Washing the crude cyclics/polymer product with 5 volumes of acetone provided a solution of pure cyclics in about 75% yield (the high molecular weight polymer and macrocyclic carbonates with more than ca. 15 repeat units are insoluble in acetone). The mixed macrocyclic oligomers have mp = 200-210 °C. FTIR shows no phenolic O—H and a strong C=O at 1770.6 cm^{-1}. ^{13}C NMR: absorptions at 28.3, 30.27, and 30.87 (methyls), 42.29 and 42.53 (quaternary carbons), 120.2-120.4 and 127.7-127.9 (unsubstituted aromatics), 148.2-149.05 (substituted aromatics), and 152.1-152.2 (carbonyls). 300 MHz ^1H NMR: Major resonances associated with bisphenol A carbonates: 7.26 (d, J = 8.8, 4 H), 7.17 (d, J = 8.8, 4 H), 1.69 (s, 6 H); minor resonances associated with cyclic dimer and trimer are also observed (vide infra). Field desorption shows parent ions at m/e 508, 762, 1016, 1270, 1524, and 1778. HPLC elution using a THF/water gradient on a C-8 reverse-phase column showed the following pattern:

component	t_R (min)	254/285 nm ratio
cyclic dimer	3.10	17.5
cyclic trimer	4.29	46.6
cyclic tetramer	5.68	49.65
cyclic pentamer	6.91	52.65
cyclic hexamer	8.07	56.26
cyclic heptamer	9.125	51.5
cyclic octamer	10.10	50.7
cyclic nonamer	11.02	50.2

Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.36; H, 5.21.

Isolation and Identification of Discrete Oligomers: Bisphenol A Cyclic Tetramer Carbonate. One hundred grams of polymer-free macrocyclic carbonates were dissolved in 500 mL of hot 70:29:1 acetone/CH_2Cl_2/2-propanol. Upon standing, 95% pure cyclic tetramer crystallized. Recrystallization from benzene afforded 15.0 g of pure cyclic tetramer with mp = 368-372 °C. FTIR shows no O—H and a strong C=O at 1770.3 cm^{-1}. ^1H NMR has a slightly broadened singlet at 1.66 ppm and a collapsed A_2B_2 pattern at 7.20 and 7.24 ppm. ^{13}C NMR: 30.849 (methyls), 42.481 (quaternary carbon), 120.231 and 127.837 (unsubstituted aromatic), 148.843 and 148.196 (substituted aromatic), and 151.999 (carbonyl carbons). A single-crystal X-ray structure has been solved.[19] High-resolution mass spectrum has a parent at 1016.3772; calcd = 1016.3708. Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.58; H, 5.21.

Bisphenol A Cyclic Trimer. The tetramer-poor filtrate from above was evaporated and the residue dissolved in hot toluene. Cooling caused cyclic dimer and trimer to crystallize. Trimer was removed by washing with 60:40 acetone/hexane, which when recrystallized from benzene gave 13.4 g of white solid with mp = 345-350 °C. The transparent plates obtained from benzene occluded benzene, and a crystal structure could not be solved. FTIR shows no O—H and a strong C=O at 1771 cm^{-1}. ^1H NMR has a slightly broadened singlet at 1.66 ppm and a collapsed A_2B_2 pattern at 7.09 and 7.14. ^{13}C NMR: 30.293 (methyls), 42.300 (quaternary carbon), 120.461, 127.717 (unsubstituted aromatics), 148.400, 149.078 (substituted aromatic), and 152.256 (carbonyl). High-resolution mass spectrum has a parent at 762.2829; calcd = 762.2825. Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.62; H, 5.76.

Bisphenol A Cyclic Dimer. The residue from above, after removal of cyclic trimer was 98% pure cyclic dimer. Recrystallization from toluene afforded 5.8 g of pure dimer with mp = 330-335 °C. FTIR had no O—H and a strong C=O at 1780.9 cm^{-1}. ^1H NMR had a singlet at 1.73 and an A_2B_2 pattern at 6.81 and 7.02 ppm (J = 9 Hz). ^{13}C NMR: 28.199 (methyls), 42.029 (quaternary carbon), 119.325 and 127.364 (unsubstituted aromatic), 148.645 and 149.485 (substituted aromatic); the carbonyl carbon was shifted upfield, and revealed by integration to be accidentally equivalent to the 148.645 absorption. A single-crystal X-ray structure has been solved and reveals significant ring strain and transannular coplanarity of the aromatic rings, explaining the shifted C=O stretch, and the NMR data. High-resolution MS: calcd for $C_{32}H_{28}O_6$ 508.1886, found 508.1897. Anal. Calcd: C, 75.57; H, 5.55. Found: C, 75.61; H, 5.86.

Preparation of Linear Oligomers. A reaction was carried out identical with that described above for preparation of macrocyclic carbonates, except that pyridine was used as the amine catalyst rather than triethylamine. Identical reaction workup provided a white solid with mp = 140-145 °C. HPLC analysis (Figure 2) indicated selective formation of linear oligomers, by comparison of retention times and 254/285 nm values to bisphenol A and to authentic linear dimer, trimer, and tetramer. HPLC elution using the same THF/water gradient as for cyclics analysis showed the following pattern:

component	t_R (min)	254/285 nm ratio
Bisphenol A	1.69	0.187
linear dimer	2.077	0.408
linear trimer	2.626	0.679
linear tetramer	3.417	0.879
linear pentamer	4.496	1.39
linear hexamer	5.635	1.47
linear heptamer	6.673	1.61
linear octamer	7.618	1.69
linear nonamer	8.496	2.16
linear decamer	9.326	2.05

FTIR showed an O—H absorption at 3597 and a C=O absorption at 1770.2 cm^{-1}. 300-MHz ^1H NMR, major resonances associated with carbonate linkages: 7.26 (d, J = 8.9, 4 H), 7.18 (d, J = 8.9, 4 H), 1.69 (s, 6 H). 300-MHz ^1H NMR, minor resonances associated with phenolic end groups (about 10%): 7.08 (m), 6.70 (m), and 4.91 (s). ^{13}C NMR: 30.892 (methyls), 42.05 and 42.54 (quaternary carbons), 114.65, 114.78 (phenolic carbon), 119.90-120.75 and 127.52-128.21 (unsubstituted aromatics), 142.20, 148.28-149.03 (substituted aromatics), 152.214 and 153.635 (carbonyls). Field-desorption mass spectrum showed parent peaks at m/e 272, 482, 736, and 990. Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.80; H, 5.42.

Acknowledgment. We thank Thomas L. Evans, Allan R. Shultz, and Rebecca Sawyers for information and technical support in polymerization and cyclization chemistry, and K. Randall Stewart for mechanistic and molecular modeling discussions.

(19) Brunelle, D. J.; Garbauskas, M. F. Manuscript in preparation.

Allene/Haloolefin Electrocyclic Reactions: A New Route to Stable Triarylmethyl Radicals

Ned A. Porter,* Derk J. Hogenkamp, and Farid F. Khouri

Contribution from the Department of Chemistry, Duke University, Durham, North Carolina 27706. *Received July 3, 1989*

Abstract: Electrocyclization of allene 1,1-diphenyl-3-[2-(2-bromoethenyl)phenyl]propadiene (**5**). followed by one-electron reduction with elemental mercury, gives β-naphthyldiphenylmethyl radical **6** in good yield. In the absence of mercury, the only product isolated is the corresponding triarylmethyl halide. Although both reactions presumably involve an intermediate *o*-quinodimethane species, no evidence for this intermediate was found by ^1H NMR or UV spectroscopy. Allene **5** was formed by isomerization of the corresponding alkyne **7** with activated basic alumina. Palladium-catalyzed coupling of iodo chloride **9** and 3,3-diphenylpropyne gave alkyne **7** in 89% yield.

Recent interest in the chemistry of stable triarylmethyl radicals has been stimulated by the suggestion that polyradicals, linked by appropriate groups, might be possible organic ferromagnets.[1] Thus, compounds having multiple carbene or radical functionality

0002-7863/90/1512-2402$02.50/0

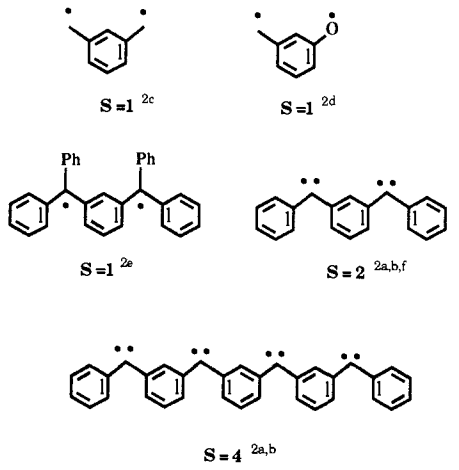
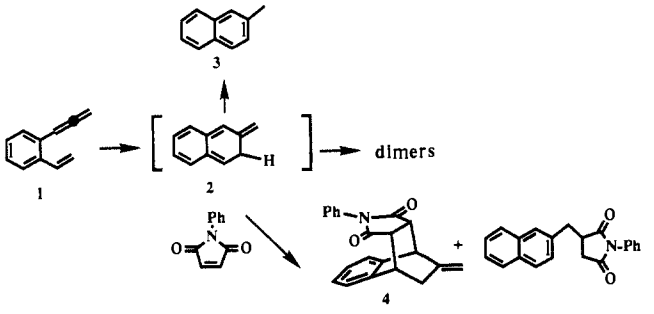


Figure 1.

Scheme I

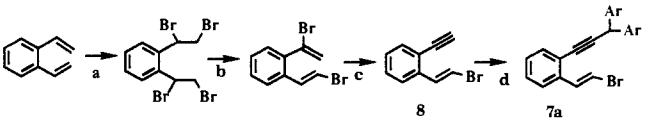


may be high spin if the link between the radical or carbene centers is appropriate.[2] For example, structures shown in Figure 1 are all meta benzene substituted carbenes or radicals, and all are suggested by theory and experiment to have high-spin ground states.

Advances in this field have been limited by synthetic routes to these polyradical and polycarbene systems. Although the polycarbenes have been the focus of many recent studies, the polyradicals have received much less attention. The preparation of triarylmethyl radicals generally involves very labile triarylmethyl halides or alcohols as intermediates and polytriarylmethyl radicals, for example, would not appear to be readily accessible by classical methods developed for the preparation of monoradicals.[3]

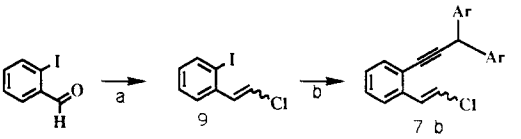
We report here a new route to triarylmethyl radicals, exemplified by β-naphthyldiphenylmethyl **6**. This new method may find application in the synthesis of polyradicals. We require that our route to the radical reveal the reactive leaving group in the last step of the sequence and that prior to this last step, the stability of the functional groups should be appropriate for the coupling reactions necessary for polymer construction. We also require

Scheme II[a]



[a] (a) $2Br_2$; (b) KO-*t*-Bu, 0 °C; (c) KO-*t*-Bu, 100 °C; (d) MeMgBr, CuBr, Ar_2CH–Br.

Scheme III[a]



[a] (a) Ph_3PCHCl; (b) $Pd(Ph_3)_2Cl_2$, CuI, Et_3N, $Ar_2CHC{\equiv}CH$.

that a polymerization strategy for polyradical synthesis should exist and that it be consistent with the synthesis of the monoradical model **6**. With this in mind, we explored the possibility of utilizing electrocyclization processes to convert very stable vinyl halides to unstable preradical species. The precedent for this approach lies in the electrocyclization of allenes, documented by Brinker et al.,[4] who found that *o*-propadienylstyrene (**1**) has a half-life of 1.7 h at 46 °C and gives dimerization, aromatization, Diels–Alder, and ene reaction trapping products resulting from the intermediate **2** (Scheme I). The strategy described here modifies the Brinker electrocyclization by substituting on the vinyl group of **1** with a halide group (X = halide) and on the allene with two terminal aromatic groups as in the structure **5**. Electrocyclization of this vinyl halide in the presence of a reducing agent leads to the stable radical species **6**.

Results

Preparation of Alkyne 7. Two approaches were taken for the synthesis of the allene **5**, both proceeding through the alkynes **7a** or **7b**. Both approaches involved conversion of the alkyne **7** to the allene **5**, a procedure that has good precedent in the isomerization of triphenylpropyne to triphenylpropadiene via base-catalyzed 1,3-H migration using amines[5] or activated basic alumina[6] or photochemically with 1,4-dicyanonaphthalene.[7] Alkyne **7a** was prepared by alkylation of 1-[2-(2(*E*)-bromoethenyl)-phenyl]acetylene[8] (**8**) with diarylbromomethane. Treatment of **8** with EtMgBr in THF in the presence of 10 mol % CuBr, gave **7a** with Ar = Ph or Ar = *p-tert*-butylphenyl, although this is a capricious reaction and yields varied from 40% to 62% for this step. The synthesis of **7a** is outlined in Scheme II.

The route to **7b** proceeds via reaction of the iodo chloride **9** with 3,3-diarylpropyne by using a catalytic palladium coupling procedure.[9] Using catalytic $Pd(PPh_3)_2Cl_2$ and CuI in Et_3N, the

(1) (a) Alexander, S. A.; Klein, D. J. *J. Am. Chem. Soc.* **1988**, *110*, 3401. (b) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1978**, *100*, 388. (c) Peterson, I. *ScienceNews* April 18, **1987**, *131*, 252. (d) Mishima, A.; Nasu, K. *Syn. Met.* **1987**, *22*, 23. (e) Breslow, R. *Pure Appl. Chem.* **1982**, *54*, 927. (f) Mataga, N. *Theor. Chim. Acta* **1968**, *10*, 372. (g) McConnell, H. M. *J. Chem. Phys.* **1963**, *39*, 1910. (h) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* **1988**, *88*, 201. (i) See also: *Abstracts of Papers*, 197th National Meeting of the American Chemical Society, Dallas, TX, April 9, 1989; American Chemical Society: Washington, DC, 1989; *Symposium on Ferromagnetic and High Spin Molecular Based Materials.*

(2) (a) Iwamura, H. *Pure Appl. Chem.* **1986**, *58*, 187. (b) Sugawara, T.; Tukada, H.; Izuoka, A.; Murata, S.; Iwamura, H. *J. Am. Chem. Soc.* **1986**, *108*, 4272. (c) Wright, B. B.; Platz, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 628. (d) Rule, M.; Mailin, A. R.; Dougherty, D. A.; Hilinsky, E.; Berson, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 5098. (e) Kothe, G.; Denkel, K.-H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 906. (f) Wasserman, E.; Murray, R. W.; Jager, W. A.; Trozzolo, A. M.; Smolinsky, G. *J. Am. Chem. Soc.* **1967**, *89*, 5076.

(3) Review of the chemistry of trityl radicals: (a) Sholle, V. D.; Rozantsev, E. G. *Russ. Chem. Rev.* **1973**, *42*, 1011. (b) McBride, J. M. *Tetrahedron* **1974**, *30*, 2009. Preparation from triarylmethyl carbinols: (c) Gomberg, M.; Cone, L. H. *Ber. Dtsch. Chem. Ges.* **1904**, *37*, 3538. (d) Neumann, W. P.; Uzick, W.; Zarkadis, A. K. *J. Am. Chem. Soc.* **1986**, *108*, 3762.

(4) (a) Brinker, U. H.; Wilk, G.; Gomann, K. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 868. Other examples of allene cyclizations: (b) Reischl, W.; Okamura, W. H. *J. Am. Chem. Soc.* **1982**, *104*, 6115. (c) Miller, B.; Baghdadchi, J. *J. Org. Chem.* **1987**, *52*, 2391. Allene electrocyclic reactions have also been used to prepare biradicals; see: (d) Garratt, P. J.; Neoh, S. B. *J. Org. Chem.* **1979**, *44*, 2667. (e) See also: Stone, K. J.; Greenberg, M. M.; Blackstock, S. C.; Berson, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 3659.

(5) Cram, D. J.; Willey, F.; Fischer, H. P.; Relles, H. M.; Scott, D. A. *J. Am. Chem. Soc.* **1966**, *88*, 2759.

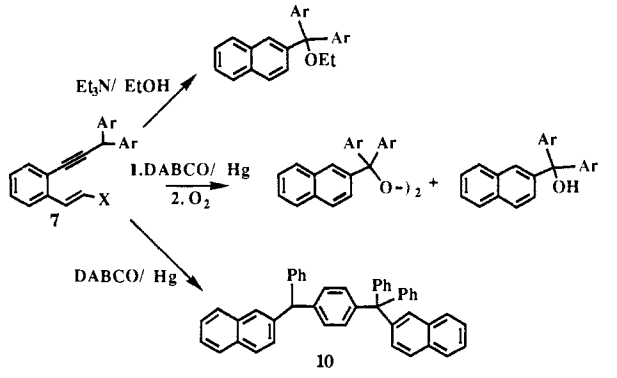
(6) Jacobs, T. L.; Danker, D.; Singer, S. *Tetrahedron* **1964**, *20*, 2177.

(7) Klett, M. W.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 6615.

(8) Behr, O. M.; Eglinton, G.; Lardy, I. A.; Raphael, R. A. *J. Chem. Soc.* **1964**, 1151.

(9) (a) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis*, **1980**, 627. (b) The preparation of 3,3-diphenylpropyne involved the alkylation of (trimethylsilyl)acetylene with diphenylbromomethane, as in the synthesis of **5b**, followed by removal of the trimethylsilyl group with $AgNO_3$ and KCN (Schmidt, H. M.; Arens, J. F. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 1138). Other methods for the deprotection led to the formation of 1,1-diphenylpropadiene.

Scheme IV



reaction is clean, spot to spot on thin layer, and a 89% yield of the alkyne **7b** is isolated after column chromatography on silica gel. The iodo chloride **9** is prepared as a mixture of cis and trans isomers and the coupling works well for either geometric isomer. The synthesis of **7b** is outlined in Scheme III.

While a synthesis of **7b** has been developed that proceeds in high yield, several modifications of the palladium coupling procedure have been reported in the literature that we have not yet explored, and the method reported here is by no means maximized.

Alkyne Isomerization. Tertiary amines[5] were found to be effective catalysts for the isomerization of alkyne **7** to propadiene **5**, X = Br or Cl. Reaction of *trans*-**7** (X = Br or Cl) with 10 equiv of Et_3N in refluxing EtOH gave β-naphthyldiphenylmethyl ethyl ether, identified by comparison with authentic material.[10,11] Isolation of this ether supports the notion that the propadiene **5** does undergo the electrocyclization to give a *o*-quinodimethane, which then reacts with EtOH (see Discussion section). The cis isomer of **7b** gave only minor amounts of ether under these conditions, and the products in the reaction may result from initial elimination of the chloride. The isomerization of *trans*-**7** was repeated in the presence of Hg as one-electron donor. Reaction of *trans*-**7** with excess 1,4-diazobicyclo[2.2.2]octane (DABCO) and mercury in THF followed by exposure of this solution to air gave β-naphthyldiphenylmethylcarbinol[10] and bis(β-naphthyldiphenylmethyl) peroxide. These products accounted for 79% of the starting alkyne **7**. Longer reaction times gave rise to increasing amounts of [4-(β-naphthyldiphenylmethyl)phenyl]-β-naphthylphenylmethane (**10**), which could not be separated from the peroxide by HPLC (Scheme IV). The hydrocarbon product **10** can be independently prepared by DABCO treatment of authentic **6** prepared from β-naphthyldiphenylmethyl chloride/mercury. Substitution of *p-tert*-butyl groups on the aryl substituents of **6** successfully avoids formation of the *p-tert*-butyl analogue of **10**.

With tertiary amine catalysts, we observed no allene under any of the conditions explored. Activated basic alumina was, however, successfully employed to isomerize **7** to the corresponding allene (**5**). Jacobs et al.[6] found that triphenylpropyne isomerizes to triphenylallene in 83% yield on a column of activated basic alumina. A solution of **7** (X = Br or Cl, Ar = Ph or *p-tert*-butylphenyl) in dry petroleum ether or toluene at −20 °C smoothly reacted over 30 min in the presence of activated Brockmann activity I alumina (further activated by heating at 400 °C for 24 h under vacuum), giving 1,1-diphenyl-3-[2-(2-bromoethenyl)-phenyl]propadiene (**5**) as the only product by ^1H NMR (Scheme V). The propadiene was isolated by adding cold (−20 °C) THF to the reaction mixture, decanting the solution from the alumina, and removing the solvent in vacuo (both operations run at −20 °C). The structure of **5** was confirmed by low-temperature ^{13}C NMR which shows a central allenic carbon at 209.5 ppm. Mass recovery is low if the alumina is not washed with THF after the reaction is complete and no isomerization of **7** is observed with THF as the solvent. When the allene **5** is allowed to warm to room temperature in the presence of alumina, β-naphthyldiphenylmethylcarbinol is isolated in 81% yield. Analogous chemistry is observed for the alkynes with X = Br or Cl.

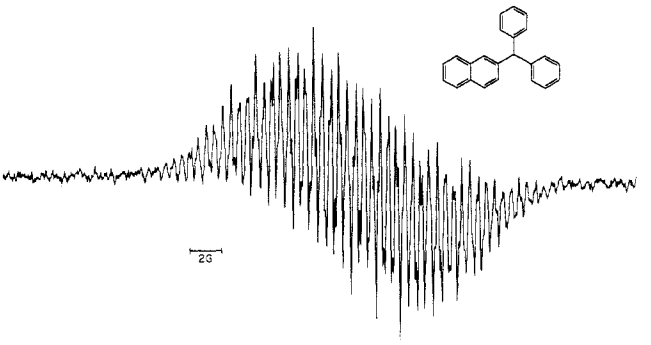
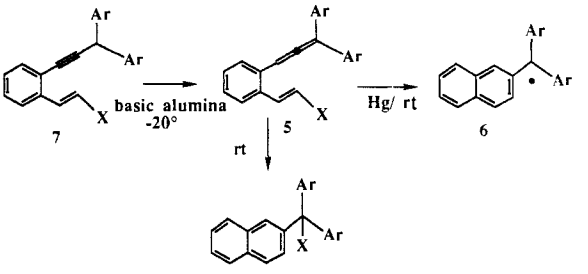


Figure 2. EPR spectrum from reaction of allene **5b** with mercury.

Scheme V



The decomposition of propadiene **5** at room temperature was followed by ^1H NMR and by UV spectroscopy. By NMR, the only product detected from **7a**, Ar = Ph, was β-naphthyldiphenylmethyl bromide,[10] no evidence for an intermediate in the reaction was found. By UV, the disappearance of the electronic spectrum of **5** (λ_{max} = 230, 270 nm) was paralleled by an increase in a species with a UV (λ_{max} = 230 nm) identical with that of the halide. An isosbestic point at 236 nm was observed, and the conversion was cleanly first order. No longer wavelength absorption that could be attributed to a *o*-quinodimethane intermediate (see Discussion section) was observed. The rate of disappearance of **5** was 10^{-4} s^{-1} (half-life = 1.9 h) at 23 °C.

The isolation of bis(triarylmethyl) peroxides and the hydrocarbon **10** in previous experiments are indirect evidence for the formation of β-naphthyldiphenylmethyl radical from alkyne **7** via propadiene **5**. For direct evidence, a THF solution of **5**, prepared by alumina isomerization of **7**, was allowed to stir with excess mercury at room temperature. A yellow-brown mixture formed almost immediately, and the color deepened as the mixture was allowed to stir. After filtration, the solution gave a very strong and highly structured EPR spectrum, identical with an EPR spectrum obtained from "authentic" β-naphthyldiphenylmethyl radical prepared from the corresponding chloride (Figure 2). The intensity of EPR signals obtained from 0.5-mmol solutions of **5** and triarylmethyl chloride were identical, indicating that the two methods give comparable yields of radical **6**. It should be emphasized that we have no data to present indicating whether the *o*-quinodimethane or the triarylmethyl halide is the immediate precursor to the triarylmethyl radical.

Discussion

The new *o*-quinodimethane halide approach to stable radicals reported here is an example of a general strategy that relies on the conversion of stable vinyl–X groups to unstable pentadienyl–X or heptadienyl–X structures as the key step in the synthesis of the immediate radical precursor.

Several concerted reaction sequences may fall into this general framework. Electrocyclic reactions and cycloadditions, for example, might be applied to the production of stable radical species by applications designed to convert vinyl-X to allyl-X. Thus, the Gomberg approach[3] to the synthesis of triarylmethyl radicals involves reductive cleavage of triarylmethyl halide to the radical while the electrocyclic and cycloaddition strategies proceed through

(10) Gomberg, M.; Sullivan, F. W., Jr. *J. Am. Chem. Soc.* **1922**, *44*, 1810.
(11) Chaundary, S. K.; Hernandez, O. *Tetrahedron Lett.* **1979**, 95.

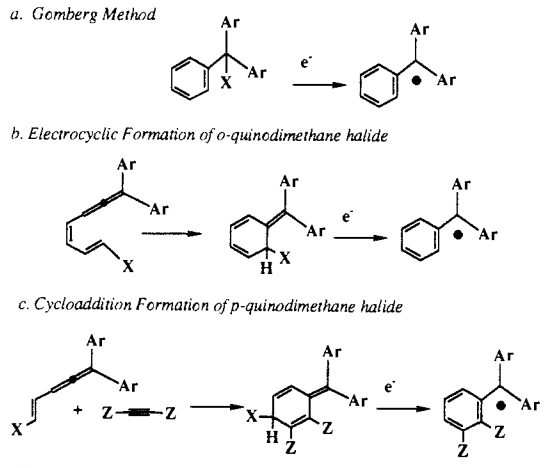


Figure 3.

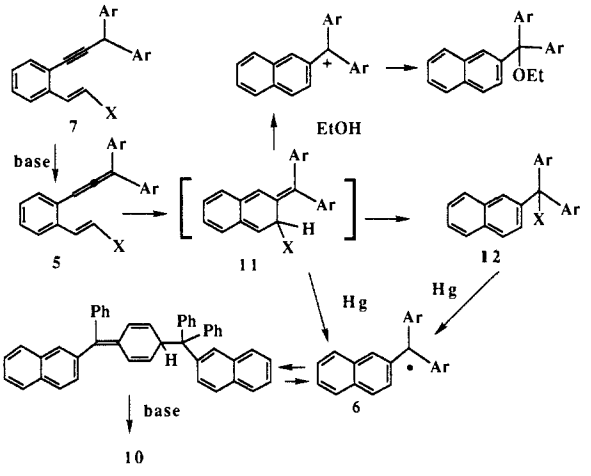


Figure 4.

formation of an *o*-quinodimethane halide as described in Figure 3.

If syntheses are designed to provide the *o*-quinodimethane halides, it seems reasonable to expect that these nonaromatic compounds will be readily converted to the stable radical species by analogy to the aromatic Gomberg precursors. This expectation is confirmed by the studies reported here. The electrocyclic approach is highly efficient. Yields in the cyclization–reduction sequence are at least comparable to those obtained in the reaction of triarylmethyl chloride with mercury. Under all conditions utilized, only aromatic compounds were isolated from the allene/olefin electrocyclization and in several of the reactions examined the naphthyldiphenylmethyl products isolated accounted for greater than 80% of the starting material.

In Figure 4 is presented a mechanistic proposal that accounts for the chemistry observed from the alkyne **7**. Electrocyclization of the allene **5** provides the *o*-quinodimethane structure **11** which then serves as a key intermediate for the formation of the aromatic triarylmethyl halide **12**, the carbocation, and the radical **6**. While **11** must be an intermediate in the conversion of **5** to the stable radical, *we have no evidence to present concerning the question of whether* ***11*** *or* ***12*** *is the immediate precursor to* ***6*** in the presence of Hg. When formed, the radical **6** is in equilibrium with the radical dimer which, in the presence of base, gives the hydrocarbon **10**. Dimerization of the naphthyldiphenylmethyl radical must occur on the phenyl rather than on the naphthyl ring since we see no hydrocarbon isomer of **10** that results from naphthyl ring coupling.

The stimulus for the development of this alternate strategy for stable radical preparation comes from interest in the preparation of meta benzene substituted polyradicals as potential ferromagnetic materials. The potential advantages of this synthesis of stable triarylmethyl radicals comes from a strategy for polymer synthesis

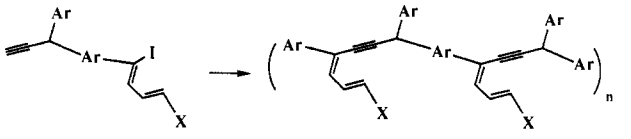


Figure 5.

that derives from this approach and that may be appropriate for polyradical synthesis. Thus, palladium-catalyzed polymerization[12] of bifunctional monomers may provide polyalkyne precursors analogous to **7**. One example of such a polymerization is described in Figure 5.

The alkyne **7** is indefinitely stable. Polymeric alkynes with structures like **7**, potentially available from Pd-catalyzed polymerizations, would thus be expected to be stable and only after base-catalyzed isomerization would the reactive halide be revealed. This general strategy may thus be useful in the preparation of multiradical structures proposed as potential organic ferromagnets, and we are currently pursuing this strategy.

Experimental Section

General Procedures. ^1H (300 MHz) and ^{13}C (75.43 MHz) NMR spectra were recorded on a Varian XL-300 spectrometer with Me_4Si as internal standard in $CDCl_3$. Electron-impact (EI), chemical-ionization (CI), and high-resolution mass spectra (HRMS) were obtained on a VG-ZAB 1F spectrometer. IR spectra were recorded on a Bomem Michelson Series FT-IR. ESR spectra were obtained on a Varian E-9 ESR spectrometer. GC analyses were performed with use of a Hewlett-Packard 5890 gas chromatograph with an HP-1 cross-linked methyl silicone gum capillary column. An ISCO Model 2350 with a Waters differential refractometer and a preparative Rainin Dynamax 60-A column were used for HPLC separations. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are corrected. THF was distilled from sodium benzophenone immediately before use. Toluene and triethylamine were distilled from sodium. Diphenylbromomethane (Aldrich, 98%) was purified by bulb-to-bulb distillation. β-Naphthyldiphenylmethyl bromide and chloride were prepared from the carbinol by using the method of Gomberg.[10] β-Naphthyldiphenylmethyl ethyl ether was prepared from the corresponding chloride by using the procedure of Chaundary et al.[11] Copper iodide was purified by using the Inorganic Synthesis procedure.[13] All other reagents were of the highest grade available and were used without further purification unless otherwise indicated. Elemental analyses were performed by Atlantic Microlab (Atlanta, GA).

1-[2-(2(*E*)-Bromoethenyl)phenyl]-3,3-diphenylpropyne (7a, Ar = Ph). To a 3.0 M solution of CH_3MgBr in ether (2.60 mL, 7.80 mmol) and 2.5 mL of THF was added a solution of 2-(2(*E*)-bromoethenyl)phenylacetylene[8] (1.54 g, 7.45 mmol) dissolved in 1.5 mL of THF. The resulting mixture was heated to 60 °C for 45 min and allowed to cool. Once at room temperature, CuBr (50 mg, 0.35 mmol) was added as a solid in one portion. After the mixture was stirred for 10 min, a solution of diphenylbromomethane (1.86 g, 7.53 mmol) in 2.0 mL of THF was added via syringe over 25 min. A brown mixture formed and was heated at 60 °C for 45 min. Once at room temperature, the reaction was treated with a saturated NH_4Cl solution and extracted with ether. The organic layer was separated, washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was adsorbed onto flash silica gel and chromatographed (flash silica gel; 100% hexane), affording 1.27 g (46%) of alkyne **7a** (Ar = Ph) as a pale yellow oil. Recrystallization from petroleum ether gave a white solid: mp 42–44 °C; ^1H NMR δ 7.47 (d, 1 H, *J* = 14.0 Hz), 7.36–7.09 (m, 14 H), 6.74 (d, 1 H, *J* = 14.0 Hz), 5.16 (s, 1 H); ^{13}C NMR 141.4, 137.4, 135.7, 132.7, 128.7, 128.2, 127.8, 126.9, 125.2, 121.6, 108.6, 95.6, 83.0, 44.0 ppm; UV (hexane, λ_{max} [E]) 242 nm (35×10^4), 272 (1.8×10^4); MS(CI) *m/e* 392 ($M + NH_4^+$), 373 ($M + H^+$). Anal. Calcd for $C_{23}H_{17}Br$: C, 74.00; H, 4.59. Found: C, 74.10; H, 4.60.

1-[2-(2(*E*)-Bromoethenyl)phenyl]-3,3-bis(4-*tert*-butylphenyl)propyne (7a, Ar = 4-*tert*-Butylphenyl). By use of the procedure described above, reaction of **8** with bis(4-*tert*-butylphenyl)bromomethane[14] gave a 64% yield of the propyne as an off-white foam: ^1H NMR δ 7.55 (d, 1 H, *J* = 13.9 Hz), 7.46–7.18 (m, 12 H), 6.86 (dd, 1 H, *J* = 14.0, 1.3 Hz), 5.20

(12) Trumbo, D. L.; Marvel, C. S. *J. Polym. Sci. A* **1987**, *25*, 1027.
(13) Kauffman, G. B.; Fang, L. Y. *Inorg. Synth.* **1983**, *22*, 101.
(14) (a) Smith, W. B.; Harris, M. C. *J. Org. Chem.* **1983**, *48*, 4959. (b) Deno, N. C.; Jaruzelski, J. J.; Schriesheim, A. *J. Am. Chem. Soc.* **1955**, *77*, 3044.

(s, 1 H), 1.29 (s, 18 H); ^{13}C NMR 149.65, 138.52, 137.43, 135.79, 132.73, 128.165, 127.78, 127.44, 125.64, 125.24, 121.81, 128.49, 96.29, 82.47, 43.14, 34.43, 31.36 ppm. Anal. Calcd for $C_{31}H_{33}Br$: C, 76.69; H, 6.85. Found: C, 76.93; H, 6.94.

2-Iodo-1-(2-chloroethenyl)benzene (9). To a suspension of (chloromethyl)triphenylphosphonium chloride (0.765 g, 2.20 mmol) in 5 mL of THF at 0 °C was added 4.5 mL (2.2 mmol) of a 0.5 M solution of potassium *tert*-butoxide in THF. The resulting red-orange mixture was allowed to warm to room temperature. A solution of 2-iodobenzaldehyde (98 mg, 0.42 mmol) in 1.0 mL of THF was added via syringe, giving a light yellow mixture. The reaction was then poured into ice-cold water/EtOAc. The organic layer was separated, washed with a saturated NaCl solution, dried (MgSO4), and concentrated in vacuo. The residue was chromatographed on flash silica gel (100% hexane), giving 96 mg (86%) of the desired vinyl chloride[16] as a 2.2:1 mixture of cis and trans isomers by GC. The two isomers were separated by normal-phase HPLC on preparative scale with a Dynamax 60A column (eluent 100% hexane, 3.00 mL/min). Retention times for the cis and trans isomers are 45.3 and 50.5 min, respectively.

The vinyl chlorides could also be prepared from the aldehyde with $Cr^{II}Cl_2$ and $CHCl_3$[15]. A solution of aldehyde (227 mg, 0.978 mmol) in 4.5 mL of dry THF containing 157 μL (234 mg, 1.957 mmol) of dry $CHCl_3$ was added to a suspension of $Cr^{II}Cl_2$ (0.693 g, 5.64 mmol) in 9.0 mL of THF at 0 °C. The reaction was allowed to come to room temperature and was then heated at 65 °C for 2.5 h. Once at room temperature, the reaction mixture was poured into an ice-cold water/ether mixture. The aqueous layer was separated and washed with ether. The organic layers were then combined, washed with water and a brine solution, dried ($MgSO_4$), and concentrated. Column chromatography (flash silica gel; 100% hexane) gave a mixture of trans and cis isomers, ratio 1.8:1 by GC (isothermal 150 °C). HPLC as described above gave 96 mg of the trans isomer and 56 mg of the cis isomer, total yield 59%.

Cis isomer: ^{1}H NMR δ 7.87 (d, 1 H, J = 7.9 Hz), 7.72 (dd, 1 H, J = 7.8, 1.5 Hz), 7.36 (dt, 1 H, J = 7.6, 0.7 Hz), 6.99 (dt, 1 H, J = 7.7, 1.7 Hz), 6.72 (d, 1 H, J = 8.1 Hz), 6.37 (d, 1 H, J = 8.0 Hz); IR (neat) 3062, 1617, 1455, 1430, 1422, 1334, 1010, 867, 841, 756, 733, 695, 657 cm^{-1}.

Trans isomer: ^{1}H NMR δ 7.83 (dd, 1 H, J = 8.0, 0.9 Hz), 7.03 (d, 1 H, J = 13.4 Hz), 6.96 (dt, 1 H, J = 7.5, 1.9 Hz), 6.53 (d, 1 H, J = 13.5 Hz); ^{13}C NMR 139.59, 138.27, 136.94, 129.56, 128.45, 126.54, 121.22, 98.83 ppm; IR (neat) 3080, 1577, 1456, 1427, 1272, 1231, 1006, 940, 923, 846, 812, 738, 645 cm^{-1}.

1-(Trimethylsilyl)-3,3-diphenylpropyne. To a 2.0 M solution of EtMgBr in THF (3.0 mL, 6.0 mmol) at 10 °C was added neat (trimethylsilyl)acetylene (0.85 mL, 0.59 g, 6.01 mmol) via syringe. The resulting mixture was allowed to warm to room temperature and then treated with CuBr (Aldrich, 99.999%; 70 mg, 0.49 mmol). After the mixture was stirred for 10 min, diphenylbromomethane (1.49 g, 6.03 mmol), dissolved in 4 mL of dry THF, was added over a 5-min period. A solution formed and was heated at 60 °C for 2 h and 20 min, while the alkylation was monitored by GC. The reaction mixture was cooled to 0 °C and poured into an ice-cold 5% HCl solution/hexane mixture. The hexane layer was separated, and the aqueous layer was washed twice with ether. The combined organic layers were then washed with water and brine, dried ($MgSO_4$), and concentrated. The crude alkyne was adsorbed on flash silica gel and chromatographed (flash silica gel; 100% hexane), affording 0.959 g (60%) of the propyne as a clear oil: ^{1}H NMR δ 7.40–7.18 (m, 10 H), 5.02 (s, 1 H), 0.20 (s, 9 H); ^{13}C NMR 141.5, 128.4, 127.8, 1326.8, 106.6, 89.0, 44.1, 0.10 ppm; IR (neat) 3062, 3028, 2959, 2171, 1598, 1493, 1452, 1250, 1042, 1025, 849, 759, 737 cm^{-1}. Anal. Calcd for $C_{18}H_{20}Si$: C, 81.76; H, 7.62. Found: C, 81.68; H, 7.64.

3,3-Diphenylpropyne. A solution of $AgNO_3$ (0.88 g, 5.18 mmol) in 13.5 mL of 2:1 EtOH/H_2O was added to 1-(trimethylsilyl)-3,3-diphenylpropyne, dissolved in 4.5 mL of EtOH. A white gelatinous mixture formed and was stirred at room temperature for 10 min and then was treated with KCN (1.67 g, 25.6 mmol), dissolved in 5.5 mL of H_2O. An additional 3 mL of EtOH was added to give a clear solution. After stirring for 1.5 h, the reaction was poured into a separatory funnel containing 50 mL of 1:1 hexane/H_2O. The aqueous layer was separated and washed with hexane (2 × 25 mL). The hexane layers were combined, washed with water and brine, and dried ($MgSO_4$). The hexane was removed in vacuo, and the residue chromatographed (100% hexane), giving 290 mg (77%) of 3,3-diphenylpropyne as a clear oil that solidified on standing: mp 50–52 °C (lit.[17] mp 48–49 °C); ^{1}H NMR δ 7.40–7.23 (m, 10 H), 5.01 (d, 1 H, J = 2.4 Hz), 2.49 (d, 1 H, J = 2.6 Hz).

1-[2-(2(*Z*)-Chloroethenyl)phenyl]-3,3-diphenylpropyne. To the *cis*-iodo chloride **9** (32.6 mg, 0.12 mmol) and 3,3-diphenylpropyne (26 mg, 0.135 mmol), dissolved in 0.75 mL of dry Et_3N, was added $Pd(PPh_3)_2Cl_2$ and CuI (<1 mg of each, ~1 mol %). The resulting mixture was stirred in the dark. After 15 min, an off-white precipitate formed. After an additional 1 h and 10 min, the mixture was concentrated in vacuo, and the residue triturated with hexane. The yellow hexane wash was added to a flash silica gel column and eluted with hexane. The *cis*-propyne (36 mg, 89%) was isolated as a light yellow oil: ^{1}H NMR δ 8.00 (d, 1 H, J = 7.9 Hz), 7.50 (d, 1 H, J = 7.7 Hz), 7.43 (d, 4 H, J = 7.7 Hz), 7.32 (t, 5 H, J = 7.6 Hz), 7.23 (t, 3 H, J = 6.8 Hz), 7.04 (d, 1 H, J = 8.2 Hz), 6.29 (d, 1 H, J = 8.2 Hz), 5.24 (s, 1 H); ^{13}C NMR 141.54, 135.66, 132.32, 128.63, 127.87, 127.86, 127.79, 127.69, 126.95, 123.37, 118.74, 95.64, 83.17, 43.94 ppm; IR (neat) 3062, 3027, 2222, 1602, 1492, 1473, 1451, 1338, 1077, 1031, 847, 767, 752, 699, 643, 611 cm^{-1}; MS (Cl) m/e 346 [(M + NH_4)$^+$, 100], 348 (35), 329 (MH^+, 10), 331 (3); HRMS calcd for (M + NH_4)$^+$ 346.1362, found 326.1370.

1-[2-(2(*E*)-Chloroethenyl)phenyl]-3,3-diphenylpropyne. By use of the procedure described for the *Z* isomer, the *E* isomer was prepared in 73% yield after column chromatography (flash silica gel; 100% hexane). Recrystallization from petroleum ether gave a light yellow solid: mp 50–51 °C; ^{1}H NMR δ 7.48–7.44 (m, 5 H), 7.37–7.30 (m, 5 H), 7.27–7.18 (m, 5 H), 6.72 (d, 1 H, J = 13.7 Hz), 5.27 (s, 1 H); ^{13}C NMR 141.46, 136.49, 132.75, 131.84, 128.73, 128.29, 127.87, 127.73, 126.99, 125.20, 121.77, 120.53, 95.59, 83.05, 43.99 ppm; MS (Cl) m/e 346 [(M + NH_4)$^+$, 100], 348 (30), 329 (MH^+, 11), 331 (3). Anal. Calcd for $C_{23}H_{17}Cl$: C, 84.01; H, 5.21. Found: C, 83.78; H, 5.24.

Reaction of 7a with EtOH/Et_3N. A suspension of the propyne **7a** (197 mg, 0.528 mmol) in 2.5 mL of dry EtOH was treated with dry Et_3N (10 equiv, 0.736 mL, 0.534 g, 5.28 mmol) and placed in an oil bath at 95 °C. After 3.5 h, TLC showed that the reaction was complete. Once at room temperature, the cloudy solution was diluted with ether and filtered to remove precipitated triethylammonium hydrobromide. The ether was evaporated from the filtrate, and the residue was dissolved in a minimum of hexane and chromatographed (flash silica gel; gradient from 100% hexane to 10% EtOAc/hexane). Ethyl β-naphthyldiphenylmethyl ether was isolated as a semisolid, weight 154 mg (86%). Recrystallization from EtOH gave a white solid: mp 110–114 °C (lit.[10] mp 114 °C); ^{1}H NMR δ 7.95 (s, 1 H), 7.76–7.67 (m, 3 H), 7.46–7.15 (m, 13 H), 3.10 (q, 2 H, J = 7.0 Hz), 1.22 (t, 3 H, J = 7.0 Hz); ^{13}C NMR 144.27, 141.97, 132.82, 132.31, 128.69, 128.38, 127.78, 127.39, 127.33, 127.05, 126.90, 125.98, 125.89, 86.66, 59.59, 15.35 ppm; MS (Cl) m/e 293 (M^+ – OEt).

Reaction of 1-[2-(2(*E*)-chloroethenyl)phenyl]-3,3-diphenylpropyne with EtOH/Et_3N under these conditions gave the ethyl ether in 92% yield.

Reaction of 7a with DABCO and Hg. A. Trapping with O_2. A solution of **7a** (140 mg, 0.375 mmol) in 20 mL of freshly distilled THF was rigorously degassed in five freeze–pump–thaw cycles. The solution was then added to mercury metal (0.205 g, 1.02 mmol) and DABCO (104 mg, 0.931 mmol). A light yellow-brown mixture formed immediately and was stirred in the dark for 12 h. The reaction was then diluted with 20 mL of dry, degassed THF, and the deeply colored mixture was decanted. Exposure of the dark yellow-brown solution to dry air gave a light yellow solution. The solvent was removed in vacuo, and the residue was absorbed on fresh silica and chromatographed (flash silica gel; 10% EtOAc/hexane). β-Naphthyldiphenylmethylcarbinol (38 mg, 33% yield) was isolated along with 54 mg (46%) of bis(β-naphthyldiphenylmethyl) peroxide, mp 161.5–163.5 °C (lit.[10] mp 166 °C), after washing with ether. These products account for a total of 79% of the starting alkyne. A smaller scale reaction gave an 85% combined yield of alcohol and peroxide.

B. Isolation of Rearranged Dimer 10. Reaction of a solution of **7a** (74 mg, 0.198 mmol) in 1.0 mL of dry, degassed ether with mercury (129 mg, 0.643 mmol) and DABCO (71 mg, 0.633 mmol) at room temperature for 48 h, after column chromatography (flash silica gel, 10% benzene/hexane) gave 33 mg (60%) of a mixture of dialkyl peroxide and **10**, identified by ^{1}H NMR (methine resonance at 5.67 ppm). Analytical HPLC allowed the separation of a small amount (<1 mg) of **10** uncontaminated by peroxide (1:2 benzene/hexane; 1.0 mL/min). The ^{1}H NMR is identical with **10** prepared as outlined below.

Preparation of 10 from β-Naphthyldiphenylmethyl Chloride. The triarylmethyl chloride (506 mg, 1.54 mmol), dissolved in 2.0 mL of dry, degassed ether, was treated with mercury (0.925 g, 4.61 mmol) and DABCO (0.794 g, 7.08 mmol). The resulting yellow-brown mixture was stirred in the dark for 72 h, giving an orange mixture which did not change color on exposure to air. The unreactive mercury and mercury salts were removed by filtration, and the filtrate was removed in vacuo. Column chromatography on the residue (flash silica gel; 20% benzene/hexane) gave 182 mg (40%) of **10**. Recrystallization from ether/petroleum ether gave a white solid: mp softens at 167 °C, melts 172–176

(15) Takai, K.; Nitta, K.; Utimoto, K. *J. Am. Chem. Soc.* **1986**, *108*, 7408.
(16) Weitzenbock, R. *Monatsh. Chem.* **1918**, *39*, 307.
(17) McComsey, D. F.; Reitz, A. B.; Maryanoff, C. A.; Maryanoff, B. E. *Synth. Commun.* **1986**, *16*, 1535.

°C dec; ^{1}H NMR δ 7.81-7.65 (m, 7 H), 7.48-7.42 (m, 5 H), 7.33-7.16 (m, 19 H), 7.05 (d, 2 H, J = 8.3 Hz), 5.68 (s, 1 H); ^{13}C NMR 146.5 (quaternary), 144.6 (quaternary), 144.4 (quaternary), 143.7 (quaternary), 141.5 (quaternary), 141.2 (quaternary), 133.3 (quaternary), 132.9 (quaternary), 132.1 (quaternary), 131.7 (quaternary), 131.2, 130.9, 129.5, 128.6, 128.33, 128.29, 128.0, 127.9, 127.8, 127.5, 127.2, 16.5, 126.4, 126.0, 125.97, 125.8, 125.6, 64.7 (quaternary), 56.5 ppm; MS(Cl) m/e 604 (M + NH_4^+). Anal. Calcd for $C_{46}H_{34}$: C, 94.16; H, 5.84. Found: C, 94.10; H, 5.85.

Reaction of 7a (Ar = 4-*tert*-Butylphenyl) with DABCO and Hg. A solution of the propyne **7a** (56 mg, 0.115 mmol) in 10 mL of dry, degassed THF was treated with Hg metal (106 mg, 0.53 mmol) and DABCO (86 mg, 0.767 mmol). The mixture was heated in a sealed tube at 70 °C for 22 h. The tube was then opened and the mixture was filtered. By ^{1}H NMR, the crude reaction showed no methine proton characteristic of rearranged dimer. Concentration in vacuo and column chromatography of the residue (flash silica gel; gradient, 2.5-50% benzene/hexane) gave 14.7 mg (30%) of bis[β-naphthyl(4-*tert*-butylphenyl)methyl] peroxide: mp 181-183 °C dec; ^{1}H NMR δ 7.74 (d, 1 H, J = 7.5 Hz), 7.60-7.58 (m, 3 H), 7.39 (m, 2 H), 7.27 (dd, J = 8.7, 1.8 Hz), 7.21 (d, 4 H, J = 8.6 Hz), 7.15 (d, 4 H, J = 8.6 Hz), 1.30 (s, 18 H).

Isomerization of Alkyne 7 to Propadiene 5 with Alumina. Alkyne **7a** (11 mg, 0.030 mmol) was added as a solid in one portion to 389 mg of basic alumina (Brockman activity I, further activated by heating at 400 °C at 0.05 mmHg for 24 h) suspended in 0.7 mL of dry toluene (or petroleum ether) at -20 °C. The resulting mixture was vigorously stirred at -20 °C for 25 min. By TLC, the alkyne was consumed and a slightly higher R_f UV-active spot was present (10% benzene/hexane). Cold THF (<-20 °C) was then added and the solvent was decanted from the alumina via cannula. The solvent was removed in vacuo to give pure propadiene as a clear oil. Recrystallization from THF/petroleum ether (-80 °C) gave a white solid: ^{1}H NMR ($CDCl_3$, -25 °C) δ 7.45-7.20 (m, 15 H), 6.92 (s, 1 H), 6.67 (d, 1 H, J = 13.7 Hz); ^{13}C NMR ($CDCl_3$, -25 °C), 209.3, 135.7, 135.3, 134.1, 130.9, 128.5, 128.4, 128.0, 127.6, 127.3, 113.0, 108.3, 94.7 ppm.

EPR Spectra of β-Naphthyldiphenylmethyl Radical 6. A. From Allene 7a. To a suspension of activated basic alumina (2.0 g) in 2.5 mL of dry toluene at -20 °C was added **7a** (34 mg, 0.091 mmol) in one portion as a solid. This mixture was vigorously stirred until TLC showed no residual alkyne (10 min). The reaction was diluted with 2.5 mL of cold (-20 °C) toluene. The supernatent liquid was transferred to an appratus consisting of two interconnected Schlenk tubes, one of which was further connected to a vacuum manifold and to an adaptor leading to an EPR cell (Wilmad glass flat cell, WG-812-Q-Suprasil). The bulb containing the allene **5** was isolated from the vacuum manifold, and the second bulb was charged with mercury metal (0.29 g, 1.45 mmol). The mercury metal was added to the toluene solution of **5**, and the yellow mixture was stirred at room temperature for 19.5 h in the dark. The resulting yellow-brown mixture was decanted into the second bulb containing 19 mL of dry, degassed toluene. The solution of **6** was poured into the EPR cell and its EPR spectrum was taken (radical concentration is 5 mM if the dimer of **6** is 100% dissociated). More fine structure was resolved if this solution was diluted 10-fold. The EPR of this 0.5 mM solution is shown in Figure 2.

B. From β-Naphthyldiphenylmethyl Chloride. Via the procedure described for the preparation of **6** from the allene **5**, reaction of β-naphthyldiphenylmethyl chloride (freshly recrystallized from petroleum ether; 33 mg, 0.10 mmol) gave an EPR signal identical with that in Figure 2. The intensity of the spectra obtained from **5** and from the triarylmethyl halide was the same within experimental error (±10%).

Acknowledgment. This work was supported by a grant from the National Science Foundation. We thank Joe Morelli for helpful discussions and valuable comments.

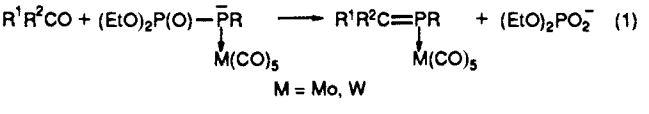
Synthesis, Structure, and Reactivity of (Phosphoranylidenephosphine)pentacarbonyltungsten Complexes. Another Access to the Phosphorus-Carbon Double Bond

Pascal Le Floch, Angela Marinetti, Louis Ricard, and François Mathey*

Contribution from the Laboratoire de Chimie du Phosphore et des Mêtaux de Transition, DCPH, Ecole Polytechnique, 91128 Palaiseau Cedex, France. *Received August 4, 1989*

Abstract: The reaction of trialkylphosphines with 7-phosphanorbornadiene $PW(CO)_5$ complexes affords the corresponding phosphoranylidenephosphine complexes $R^1{}_3P{=}P(R){\rightarrow}W(CO)_5$. One such complex (R = CO_2Et, R^1 = Et) has been investigated by X-ray crystal structure analysis. It shows a zwitterionic character with a long P=P bond (2.156 (2) Å). These phosphoranylidenephosphine complexes cleanly react at room temperature with aldehydes to give the corresponding phosphaalkene complexes via a "phospha-Wittig" reaction. These phosphaalkene complexes are either isolated as such or trapped by MeOH, dimethylbutadiene, or benzoic acid.

We have recently developed what we called the "phospha-Wittig" reaction that directly converts a carbonyl compound into a phosphaalkene complex[1-3] (eq 1). In this scheme, the com-



(1)

plexing group serves to stabilize both the starting phosphorylphosphine and the final phosphaalkene. Without it, both species are unstable with "ordinary" (i.e., neither bulky nor conjugating) substituents. Stricto sensu, this phospha-Wittig reaction is, in fact, a transposition of the Wittig-Horner synthesis of olefins. It was tempting to generalize this transposition to the genuine Wittig reaction itself. For that purpose, it was necessary to devise a general access to phoshoranylidenephosphines. Indeed, at the beginning of our work, only a few such compounds were known,[4-7] some of which are listed here. Their syntheses obviously depend on either the electron-accepting properties or the steric bulk of

(1) Marinetti, A.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1382.
(2) Marinetti, A.; Bauer, S.; Ricard, L.; Mathey, F., *Organometallics*, in press.
(3) Marinetti, A.; Ricard, L.; Mathey, F., *Organometallics*, in press.
(4) Burg, A. B.; Mahler, W. *J. Am. Chem. Soc.* **1961**, *83*, 2388.
(5) Zurmühlen, F.; Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 83; *New J. Chem.* **1989**, *13*, 335.
(6) Weber, D.; Fluck, E. *Z. Anorg. Allg. Chem.* **1976**, *424*, 103.
(7) Schmidpeter, A.; Lochschmidt, S. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 253.

0002-7863/90/1512-2407$02.50/0