, 9.67. Found: C, 69.29; H, 9.95.

1-[*p*-((Trimethylsilyl)methyl)phenyl]ethyl Acetate (13). 13 was prepared in an 87% yield from 1-[*p*-((trimethylsilyl)methyl)phenyl]-ethanol (50 mg, 0.24 mmol) with the procedure used for the above preparation of [*p*-((trimethylsilyl)methyl)phenyl]methyl acetate. ^{1}H NMR (400 MHz, CD_3CN) δ 7.196 and 7.002 (AA′BB′q, J = 8 Hz, 4H), 5.763 (q, J = 6.8 Hz, 1H), 2.085 (s, 2H), 1.991 (s, 3H),1.456 (d, J = 6.8 Hz, 3H), −0.038 (s, 9H); ^{13}C NMR (100 MHz, CD_3CN) δ 171.0, 141.3, 138.5, 129.0, 126.8, 72.8, 26.9, 22.4, 21.5, −1.9.

α-Methyl-*p*-xylylene (10) in Partially Degassed CD_3CN. 10 was prepared from acetate **13** (1.2 μmol), TBAF (25 μmol), and naphthalene (0.30 μmol) with the procedure used for the above preparation of *p*-xylylene (**1**) in partially degassed CD_3CN. A ^{1}H NMR spectrum was obtained 15 min after the addition of the TBAF. ^{1}H NMR (400 MHz, CD_3CN) δ 6.713 (br d, J = 9.6 Hz, 1H), 6.466 (br d, J = 9.6 Hz, 1H), 6.314 (br s, 2H) 5.619 (q, J = 8 Hz, 1H), 4.963 (br s, 2H), 1.848 (d, J = 8 Hz, 3H). Upon standing, the ^{1}H NMR spectrum showed signals consistent with oxygen adducts and trace amounts of dimers and trimers.

α-Methyl-*p*-xylylene (10) in Deoxygenated CD_3CN. 10 was prepared from acetate **13** (5.7 μmol), TBAF (25 μmol), and naphthalene (0.41 μmol) in 20 mL of CH_3CN with the procedure used for the above preparation of *p*-xylylene (**1**) in deoxygenated CD_3CN. The ^{1}H NMR spectrum after 15 min is very similar to the spectrum obtained for *p*-QDM **10** in partially degassed CD_3CN. As the solution was allowed to stand, insoluble oligomers were formed. After 14 h, another ^{1}H NMR spectrum was obtained. It showed signals with chemical shifts similar to those of the dimer, trimer, and oxygen adducts of parent *p*-QDM **1**. The spectrum showed no signals for *p*-QDM **10**.

α-Methyl-*p*-xylylene (10) in Deoxygenated CH_3CN. 10 was prepared from acetate **13** (20 μmol) and TBAF (45 μmol) in 20 mL of CH_3CN with the procedure used for the above preparation of *p*-xylylene (**1**) in deoxygenated CD_3CN. As the solution was allowed to stand, the *p*-QDM **10** was consumed, and three dimers **14**, four trimers **15**, oxygen adducts, and insoluble oligomers were formed. The product mixture was extracted with pentane, and the extract was analyzed by GC/MS. Dimer A **14** (7.3% yield): GC/MS *m*/*z* (relative intensity) 237 (6), 236 (31) M^+, 119 (29), 118 (100), 117 (66), 115 (24), 113 (3), 105 (2), 103 (3), 102 (3), 89 (7), 88 (6). Dimer B **14** (2.6% yield): GC/MS *m*/*z* (relative intensity) 237 (2), 236 (3) M^+, 119 (58), 118 (100), 117 (93), 115 (26), 103 (3), 90 (6), 89 (9), 88 (8). Dimer C **14** (5.0% yield): GC/MS *m*/*z* (relative intensity) 236 (9) M^+, 120 (3), 119 (36), 118 (97), 117 (100), 115 (24), 103 (3), 89 (12), 88 (7), 86 (6). Trimer A **15** (1.3% yield): GC/MS *m*/*z* (relative intensity) 354 (2) M^+, 238 (16), 237 (100), 236 (60), 189 (2), 131 (2), 129 (2), 128 (3), 119 (42), 118 (56), 117 (99), 115 (34), 107 (2), 103 (3), 90 (6), 89 (10), 88 (10), 86 (4). Trimer B **15** (2.2% yield): GC/MS *m*/*z* (relative intensity) 354 (6) M^+, 238 (15), 237 (100), 236 (51), 232 (2), 189 (2), 131 (2), 129 (2), 128 (2), 122 (4), 118 (60), 117 (89), 115 (35), 106 (2), 105 (2), 103 (3), 89 (9), 87 (4), 86 (3), 77 (3), 75 (2), 74 (3). Trimer C **15** (1.1% yield): GC/MS *m*/*z* (relative intensity) 354 (2) M^+, 238 (15), 237 (92), 236 (57), 131 (2), 128 (3), 119 (41), 118 (56), 117 (100), 115 (37), 103 (2), 91 (4), 89 (12), 88 (10), 87 (5), 86 (4). Trimer D **15** (2.4% yield): GC/MS *m*/*z* (relative intensity) 355 (2), 354 (7) M^+, 353 (2), 239(2), 238 (15), 237 (97), 236 (36), 233(4), 232 (3), 189 (2), 131 (2), 128 (3), 119 (38), 118 (569), 117 (100), 115 (39), 112 (2), 108 (2), 105 (2), 103 (2), 91 (6), 90 (7), 89 (10), 88 (9), 86 (3), 77 (4), 76 (3), 74 (2). The pentane was removed under vacuum from the extract. The resulting residue was dissolved in CD_3CN, and a ^{1}H NMR spectrum was obtained.

3,5-Dimethyl-4-[(trimethylsilyl)methyl]benzyl Alcohol. 3,5-Dimethyl-4-[(trimethylsilyl)methyl]benzyl alcohol was prepared in a 92% yield by lithium aluminum hydride (1.23 mmol) reduction of 3,5-dimethyl-4-[(trimethylsilyl)methyl]benzoic acid (0.5 mmol) following a procedure similar to that outlined by Nystrom and Brown[26] for the reduction of phenylacetic acid to β-phenylethanol that was used above for 4-[(trimethylsilyl)methyl]benzyl alcohol. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.967 (s, 2H), 4.538 (s, 2H), 2.224 (s, 6H), 2.138 (s, 2H) 0.014 (s, 9H).

[3,5-Dimethyl-4-((trimethylsilyl)methyl)phenyl]methyl Acetate (17). 17 was prepared in an 85% yield from 3,5-dimethyl-4-[(trimethylsilyl)methyl]benzyl alcohol (0.4 mmol) following the procedure used for the above preparation of [*p*-((trimethylsilyl)-methyl)phenyl]methyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.954 (s, 2H), 4.925 (s, 2H), 2.209 (s, 6H), 2.170 (s, 2H), 2.008 (s, 3H), −0.003 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 138.5, 131.4, 127.8, 117.4, 66.0, 20.4, 20.2, 19.4, −1.1. GC/MS *m*/*z* (relative intensity) 264 (2) M^+, 249 (5), 207 (5), 206 (14), 205 (100), 202 (9), 201 (6), 197 (3), 195 (2), 135 (3), 132 (20), 130 (15), 128 (13), 125 (7), 117 (2), 115 (4), 113 (2), 112 (2); HRMS calcd for $C_{15}H_{24}O_2Si$ 264.1546, found 264.1550.

2,6-Dimethyl-*p*-xylylene (11) in Partially Degassed CD_3CN. 11 was prepared from [3,5-dimethyl-4-((trimethylsilyl)methyl)-phenyl]methyl acetate (**17**) (1.6 μmol), TBAF (25 μmol) and naphthalene (0.47 μmol) following the procedure used for the above preparation of *p*-xylylene (**1**) in partially degassed CD_3CN. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.331 (s, 2H), 5.262 (s, 2H), 5.007 (s, 2H), 1.997 (s, 6H). As the solution was allowed to stand, the 2,6-dimethyl-*para*-xylylene (**14**) was consumed and head-to-head dimer **18** (7.7% yield), head-to-tail dimer **23** (7.3% yield), trimer **20a** (1.3% yield), and insoluble oligomers were formed. Dimer **18**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.166 (s, 4H), 3.292 (s, 4H), 2.850 (s, 4H), 2.020 (s, 12H); GC/MS *m*/*z* (relative intensity) 264 (13) M^+, 249 (10), 133 (19), 132 (100), 129 (19), 128 (13), 117 (18), 115 (26), 114 (12). Dimer **19**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.348 (s, 4H), 2.97−2.93 (m, 4H), 2.85−2.80 (m, 4H), 2.210 (s, 12H); GC/MS *m*/*z* (relative intensity) 264 (18) M^+, 249 (5), 133 (23), 132 (100), 129 (12), 128 (10), 117 (47), 115 (44). Trimer **20a**: ^{1}H NMR[35] (400 MHz, $CDCl_3$) δ 6.630 (s, 2H), 6.489 (s, 2H), 6.278 (s, 2H); GC/MS *m*/*z* (relative intensity) 397 (2), 396 (6) M^+, 147 (4), 146 (2), 145 (2), 143 (2), 134 (3), 133 (26), 132 (100), 129 (9), 128 (6), 127 (3), 126 (2), 117 (19), 115 (21), 111 (2), 103 (2), 89 (5), 88 (10), 86 (2), 85 (2), 53 (2).

***p*-Xylylene (1) and 2,6-Dimethyl-*p*-xylylene (11) in Partially Degassed CD_3CN. 1** and **11** were prepared from [*p*-((trimethylsilyl)methyl)phenyl]methyl acetate (**12**) (0.67 μmol), [3,5-dimethyl-4-((trimethylsilyl)methyl)phenyl]methyl acetate (**17**) (1.5 μmol), TBAF (50 μmol), and naphthalene (0.47 μmol) following the procedure used for the above preparation of *p*-xylylene (**1**) in partially degassed CD_3CN. As the solution was allowed to stand, the *p*-xylylene and 2,6-dimethyl-*para*-xylylene (**11**) were consumed and *p*-xylylene dimer **3** (2.8×10^{-8} mol), head-to-head dimers **18**

(35) Benzylic hydrogens were masked by other signals and were not observed.

(1.1×10^{-7} mol), head-to-tail dimer **19** (9.1×10^{-8} mol), mixed dimer **21** (1.6×10^{-7} mol), and insoluble oligomers were formed. Mixed dimer **21**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.811 (d, $J = 8$ Hz, 2H), 6.433 (d, $J = 8$ Hz, 2H), 6.348 (s, 2H), 3.005 (s, 4H), 2.97−2.93 (m, 2H), 2.85−2.80 (m, 2H), 2.053 (s, 6H); GC/MS *m*/*z* (relative intensity) 236 (64) M^+, 233 (5), 132 (100), 131 (30), 129 (24), 126 (7), 117 (17), 115 (23), 114 (17), 113 (13), 112 (9), 111 (5).

Acknowledgment. This work (Paper IS-J 7047) was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract W-7405-ENG-82.

Supporting Information Available: Experimental procedures for the syntheses of acetates **12**, **13**, and **17**. Spectroscopic data for the acetates, *p*-QDMs **1**, **10**, and **11**, and their oligomerization products. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0516279