Synthesis of (4*Z*)-1,1-Diphenyl-1,2,4-heptatrien-6-ynes and Their Facile Cycloaromatizations to α,3-Didehydrotoluene Biradicals Having a Triarylmethyl Radical Center

Bin Liu, Kung K. Wang,* and Jeffrey L. Petersen†

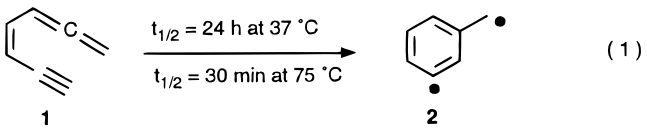
Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506

Received June 7, 1996⊗

The Horner reaction between enynyl aldehydes **12** and phosphinoxy carbanion **11** provided enyne−allenes **14**. Thermolysis (37−80 °C) of 1,4-cyclohexadiene solutions of **14** gave **20** via α,3-didehydrotoluene biradicals **19** having a reactive aryl radical center and a stabilized triarylmethyl radical center. In the absence of 1,4-cyclohexadiene, **19e** underwent intramolecular H-atom transfer between the proximal benzylic methyl group and the aryl radical center to give the more stable biradical **21**, the ultimate precursor of **22**.

Introduction

The Myers cyclization of (*Z*)-1,2,4-heptatrien-6-ynes (enyne−allenes) to α,3-didehydrotoluene biradicals occurs under mild thermal conditions (eq 1).[1] The resulting α,3-

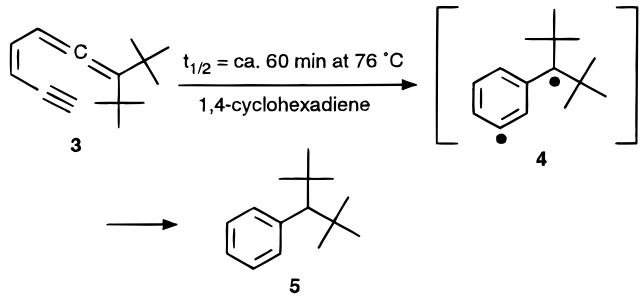


1 2 (1)

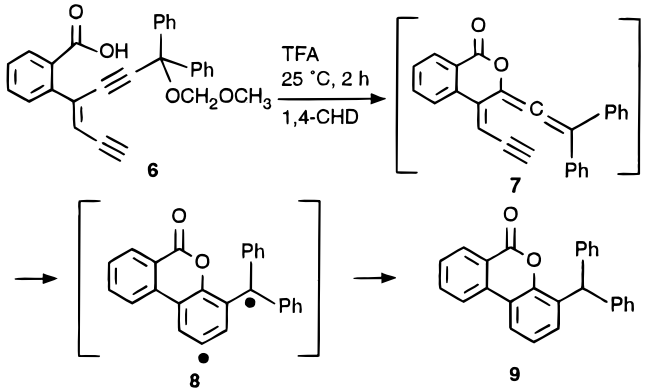
didehydrotoluene biradicals contain a highly reactive aryl radical center and a stabilized benzylic radical center. While there is little chance of producing a persistent aryl radical because H-atom abstraction generates a strong aryl C−H bond, the benzylic radical center could become persistent or even stable[2] if proper substituents are placed at the terminus of the allenic end of **1**.

We recently reported that enyne−allene **3** undergoes a facile Myers cyclization reaction in the presence of 1,4-cyclohexadiene (1,4-CHD) to furnish **5** in 58% yield (Scheme 1).[3] The reaction presumably proceeds through biradical **4** having an α,α-di-*tert*-butylbenzylic radical center, which was reported to be persistent in dilute solution at rt for several days.[4] It is worth noting that the presence of two sterically demanding *tert*-butyl groups in **3** does not significantly affect the rate of cycloaromatization when compared to that of **1**. Presumably, the small size of the hydrogen atom at the acetylenic terminus minimizes the steric interactions even with the *tert*-butyl group, and the formation of a more stable

Scheme 1



Scheme 2



tertiary benzylic radical in **4** partially compensates for the increased steric interactions.

In a recent report by Shibuya and co-workers, the enediyne **6** was treated with trifluoroacetic acid in the presence of 1,4-CHD at 25 °C to form **9** (85% yield) in 2 h (Scheme 2).[5] The reaction was proposed to proceed through an initial acid-catalyzed reaction to form the *s-cis* enyne−allene **7** followed by cycloaromatization to biradical **8** having a triarylmethyl radical center. While the intrinsic rate of transformation from **7** to **8** was not determined, the process was clearly facile at 25 °C due mainly to the fixed *s-cis* structure in **7** and the stability of the resulting triarylmethyl radical in **8**.

As a part of our continuing efforts in using the Myers cyclization reaction to produce α,3-didehydrotoluene biradicals having a persistent or stable benzylic radical

† To whom correspondence concerning the X-ray structure should be addressed.

⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1996.

(1) (a) Myers, A. G.; Kuo, E. Y.; Finney, N. S. *J. Am. Chem. Soc.* **1989**, *111*, 8057−8059. (b) Myers, A. G.; Dragovich, P. S. *J. Am. Chem. Soc.* **1989**, *111*, 9130−9132. (c) Nagata, R.; Yamanaka, H.; Okazaki, E.; Saito, I. *Tetrahedron Lett.* **1989**, *30*, 4995−4998. (d) Nagata, R.; Yamanaka, H.; Murahashi, E.; Saito, I. *Tetrahedron Lett.* **1990**, *31*, 2907−2910. (e) Nicolaou, K. C.; Maligres, P.; Shin, J.; de Leon, E.; Rideout, D. *J. Am. Chem. Soc.* **1990**, *112*, 7825−7926. For recent reviews, see: (f) Wang, K. K. *Chem. Rev.* **1996**, *96*, 207−222. (g) Grissom, J. W.; Gunawardena, G. U.; Klingberg, D.; Huang. D. *Tetrahedron* **1996**, *52*, 6453−6518.

(2) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1976**, *9*, 13−19.

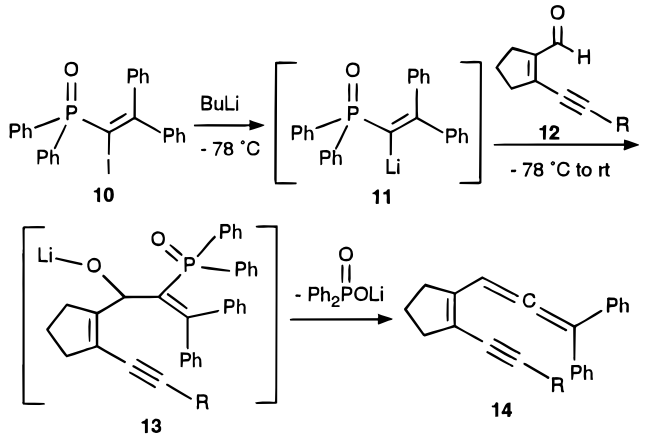
(3) Wang, K. K.; Wang, Z.; Sattsangi, P. D. *J. Org. Chem.* **1996**, *61*, 1516−1518.

(4) Schreiner, K.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 144−145.

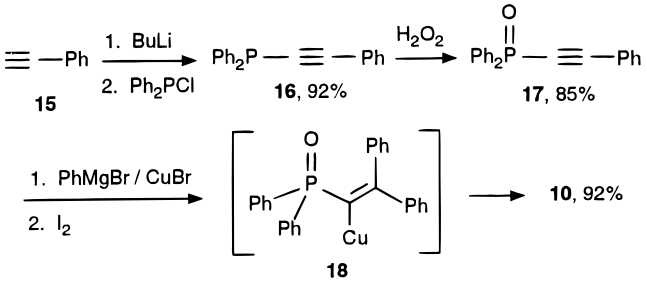
(5) Naoe, Y.; Kikuishi, J.; Ishigaki, K.; Iitsuka, H.; Nemoto, H.; Shibuya, M. *Tetrahedron Lett.* **1995**, *36*, 9165−9168.

S0022-3263(96)01073-0 CCC: $12.00

Scheme 3



Scheme 4



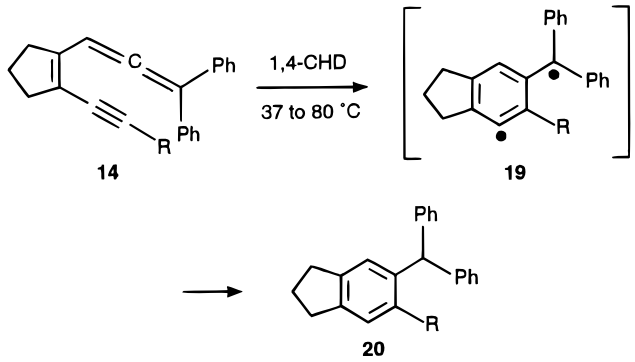
center, we developed a new synthetic route to enyne−allenes substituted with two phenyl groups at the terminus of the allenic end. Cycloaromatization of these enyne−allenes to form biradicals containing a stabilized triarylmethyl radical center was also investigated.

Results and Discussion

Our strategy for the synthesis of enyne−allenes **14** involved using the readily available enynyl aldehydes **12**[6] for the Horner reaction[7] with phosphinoxy carbanion **11** (Scheme 3). Carbanion **11** was prepared by treatment of diphenyl(2,2-diphenyl-1-iodoethenyl)phosphine oxide (**10**) with *n*-butyllithium at −78 °C. The condensation reactions between **11** and **12** to form **13** appeared to be very facile at −78 °C. When enynyl aldehydes **12** were introduced, the dark red color of **11** disappeared almost instantaneously. Elimination of lithium diphenylphosphinate from **13** also occurred spontaneously when the reaction mixture was allowed to warm to rt, producing enyne−allenes **14** in excellent isolated yields (Table 1).

10 was synthesized via the sequence outlined in Scheme 4. Treatment of phenylacetylene (**15**) with *n*-butyllithium followed by chlorodiphenylphosphine afforded **16**.[8] Subsequent oxidation of **16** with 30% H_2O_2 furnished diphenyl(phenylethynyl)phosphine oxide (**17**).[8] Treatment of **17** with phenylmagnesium bromide in the presence of cuprous bromide produced **18**,[9] which was converted to **10** with iodine.[10]

Scheme 5



While it was reported that treatment of benzaldehyde with **18** led to the formation of triphenylallene in 85% yield,[9a] attempts to transform **12a** to **14a** and **12b** to **14b** with **18** gave very low yields (<4%). This difficulty was circumvented by converting **18** to the iodide **10** followed by treatment of **10** with *n*-butyllithium to produce the corresponding alkenyllithium **11** for the subsequent condensation with **12**. It is worth noting that the iodide **10** is stable and can be prepared in large quantity for subsequent use.

Enyne−allene **14a** is thermally stable due to the presence of a sterically demanding trimethylsilyl group at the acetylenic terminus. However, when **14a** in 1,4-CHD was desilylated with tetrabutylammonium fluoride (TBAF) to form the corresponding enyne−allene having a hydrogen atom at the acetylenic terminus (R = H), cycloaromatization occurred at 37 °C in 4 h to furnish **20a** (R = H) in 41% yield (Scheme 5). Presumably, the reaction proceeded through biradical **19a** (R = H) having a triarylmethyl radical center followed by H-atom abstractions from 1,4-CHD. Similarly, enyne−allenes **14b**−**e** cyclized at 65−80 °C in 1,4-CHD to afford **20b**−**e** (Table 1). As in the case of **14a**, the presence of a sterically demanding *tert*-butyl group in **14f** prevented cycloaromatization to **20f** from occurring at 75 °C even after prolonged heating.

The presence of the appropriately positioned benzylic methyl group in **14e** provides a route for intramolecular H-atom abstraction to compete with intermolecular H-atom transfer from 1,4-CHD leading to **20e**. Indeed, when enyne−allene **14e** was heated under reflux in benzene at 80 °C in the absence of 1,4-CHD for 96 h, **22** was produced in 40% isolated yield (Scheme 6). The structure of **22** was unequivocally established by an X-ray structure determination.[11] Apparently, **19e** leads to the more stable biradical **21**, which then undergoes an intramolecular radical−radical combination to furnish **22**. The fact that **22** was produced from **14e** lends support to the formation of α,3-didehydrotoluene biradicals **19** as the transient reaction intermediates from enyne−allenes **14**. A cascade sequence similar to that outlined in Scheme 6 to demonstrate the involvement of

(6) (a) Saito, I.; Yamaguchi, K.; Nagata, R.; Murahashi, E. *Tetrahedron Lett.* **1990**, *31*, 7469−7472. (b) Wang, K. K.; Liu, B.; Lu, Y.-d. *Tetrahedron Lett.* **1995**, *36*, 3785−3788. (c) Wang, K. K.; Liu, B.; Petersen, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 6860−6867.

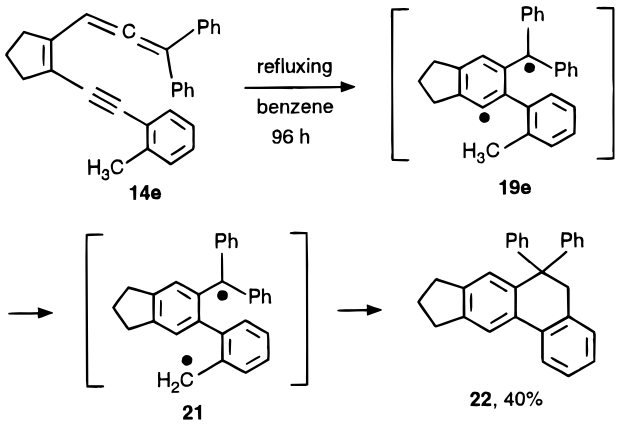
(7) Johnson, A. W.; Kaska, W. C.; Starzewski, K. A. O.; Dixon, D. A. *Ylides and Imines of Phosphorus*; Wiley-Interscience: New York, 1993; p 314.

(8) Charrier, C.; Simonnin, M.-P.; Chodkiewicz, W.; Cadiot, P. *Compt. Rend.* **1964**, *258*, 1537−1540.

(9) (a) Marszak, M. B.; Simalty, M.; Seuleiman, A. *Tetrahedron Lett.* **1974**, 1905−1908. (b) Aguiar, A. M.; Irelan, J. R. S. *J. Org. Chem.* **1969**, *34*, 4030−4031.

(10) Alexakis, A.; Cahiez, G.; Normant, J. F. *Org. Synth.* **1984**, *62*, 1−8.

Scheme 6



biradical species was previously employed in the Moore cyclization of enyne−ketenes.[12]

Conclusions

We have developed a new synthetic pathway to enyne−allenes having two phenyl substituents at the allenic terminus. Thermolysis of these enyne−allenes produced α,3-didehydrotoluene biradicals containing a reactive aryl radical center and a stabilized triarylmethyl radical center. The feasibility of converting the aryl radical center in **19e** to a more stable benzylic radical via an intramolecular 1,5-hydrogen shift was also demonstrated. The mildness of the thermal conditions makes cycloaromatization of enyne−allenes an especially attractive process for designing entirely different strategies for the synthesis of organic compounds containing multiple stable radical centers, an area of intense current interest.[13]

Experimental Section

All reactions were conducted in oven-dried (120 °C) glassware under a nitrogen atmosphere. Tetrahydrofuran (THF) was distilled from benzophenone ketyl prior to use. *n*-Butyllithium (2.5 M) in hexanes, chlorodiphenylphosphine, and phenylacetylene were purchased from Aldrich Chemical Co., Inc. and were used as received. Silica gel (70−230 mesh) and Florisil (100−200 mesh) for column chromatography were purchased from Aldrich and Fisher, respectively. 1,4-Cyclohexadiene was purchased from Wiley Organic, Inc. and was used as received. Diphenyl(phenylethynyl)phosphine (**16**),[8] diphenyl(phenylethynyl)phosphine oxide (**17**),[8] and enynyl aldehydes **12**[6] were prepared according to the reported procedures. ^{1}H (270 MHz) and ^{13}C (67.9 MHz) NMR spectra were recorded in $CDCl_3$ using $CHCl_3$ (^{1}H δ 7.26) and $CDCl_3$ (^{13}C δ 77.02) as internal standard.

Diphenyl(phenylethynyl)phosphine (16).[8] To a solution of 2.50 g (25 mmol) of phenylacetylene in 20 mL of THF at −20 °C was added 10 mL (25 mmol) of *n*-BuLi (2.5 M in hexanes), and the mixture was stirred for 30 min. Then 5.1 g (4.1 mL, 23 mmol) of chlorodiphenylphosphine was added at −20 °C, and the reaction mixture was allowed to warm to rt. After 2 h, the mixture was poured into 40 mL of water and was extracted with methylene chloride (3 × 30 mL), dried over $MgSO_4$, and concentrated to furnish 6.29 g (92%) of **16** as a yellow liquid: IR (neat) 2160, 1586, 1488, 1434, 1096, 1026, 839, 739, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.85−7.78 (4 H, m), 7.67−7.63 (2 H, m), 7.49−7.40 (9 H, m); ^{13}C NMR ($CDCl_3$) δ 136.19 (d, J = 6.7 Hz), 132.48 (d, J = 20.9 Hz), 131.71, 128.95, 128.82, 128.55 (d, J = 7.6 Hz), 128.26, 122.64, 107.71 (d, J = 3.8 Hz), 85.83 (d, J = 6.7 Hz).

Diphenyl(phenylethynyl)phosphine Oxide (17).[8] To a solution of **16** (2.86 g, 10.0 mmol) in 30 mL of THF was added 2.5 mL of 30% H_2O_2 at 0 °C, and the mixture was stirred at 0 °C for 30 min. After an additional 2 h at rt, the mixture was poured into a separatory funnel containing 50 mL of CH_2Cl_2 and 20 mL of water. The organic layer was separated, dried over $MgSO_4$, and concentrated to afford 2.57 g (85%) of **17** as a yellow solid: IR (neat) 2173, 1589, 1486, 1438, 1200, 1115, 920, 847, 697, 644 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.91−7.83 (4 H, m), 7.56−7.29 (11 H, m); ^{13}C NMR ($CDCl_3$) δ 132.96 (d, J = 122.0 Hz), 132.47 (d, J = 1.4 Hz), 132.20 (d, J = 2.9 Hz), 130.91 (d, J = 11.4 Hz), 130.67, 128.71, 128.52, 119.86 (d, J = 3.8 Hz), 105.38 (d, J = 30.0 Hz), 82.79 (d, J = 169.7 Hz).

Diphenyl(2,2-diphenyl-1-iodoethenyl)phosphine Oxide (10). To a solution containing 0.906 g (3.0 mmol) of **17** and 0.50 g (3.5 mmol) of CuBr was added 3.0 mL (3.0 mmol) of a 1.0 M solution of phenylmagnesium chloride in THF, and the resulting mixture was stirred at 50 °C for 6 h.[9a] Then 1.0 g (3.3 mmol) of iodine in 10 mL of THF was added at rt. After 3 h, the solution was poured into an aqueous solution of $Na_2S_2O_3$. The precipitate that formed was filtered, washed with water (3 × 50 mL), and dried under vacuum to afford 1.4 g (92%) of **10** as a yellow solid: IR (KBr) 3052, 1529, 1488, 1438, 1181, 1113, 830, 750, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.75−7.68 (4 H, m), 7.40−7.19 (11 H, m), 7.10−7.05 (2 H, m), 6.99−6.88 (3 H, m); ^{13}C NMR ($CDCl_3$) δ 167.18 (d, J = 6.7 Hz), 147.81 (d, J = 12.4 Hz), 139.72 (d, J = 5.2 Hz), 133.53 (d, J = 109.2 Hz), 131.69 (d, J = 9.5 Hz), 131.30, 129.58, 128.57, 128.40, 128.19, 128.02, 127.66, 97.72 (d, J = 85.8 Hz); MS (*m*/*e*) 506 (M^+), 429, 379, 201.

1,1-Diphenyl-3-[[2-(trimethylsilyl)ethynyl]-1-cyclopentenyl]-1,2-propadiene (14a). The following procedure for the preparation of **14a** is representative. To a solution of **10** (0.253 g, 0.50 mmol) in 20 mL of THF was added 0.20 mL (0.50 mmol) of a 2.5 M solution of *n*-BuLi in hexanes at −78 °C, and the color of the solution changed to dark red immediately. After 30 min at −78 °C, 0.096 g (0.50 mmol) of the enynyl aldehyde **12a** in 5 mL of THF was added. The color of the solution changed to light yellow immediately. After 3 h, the mixture was gradually warmed to rt, and a solid precipitate appeared when the temperature reached 5 °C. After an additional 1 h at rt, 100 mL of diethyl ether and 40 mL of water were added. The organic layer was separated, washed with water (2 × 20 mL), dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (Florisil/hexanes) to afford 0.131 g (74%) of **14a** as a yellow liquid: IR (neat) 2128, 1490, 1440, 1247, 842, 758, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.37−7.24 (10 H, m), 6.90 (1 H, s), 2.59 (2 H, t, J = 7.5 Hz), 2.54 (2 H, t, J = 7.5 Hz), 1.89 (2 H, quintet, J = 7.5 Hz), 0.22 (9 H, s); ^{13}C NMR ($CDCl_3$) δ 210.55, 145.07, 136.30, 128.55, 128.51, 127.47, 121.47, 112.01, 101.47, 93.71, 37.14, 33.69, 22.46, 0.22; MS (*m*/*e*) 354 (M^+), 277, 261, 207, 175, 159, 135, 105.

1,1-Diphenyl-3-[2-(1-hexynyl)-1-cyclopentenyl]-1,2-propadiene (14b): isolated in 71% yield as a yellow liquid; ^{1}H NMR ($CDCl_3$) δ 7.40−7.25 (10 H, m), 6.89 (1 H, s), 2.58−2.51 (4 H, m), 2.42 (2 H, t, J = 6.9 Hz), 1.90 (2 H, quintet, J = 7.5 Hz), 1.62−1.39 (4 H, m), 0.94 (3 H, t, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ 210.28, 141.46, 136.56, 128.56, 128.48, 127.37, 122.37, 111.80, 97.65, 93.70, 76.86, 37.54, 33.52, 31.13, 22.35, 22.11, 19.59, 13.75.

1,1-Diphenyl-3-[2-(3-methyl-3-buten-1-ynyl)-1-cyclopentenyl]-1,2-propadiene (14c): isolated in 80% yield as a yellow liquid; IR (neat) 2187, 1921, 1613, 1597, 1491, 1450, 1072, 1029, 897, 835, 768, 695, 633 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.38−7.25 (10 H, m), 6.93 (1 H, s), 5.35 (1 H, br s), 5.26 (1 H, br s), 2.62 (2 H, t, J = 8.6 Hz), 2.59 (2 H, t, J = 8.4 Hz), 1.98 (3 H, s), 1.94 (2 H, quintet, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 210.40, 143.34, 136.31, 128.48, 128.43, 127.37, 121.44, 111.92, 97.57, 93.64, 84.78, 77.23, 37.15, 33.67, 23.65, 22.38.

(11) The authors have deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

(12) Chow, K.; Nguyen, N. V.; Moore, H. W. *J. Org. Chem.* **1990**, *55*, 3876−3880.

(13) Rajca, A. *Chem. Rev.* **1994**, *94*, 871−893.

Table 1. Synthesis of Enyne−Allenes 14 and the Cycloaromatized Adducts 20

R	**14**	isolated yield, %	**20**	isolated yield, %	reaction temp, °C	reaction time, h
Me_3Si	**14a**	74	**20a** (R = H)	41	37[a]	4
Bu	**14b**	71	**20b**	57	65	6
isopropenyl	**14c**	80	**20c**	44	75	17
Ph	**14d**	87	**20d**	52	75	32
2-methylphenyl	**14e**	84	**20e**	61	80	72
tert-Bu	**14f**	82				

[a] Enyne−allene **14a** was first treated with TBAF followed by heating at 37 °C.

1,1-Diphenyl-3-[2-(phenylethynyl)-1-cyclopentenyl]-1,2-propadiene (14d): isolated in 87% yield as a yellow solid; IR (neat) 2194, 1921, 1597, 1489, 1442, 1070, 1028, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.53−7.47 (2 H, m), 7.44−7.28 (13 H, m), 7.05 (1 H, s), 2.73 (2 H, t, J = 7.4 Hz), 2.64 (2 H, t, J = 7.4 Hz), 1.99 (2 H, t, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 210.45, 143.57, 136.28, 131.41, 128.48, 128.43, 128.29, 128.03, 127.38, 123.53, 121.44, 111.96, 96.33, 93.70, 85.84, 37.20, 33.75, 22.41.

1,1-Diphenyl-3-[[2-(2-methylphenyl)ethynyl]-1-cyclopentenyl]-1,2-propadiene (14e): isolated in 84% yield as a yellow oil; IR (neat) 2191, 1920, 1597, 1490, 1451, 1030, 908, 834, 756, 694, 633 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.48−7.13 (14 H, m), 7.04 (1 H, s), 2.73 (2 H, t, J = 7.4 Hz), 2.64 (2 H, t, J = 7.5 Hz), 2.51 (3 H, s), 1.99 (2 H, quintet, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 210.52, 143.04, 139.73, 136.30, 131.72, 129.40, 128.49, 128.44, 128.09, 127.40, 125.56, 123.33, 121.75, 111.95, 95.28, 93.73, 89.75, 37.34, 33.75, 22.42, 20.97.

3-[2-(3,3-Dimethyl-1-butynyl)-1-cyclopentenyl]-1,1-diphenyl-1,2-propadiene (14f): isolated in 82% yield as a yellow solid; IR (neat) 2209, 1921, 1670, 1597, 1490, 1447, 1360, 1272, 1202, 1176, 1119, 1072, 1029, 918, 900 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.42−7.24 (10 H, m), 6.90 (1 H, s), 2.56 (2 H, t, J = 7.7 Hz), 2.54 (2 H, t, J = 7.1 Hz), 1.90 (2 H, quintet, J = 7.5 Hz), 1.31 (9 H, s); ^{13}C NMR ($CDCl_3$) δ 210.18, 141.32, 136.46, 128.47, 128.39, 127.28, 122.28, 111.72, 105.84, 93.63, 75.13, 37.45, 33.40, 31.23, 28.32, 22.28; MS (*m*/*e*) 338 (M^+), 323, 261, 245, 205, 183, 143, 115, 91; HRMS calcd for $C_{26}H_{26}$ 338.2035, found 338.2043.

5-(Diphenylmethyl)indan (20a). To a solution of enyne−allene **14a** (48.0 mg, 0.136 mmol) in 2.5 mL of 1,4-CHD was added 0.3 mL of a 1.0 M solution of TBAF (0.3 mmol) in THF at 0 °C. The mixture was then heated to 37 °C, and the progress of the reaction was followed by TLC. After 4 h, the starting material (the desilylated product of **14a**) disappeared completely. The reaction mixture was concentrated, and the residue was extracted with hexanes (2 × 20 mL), washed with water (2 × 20 mL), dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (silica gel/2% diethyl ether in hexanes) and then by HPLC (silica/2% diethyl ether in hexanes) to afford 16 mg (41%) of **20a** as a colorless liquid: IR (neat) 1599, 1493, 1448, 1077, 1031, 909, 819, 732, 699, 612 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38−7.08 (11 H, m), 6.99 (1 H, s), 6.89 (1 H, d, J = 7.7 Hz), 5.53 (1 H, s), 2.88 (2 H, t, J = 7.7 Hz), 2.84 (2 H, t, J = 7.7 Hz), 2.05 (2 H, quintet, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$) δ 144.38, 144.30, 142.20, 141.80, 129.44, 128.24, 127.36, 126.15, 125.39, 124.07, 56.75, 32.84, 32.47, 25.47; MS (*m*/*e*) 284 (M^+), 256, 241, 207, 178, 165, 128, 115, 91; HRMS calcd for $C_{22}H_{20}$ 284.1565, found 284.1559.

5-Butyl-6-(diphenylmethyl)indan (20b). The following procedure for the preparation of **20b** is representative. A solution of enyne−allene **14b** (61 mg, 0.18 mmol) in 2.5 mL of 1,4-CHD was heated at 65 °C, and the progress of the reaction was followed by TLC. After 6 h at 65 °C, the starting enyne−allene **14b** disappeared completely. The reaction mixture was concentrated, and the residue was purified by column chromatography (silica gel/hexanes) to afford 35 mg (57%) of **20b** as a colorless liquid and 14 mg (22%) of an unidentified yellow liquid. **20b**: IR (neat) 1599, 1492, 1447, 1076, 1030, 749, 699, 624 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.34−7.15 (6 H, m), 7.1−7.03 (5 H, m), 6.69 (1 H, s), 5.74 (1 H, s), 2.86 (2 H, t, J = 7.4 Hz), 2.76 (2 H, t, J = 7.4 Hz), 2.52 (2 H, t, J = 8.0 Hz), 2.01 (2 H, quintet, J = 7.4 Hz), 1.52−1.40 (2 H, m), 1.32 (2 H, sextet, J = 7.3 Hz), 0.86 (3 H, t, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 144.25, 142.25, 141.47, 139.39, 138.95, 129.60, 128.20, 126.05, 125.74, 125.39, 52.64, 33.82, 32.70, 32.64, 32.58, 25.41, 22.90, 13.99; MS (*m*/*e*) 340 (M^+), 283, 219, 205, 191, 165, 131, 115, 91; HRMS calcd for $C_{26}H_{28}$ 340.2191, found 340.2185.

5-(Diphenylmethyl)-6-(1-methylethenyl)indan (20c): isolated by column chromatography (silica gel/2% diethyl ether in hexanes) and HPLC (silica/1% diethyl ether in hexanes) in 44% yield as a white solid; IR (KBr) 1637, 1598, 1487, 1444, 893, 747, 728, 694 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.27−7.13 (6 H, m), 7.06 (4 H, d, J = 6.9 Hz), 6.98 (1 H, s), 6.85 (1 H, s), 5.82 (1 H, s), 5.12 (1 H, m, J = 1.8 Hz), 4.66 (1 H, m, J = 1 Hz), 2.85 (2 H, t, J = 7.4 Hz), 2.78 (2 H, t, J = 7.5 Hz), 2.02 (2 H, quintet, J = 7.4 Hz), 1.84 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 145.90, 144.88, 142.81, 142.15, 141.99, 138.05, 129.50, 128.12, 125.89, 123.88, 115.09, 52.53, 32.77, 32.54, 25.62, 25.43; MS (*m*/*e*) 324 (M^+) 309, 294, 265, 233, 218, 202, 165, 133, 115; HRMS calcd for $C_{25}H_{24}$ 324.1878, found 324.1861.

5-(Diphenylmethyl)-6-phenylindan (20d): isolated by column chromatography (silica gel/2% diethyl ether in hexanes) and HPLC (silica/4% diethyl ether in hexanes) in 52% yield as a light yellow oil; IR (neat) 1598, 1493, 1445, 1075, 1030, 890, 749, 728, 689 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.36−7.18 (10 H, m), 7.13−7.09 (3 H, m), 7.03−6.97 (4 H, m), 5.57 (1 H, s), 2.93 (2 H, t, J = 7.3 Hz), 2.89 (2 H, t, J = 7.2 Hz), 2.10 (2 H, quintet, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 144.62, 143.39, 142.23, 142.04, 140.54, 139.24, 129.49, 129.43, 128.09, 127.79, 126.65, 125.91, 125.85, 52.94, 32.84, 32.55, 25.47; MS (*m*/*e*) 360 (M^+), 331, 309, 299, 265, 254, 205, 166, 152, 138, 127, 115; HRMS calcd for $C_{28}H_{24}$ 360.1878, found 360.1854.

5-(Diphenylmethyl)-6-(2-methylphenyl)indan (20e): isolated by column chromatography and HPLC in 61% yield as a light yellow oil; IR (neat) 1599, 1494, 1446, 1077, 1032, 908, 754, 729, 699, 650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35−7.02 (10 H, m), 6.98−6.90 (5 H, m), 6.85 (1 H, d, J = 7.3 Hz), 5.28 (1 H, s), 2.90 (2 H, t, J = 7.1 Hz), 2.88 (2 H, t, J = 7.3 Hz), 2.09 (2 H, quintet, J = 7.4 Hz), 1.85 (3 H, s); ^{13}C ($CDCl_3$) δ 144.25, 143.71, 143.15, 141.97, 141.33, 139.87, 139.76, 136.35, 130.06, 129.72, 129.55, 129.43, 128.01, 127.99, 127.03, 125.90, 125.85, 125.47, 125.06, 53.22, 32.86, 32.54, 25.40, 20.03; MS (*m*/*e*) 374 (M^+), 359, 331, 295, 281, 252, 219, 203, 165, 134, 91, 77. Because of steric interactions, there is a high energy barrier for the the rotation about the carbon−carbon single bonds attaching the diphenylmethyl group and the methylphenyl group to the benzene ring of indan. Consequently, additional ^{13}C NMR signals due to the two nonequivalent phenyls of the diphenylmethyl group were observed.

7,7-Diphenyl-6,7,16,17-tetrahydro-15*H*-cyclopenta[*b*]-phenanthrene (22). To a flask attached with a reflux condenser containing 102 mg (0.274 mmol) of **14e** was added 220 mL of distilled benzene. The mixture was degassed by bubbling nitrogen through it for 5 min and then was heated to reflux. The progress of the reaction was followed by TLC, and the starting enyne−allene **14e** disappeared after 4 days. Benzene was removed by distillation, and the residue was filtered through a short silica gel column using 2% diethyl ether in hexanes as the eluting solvent to furnish a yellow oil in 56% yield. In addition, a brown mixture which was insoluble in hexanes was also obtained in 26% yield by weight. The yellow oil was further purified by column chromatography (silica gel/2% diethyl ether in hexanes) and HPLC (silica/1% diethyl ether in hexanes) to afford 41 mg (40%) of **22** as a light yellow oil along with an unidentified yellow oil in 11% yield by weight. When **22** was redissolved in diethyl ether and the solvent was then evaporated *in vacuo*, a colorless crystal was formed. **22:** IR (neat) 1597, 1487, 1445, 1117, 1035, 994, 882, 754, 732, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.69 (1 H, s), 7.60 (1 H, d, J = 7.5 Hz), 7.22−7.05 (13 H, m), 6.99 (1 H, s), 3.74 (2

H, s), 2.98 (2 H, t, $J = 7.4$ Hz), 2.83 (2 H, t, $J = 7.4$ Hz), 2.09 (2 H, quintet, $J = 7.5$ Hz); ^{13}C NMR ($CDCl_3$) δ 146.13, 143.48, 143.20, 141.58, 135.43, 134.84, 132.98, 129.22, 128.08, 127.65, 126.97, 126.73, 126.07, 125.60, 123.18, 120.24, 53.16, 43.26, 32.94, 32.73, 25.44; MS (*m*/*e*) 372 (M^+), 295, 267, 252, 165, 126, 77; HRMS calcd for $C_{29}H_{24}$ 372.1878, found 372.1871. **22** was recrystallized from a mixture of diethyl ether and hexanes (7:3) for the X-ray structure determination.[11]

Acknowledgment. The financial support of the National Science Foundation (Grant CHE-9307994) to K.K.W. is gratefully acknowledged. J.L.P. acknowledges financial support by the Chemical Instrumentation Program of the National Science Foundation (Grant CHE-9120098) for the acquisition of a Siemens P4 X-ray diffractometer by the Department of Chemistry at West Virginia University.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of **10**, **14a**−**f**, **20a**−**e**, and **22** (27 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO961073X