208-209.5 °C (EtOH); IR 2900, 1600, 1570, 1520, 1450, 1260 cm^{-1}; ^1H NMR (80 MHz) δ 7.7-7.1 (m, 10 H, ArH), 5.47 (s, 4 H, $ArCH_2OAr'$), 2.59 (s, 6 H, $ArCH_3$); MS, *m/e* (%) 340 (M^+, 100), 325 (9), 224 (27), 220 (5), 212 (25), 205 (9), 181 (18), 179 (16), 165 (36), 129 (36), 119 (5), 104 (32), 103 (21), 78 (18); UV (CH_2Cl_2) λ_{max} 264 (log ε 4.48), 291 (4.55), 324 (3.96), 354 (2.98), 370 (2.90) nm.

Anal. Calcd for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.91; H, 5.97.

Compound 9e. The resulting residue was worked-up in the same way as compound **9d**, but with CH_2Cl_2 as eluent. Two bands were extracted, the more polar of the two consisting of starting compound **8e** (16% yield) and the less polar consisting of phenanthrene **9e** (54% yield, 64% after correcting for recovery of starting material): mp 229.5-230.5 °C (EtOH); IR 2845, 1600, 1580, 1520, 1440, 1270, 1140 cm^{-1}; ^1H NMR (80 MHz) δ 7.7-7.0 (m, 11 H, ArH), 5.70 (s, 2 H, $ArCH_2OAr'$), 5.47 (s, 2 H, $ArCH_2OAr'$), 4.04 (s, 3 H, CH_3OAr); MS, *m/e* (%) 342 (M^+, 100), 223 (54), 214 (21), 195 (28), 167 (23), 139 (51), 129 (40), 119 (12), 104 (49), 103 (30), 91 (12), 78 (28); UV (CH_2Cl_2) λ_{max} 262 (log ε 4.51), 294 (4.26), 320 (3.97), 346 (3.39), 374 (3.38) nm.

Anal. Calcd for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30. Found: C, 80.53; H, 5.26.

Compound 9f. The resulting residue was purified in a short column of silica gel, eluting with CH_2Cl_2, followed by crystallization from EtOH to obtain a 78% yield of phenanthrene **9f**: mp 215-217 °C; IR 2900, 1615, 1595, 1435, 1265, 1175, 1135, 825 cm^{-1}; ^1H NMR (80 MHz) δ 7.6-7.1 (m, 8 H, ArH), 6.74 (s, 2 H, ArH), 5.67 (s, 2 H, $ArCH_2OAr'$), 5.44 (s, 2 H, $ArCH_2OAr'$), 4.04 (s, 3 H, CH_3OAr), 3.88 (s, 3 H, CH_3OAr); MS, *m/e* (%) 372 (M^+, 100), 340 (15), 297 (14), 253 (81), 225 (21), 159 (21), 154 (19), 126 (21), 104 (38), 103 (23), 78 (23); UV (EtOH) λ_{max} 268 (log ε 4.50), 286 (4.52), 327 (3.87, sh), 354 (2.99), 374 (2.66) nm.

Anal. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41. Found: C, 77.32; H, 5.00.

Preparation of Phenanthrene 9f by Irradiation of Cyclophane 8f, with I_2-O_2 as the Oxidant System. A stirred solution of 650 mg (1.74 mmol) of cyclophane **8f** and 50 mg of I_2 in 500 mL of Et_2O was irradiated with a 450-W Hanovia medium-pressure mercury lamp through a Pyrex filter for 1 h. The solution was washed with a sodium thiosulfate solution to eliminate the peroxides and the solvent was removed in the rotatory evaporator. The residue was loaded on a silica gel column, which was eluted with CH_2Cl_2. In this way, after crystallizing from EtOH-CH_2Cl_2, 474 mg (73% yield) of phenanthrene **9f** was obtained.

Cannithrene II (10). Phenanthrene **9f** was (90 mg, 0.24 mmol) dissolved in 6 mL of dioxane. EtOH (10 mL), 10 mg of Pd/C (10%), and two drops of concentrated HCl were added. The solution was stirred for 18 h at room temperature under 760 mmHg of H_2. The catalyst was filtered and the solvent eliminated in vacuo. The residue was purified on a silica gel plate with CH_2Cl_2-EtOH (1:1, v/v) as eluent. In this way 59 mg (90% yield) of an oil identified as pure cannithrene II (**10**) by direct comparison (TLC, ^1H NMR, MS, UV) with a natural sample were obtained. A crystalline sample obtained by distillation of the oil (ca. 170 °C (3 mmHg)) followed by crystallization from Et_2O-hexane produced no depression of the melting point when mixed with a natural sample of cannithrene II.

Acknowledgment. We thank the Comisiôn Asesora (Spain) for its financial support, the Ministry of Education and Science (Spain) for a Grant to J. A. Seijas, and Prof. L. Crombie of the University of Nottingham (England) for a natural sample of cannithrene II.

Registry No. **4**, 89052-09-5; **5a**, 88-95-9; **5b**, 612-12-4; **6a**, 621-59-0; **6b**, 100-83-4; **6c**, 121-71-1; **6d**, 57179-35-8; **7a**, 95912-29-1; **7b**, 95912-30-4; **7c**, 95912-31-5; **7d**, 95912-32-6; **7e**, 95912-33-7; **7f**, 89052-11-9; **8a**, 95912-34-8; **8b**, 95912-35-9; **8c**, 95912-36-0; **8d**, 95912-37-1; **8e**, 95912-38-2; **8f**, 95912-39-3; **9b**, 95912-40-6; **9c**, 95912-41-7; **9d**, 95912-42-8; **9e**, 95912-43-9; **9f**, 89052-08-4; **10**, 83016-16-4; 3,5-dimethoxybenzaldehyde, 7311-34-4; decanoic acid, 334-48-5; copper(II) decanoate, 28567-33-1.

Palladium-Catalyzed Dimerization of Allenes to 2,3-Bis(chloromethyl)butadienes. Synthesis of Conjugate Exocyclic Dienes

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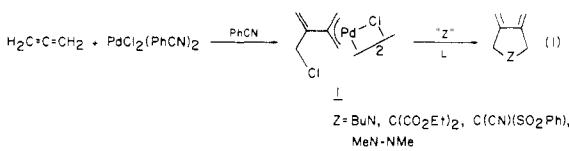
Treatment of allene with copper(II) chloride in the presence of palladium(II) chloride as catalyst (1%) produced 2,3-bis(chloromethyl)butadiene in good yield. Greater than 10 g of this material was produced in 24 h. 1-Phenylallene behaved in a similar manner, although in this case, mixtures of isomers were obtained. 1-*n*-Hexylallene underwent reaction to give an inseparable mixture of all possible regio- and stereoisomers of the coupling product. 1,1-Dimethylallene underwent polymerization, as did 1-ethoxyallene. 1-Bromoallene underwent a catalytic *trimerization*. The 2,3-bis(chloromethyl)-1,3-butadiene formed in the above catalytic reaction underwent reaction with a variety of bifunctional nucleophiles to produce five-, six-, and seven-membered rings containing exocyclic conjugated dienes.

Reaction of allene with dichlorobis(benzonitrile)palladium(II) in benzonitrile produces a high yield of a π-allylpalladium complex containing two units of allene connected at their central carbons.[1] We recently reported[2] the conversion of this complex into a variety of conjugated exocyclic dienes by reaction with "bifunctional" nucleophiles (eq 1). Although this led to the desired exocyclic dienes in fair yield, the range of nucleophiles was limited, and the process consumed a stoichiometric amount of palladium. To circumvent this problem, an approach to these same exocyclic dienes using only catalytic quantities of palladium salts was developed and is detailed herein.



Results and Discussion

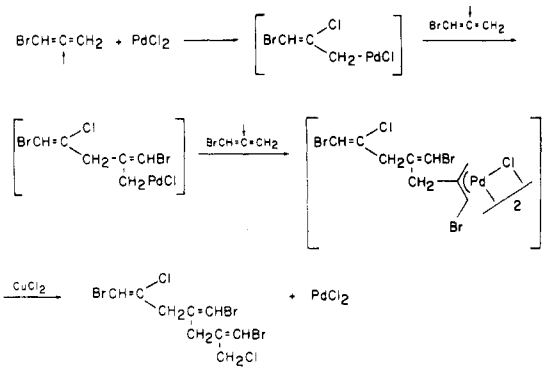
π-Allylpalladium complexes are oxidatively cleaved to allylic chlorides by treatment with copper(II) chloride,[3]

(1) (a) Schultz, R. G. *Tetrahedron Lett.* **1964**, *301*. (b) Schultz, R. G. *Tetrahedron* **1964**, *20*, 2809. (c) Lupin, N. S.; Shaw, B. L. *Tetrahedron Lett.* **1965**, 883.

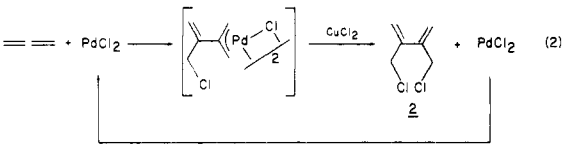
(2) Hegedus, L. S.; Kambe, N.; Tamura, R.; Woodgate, P. D. *Organometallics* **1983**, *2*, 1658.

0022-3263/85/1950-2240$01.50/0

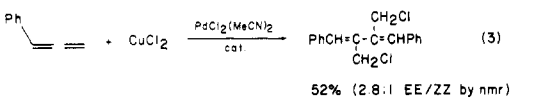
Scheme I



releasing palladium(II) chloride. Since palladium(II) chloride is required for the dimerization of allene, this provided a catalytic approach to 2,3-bis(chloromethyl)-1,3-butadiene. Treatment of allene with copper(II) chloride (2 equiv) in acetonitrile in the presence of 0.5% $PdCl_2(CH_3CN)_2$ as catalyst produced 2,3-bis(chloromethyl)-1,3-butadiene (**2**) in excellent yield (95% crude yield, 68% recrystallized, analytically pure) (eq 2). In the



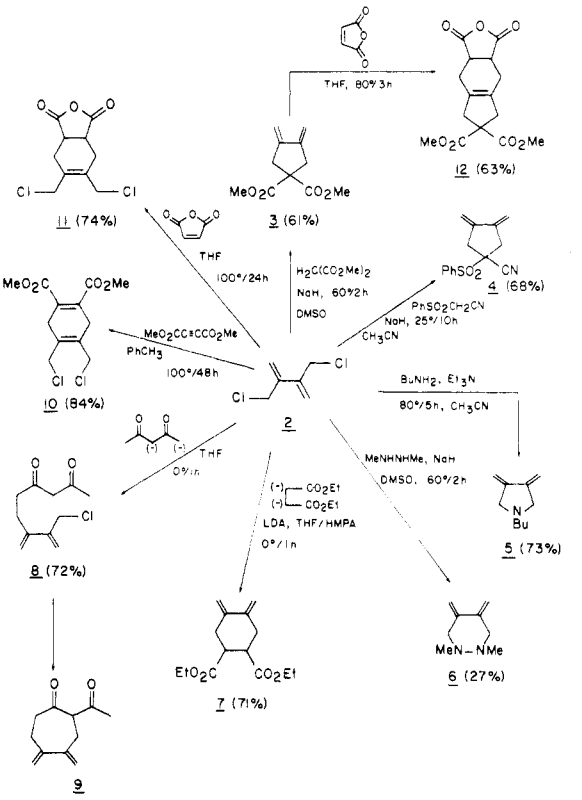
absence of the palladium catalyst no product was formed. In this manner over 10 g of pure material could be made in less then 24 h.[4] 1-Substituted allenes also underwent this coupling reaction although these reactions were complicated by the formation of mixtures of geometric olefin isomers as well as small amounts of regioisomers. Thus, with 1-phenylallene, a 52% isolated yield of the 1,4-diphenylbutadiene isomer was obtained as a 2.8:1 mixture of *E,E* and *Z,Z* isomers (by NMR spectroscopy) (eq 3).



The 1,4-diphenyl isomers were easily separated from other components of the mixture, but were difficult to separate from each other. In contrast, 1-*n*-hexylallene underwent coupling to give an intractable and inseparable mixture of all possible stereo- and regioisomers. 1,1-Dimethylallene was polymerized rather than converted to butadienes. 1-Bromoallene underwent a clean *trimerization* in 86% yield when exposed to this same catalyst system. The structure of the product indicates that the initial chloropalladation had occurred with regiochemistry *opposite* that of allene itself; that is, chlorination occurred at the *central* carbon of the bromoallene, rather than the terminal carbon (Scheme I). It appears as if a single geometric isomer was formed in this process, but its stereochemistry cannot be assigned from the available spectroscopic data.

Attempts to prepare the corresponding bis(bromomethyl) compound, a much more reactive compound, were also successful. Using copper(II) bromide in place of the dichloride and carrying the reaction out at −15 °C resulted in the production of 2,3-bis(bromomethyl)-1,3-butadiene

Scheme II



in 32% yield. In addition, 2,3-dibromopropene (5%) and tetrakis(bromomethyl)ethylene (2%) were isolated. Although the yield for this reaction was only modest, it still is the most direct synthesis of the functionalized butadiene.[5]

With a ready source of **2** at hand, its reaction chemistry was studied in some detail. The results are summarized in Scheme I. In contrast to π-allylpalladium complex 1,[2] chloromethyl diene **2** underwent clean, high yield reaction with a number of "bifunctional" nucleophiles making a number of conjugated, exocyclic dienes available. Five- and six-membered ring systems were available by this chemistry, and both carbon and nitrogen nucleophiles could be used. The chloro compound **2** was sufficiently reactive for these transformations, and the less stable bromo compound was not further examined. Seven-membered ring compounds were not readily available by this procedure. Although acetylacetone dianion underwent clean monoalkylation by **2**, ring closure of **8** to **9** was difficult and pure **9** was never obtained.

In addition, diene **2** was sufficiently stable to permit thermal Diels–Alder reactions to take place with activated dienophiles such as maleic anhydride and dimethyl acetylenedicarboxylate, to produce cyclic bis(allylic chlorides). All of these products are highly functionalized and should be useful, both for further elaboration and for use as monomers or comonomers for both diene polymerization reactions and low valent metal-catalyzed couplings of allylic halides.

Experimental Section

General Procedures. All melting points were obtained with a Mel-Temp melting point apparatus and are uncorrected. In-

(3) Castanet, Y.; Petit, F. *Tetrahedron Lett.* **1979**, 3221.

(4) 2,3-Bis(chloromethyl)-1,3-butadiene has been made in 32% yield from 1,1,2,2-tetrakis(chloromethyl)ethane, which in turn was made from the alcohol (59% yield), the tetraester (73% yield), and initially diethyl malonate (75% yield). See: Weinges, K.; Spanig, R. *Chem. Ber.* **1968**, *101*, 3010.

(5) 2,3-Bis(bromoethyl)-1,3-butadiene has been made in 31% overall yield and three steps from 2,3-dimethyl-1,3-butadiene (Butler, G. B.; Ottenbrite, R. M. *Tetrahedron Lett.* **1967**, 4873) and by reductive elimination of Br_2 from tetrakis(bromomethyl)ethylene (Gaoni, Y.; Sadeh, S. *J. Org. Chem.* **1980**, *45*, 870 and references cited therein).

frared spectra were recorded on a Beckman 4200 spectrophotometer. All 60-MHz ^1H NMR spectra were recorded on either a Varian Model EM360 or a Varian Model T-60 spectrometer with Me_4Si as an internal standard and are reported in δ. All ^{13}C NMR spectra were recorded on an IBM-WP270 Fourier Transform spectrometer. High-field NMR spectra were recorded on a Nicolet NT360 spectrometer or an IBM WP270 NMR spectrometer. Mass spectra were recorded on a V. G. Micromass 16F spectrometer. All chromatographic isolations were accomplished by radial-layer chromatography by using a Chromatotron Model 7924 with Kiesel gel 60 PF silica gel. Analyses were performed by M-H-W Laboratories, Phoenix, AZ.

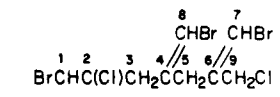
All solvents were freshly distilled and stored under an argon atmosphere. Immediately before use they were degassed and saturated with argon. Tetrahydrofuran (THF) (Fischer, Spectra Grade) was predried over Na wire, heated at reflux over Na wire with benzophenone, and distilled at atmospheric pressure under an N_2 atmosphere. Diethyl ether (Fischer, Reagent Grade) was predried over $MgSO_4$, heated at reflux over Na with benzophenone, and distilled at atmospheric pressure under an N_2 atmosphere. Petroleum ether (Skelly solve F, petroleum naphtha) was heated at reflux over CaH_2 and distilled at atmospheric pressure under an N_2 atmosphere.

Preparation of 2,3-Bis(chloromethyl)-1,3-butadiene[4] (2). To an acetonitrile solution (160 mL) of $PdCl_2(CH_3CN)_2$ (0.5 mmol, 0.130 g) was added anhydrous $CuCl_2$ (400 mmol, 53.8 g) with vigorous stirring and the system was degassed. Allene (200 mmol, 4.8 l) was introduced under atmospheric pressure at 25 °C. Reaction was continued for 24 h. The resulting dark brown homogeneous solution was poured into 200 mL of ether and the resulting black precipitate was removed by filtration. The filtrate was concentrated to ca. 30 mL and diluted with 100 mL of ether to precipitate the remaining complexes. Evaporation of the filtrate gave a dark brown solid, which was then subjected to medium-pressure liquid chromatography (silica gel, pentane). Recrystallization from hexane (2 mL/g, 40 to −14 °C) gave 10.14 g of a white crystalline solid (67%, 67 mmol): mp 28.0–28.5 °C); ^1H NMR ($CDCl_3$, 360 MHz, Me_4Si) δ 5.49 (2 H, s, =CH), 5.48 (2 H, s, =CH), 4.27 (4 H, s, CH_2Cl); IR (neat) 3098, 2964, 2344, 1843, 1630, 1598, 1449, 1407, 1262, 1121, 808, 743 cm^{-1}; mass spectrum, m/e (relative intensity) 150 (M^+) (18), 115 (16), 114 (29), 101 (12), 79 (100), 65 (26). This material was stable for months at 0 °C in the dark but polymerized in a matter of days at 25 °C in room light.

Dimerization of 1-Phenylallene by $CuCl_2/PdCl_2$. To a mixture of $CuCl_2$ (1.35 g, 10.0 mmol) and $PdCl_2(CH_3CN)_2$ (0.013 g, 0.05 mmol) in CH_3CN (10 mL) was added 1-phenylallene[6] (0.58 g, 5.0 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for three days and became almost homogeneous. The resulting dark brown solution was poured into 100 mL of ether and the resulting precipitate was removed by filtration. The solvent was removed in vacuo to yield crude products (0.75 g) as pale yellow viscous oil, which was purified by Chromatotron after passing through a silica gel short column eluting with ether. Radial-layer chromatography (petroleum ether–$CHCl_3$, 30:1) followed by evaporation of solvent gave 287 mg (38%) of compound A and 106 mg (14%) of compound B.

Compound A: (*E,E*)-2,3-Bis(chloromethyl)-1,4-diphenyl-1,3-butadiene: R_f 0.134, petroleum ether; ^1H NMR ($CDCl_3$, 270 MHz, Me_4Si) δ 7.42 (4 H, d, ArH), 7.25 (6 H, m, ArH), 6.86 (2 H, s, =CH), 4.17 (4 H, s, CH_2Cl); IR (neat) 3020, 1498, 1440, 1255, 800, 745, 725, 685 cm^{-1}. Anal. Calcd for $C_{18}H_{16}Cl_2$: C, 71.30; H, 5.32; Cl, 23.38. Found: C, 71.41; H, 5.25; Cl, 23.34.

Compound B: (*Z,Z*)-2,3-Bis(chloromethyl)-1,4-diphenyl-1,3-butadiene; R_f 0.24, petroleum ether; ^1H NMR ($CDCl_3$, 270 MHz, Me_4Si) δ 7.65 (4 H, d, ArH), 7.35 (6 H, m, ArH), 6.84 (2 H, s, =CH), 4.35 (4 H, s, CH_2Cl); IR (neat) 3020, 1485, 1445, 1428, 1262, 1158, 1095, 750, 685 cm^{-1}. Anal. Calcd for $C_{18}H_{16}Cl_2$: C, 71.30; H, 5.32; Cl, 23.38. Found: C, 71.18; H, 5.05; Cl, 23.62. This was assigned as the *Z,Z* isomer because of the downfield position of the CH_2Cl peak, being deshielded by the *cis*-phenyl group.



Trimerization of 1-Bromoallene to $C_9H_9Br_3Cl_2$. Into a mixture of $CuCl_2$ (0.896 g, 6.7 mmol) and $PdCl_2(CH_3CN)_2$ (8.7 mg, 0.033 mmol) in CH_3CN (10 mL) was added 1-bromoallene[7] (0.517 g, 4.30 mmol) at 0 °C. The reaction was stirred at this temperature for 24 h, giving a dark brown, homogeneous solution. This reaction mixture was poured into ether (50 mL) to precipitate CuCl. After the filtration, the filtrate was dried over $MgSO_4$ and filtered, and solvent removed under vacuum to give a pale yellow solid (0.530 g, 86%). Recrystallization from petroleum ether–ether solution afforded white needles: mp 60–61 °C; R_f 0.483 (petroleum ether–$CHCl_3$ = 10:3); ^{13}C NMR (270 MHz, $CDCl_3$, Me_4Si) δ 138.7, 136.1 (C_4C_6), 122.9 (C2), 113.0 ($C_{1,7,8}$), 112.8 ($C_{1,7,8}$), 112.7 ($C_{1,7,8}$), 41.1 (C_9), 38.5 (C_3C_5), 27.9 (C_3C_5); ^1H NMR (360 MHz, $CDCl_3$, Me_4Si) δ 6.70 (1 H, s), 6.68 (1 H, s), 6.50 (1 H, s), 4.40 (4 H, s), 4.26 (2 H, s); IR (NaCl, neat) 3065, 2950, 1595, 1435, 1280, 1255, 1208, 930, 793, 730 cm^{-1}; mass spectrum, m/e (relative intensity) 354 (1.9), 352 (1.9), 310 (5.6), 308 (5.8), 275 (5.9), 273 (9.1), 229 (19.3), 227 (11.9), 185 (8.1), 183 (8.4). Anal. Calcd for $C_9H_9Br_3Cl_2$: C, 25.27; H, 2.12. Found: C, 25.05; H, 2.34.

Attempted Dimerization of 1-*n*-Hexylallene.[8] To a mixture of $CuCl_2$ (1.35 g, 10 mmol) and $PdCl_2(CH_3CN)_2$ (7 mg, 0.026 mmol) in CH_3CN (10 mL) was added 1-*n*-hexylallene (645 mg, 0.52 mmol) at 22–23 °C. The reaction was run for 16 h, and the solution became homogeneous dark brown.

The reaction mixture was poured to 100 mL of ether and the precipitate was removed by filtration. The filtrate was dried over $MgSO_4$ and the solvent was removed by evaporation to give crude product (600 mg) as a pale yellow viscous oil.

The crude product was separated by radial chromatography (petroleum ether–chloroform 20:1) to give 444 mg (53%) of a fraction containing what appeared to be all possible regio- and stereoisomers of the desired coupling product. Separation of *this* mixture proved difficult and was not achieved.

Preparation of 2,3-Bis(bromomethyl)-1,3-butadiene. Allene (10 mmol, 240 mL gaseous) was dissolved in acetonitrile (25 mL) containing $CuBr_2$ (2.23 g, 10 mmol) and $PdCl_2(CH_3CN)_2$ (0.013 g, 0.05 mmol) at 0 °C, and the heterogeneous mixture was stirred at this temperature for 7 h. The solvent was removed in vacuo, ether (20 mL) was added, and the mixture was filtered through a short column of silica gel to give 657 mg of a yellow solid. Separation by Chromatotron (silica gel, hexane) gave 370 mg (31%) of a white relatively unstable solid, mp 57–58 °C (lit.[5] mp 57–58 °C), identical in all respects with 2,3-bis(bromomethyl)-1,3-butadiene obtained by an alternate route.[5]

Reactions of 2 with Bifunctional Nucleophiles. (a) With Dimethyl Malonate To Form 3. To a mixture of 2,3-bis-(chloromethyl)-1,3-butadiene (1 mmol, 151 mg) and sodium hydride (2.2 mmol, 53 mg) in Me_2SO (10 mL) was added dimethyl malonate (1 mmol, 114 μL). The mixture was stirred at 25 °C for 3 min then warmed to 60 °C. Reaction was continued at this temperature for 2 h.

After the reaction was complete, the product was extracted with ether (5 × 7 mL) and dried over Drierite. Evaporation of the solvent gave 154 mg of colorless liquid, which was purified by radial-layer chromatography (silica gel, ether–pentane 1:3) to give 128 mg of pure product (0.61 mmol, 61%), identical in all respects with authentic material.[2]

(b) With (Phenylsulfonyl)cyanomethane To Form 4. To a mixture of (phenylsulfonyl)cyanomethane (1 mmol, 181 mg), sodium hydride (2.1 mmol, 50 mg), and the starting diene 2 (1 mmol, 151 mg) at −50 °C was added acetonitrile. The mixture was allowed to warm to 25 °C slowly and the reaction was continued at this temperature for 10 h.

After the reaction was complete, solvent was removed by evaporation. To the residue was added 10 mL of ether and the insoluble solid was removed by filtration. Evaporation of the solvent gave 258 mg of yellow damp solid, which was then purified on radial-layer chromatography (silica gel, ether–pentane 1:1) to

(6) Vermeer, P.; Meijer, J.; Brandsma, L. *Recl. Trav. Chim. Pays-Bas* **1975**, *94*, 112. The precursor to this material was prepared by the method of Macdonald: Macdonald, T. L.; Reagan, D. R. *J. Org. Chem.* **1980**, *45*, 740.

(7) Jacobs, T. L.; Brill, W. F. *J. Am. Chem. Soc.* **1953**, *75*, 1314.

(8) Pasto, D. J.; Chow, S. K.; Waterhouse, A.; Schultz, R. H.; Hennion, G. F. *J. Org. Chem.* **1967**, *43*, 1385.

give 177 mg of the desired product (0.68 mmol, 68%), identical in all respects with authentic material.[2]

(c) With *n*-Butylamine To Form 5. In a 5-mL sealed tube were placed the starting diene **2** (0.5 mmol, 76 mg), acetonitrile (5 mL), triethylamine (5 mmol, 0.70 mL), and butylamine (1.25 mmol, 125 μL) in this order. Reaction was carried out at 80 °C for 5 h.

After the reaction was complete, the resulting mixture was poured into a mixture of 20 mL of ether and 1 mL triethylamine. Then the insoluble precipitate was removed by passing through a short silica gel column (2 cm × 1.4 mL) to give 69 mg of slightly yellow liquid which was then purified by radial-layer chromatography (silica gel, ether–pentane 1:1) to give 55 mg (73%) of **5**, identical in all respects with authentic material.[2].

(d) With *sym* Dimethylhydrazine To Give 6. To a mixture of the starting diene **2** (1.0 mmol, 151 mg), MeNHNHMe·2HCl (1.1 mmol, 147 mg), and sodium hydride (2.4 mmol, 106 mg) was added Me_2SO (10 mL). The white suspension was heated at 60 °C for 4 h.

The product was extracted with ether (5 × 10 mL) from basic aqueous layer (pH 13–14, basified by KOH pellet) and dried over Drierite. The solvent was evaporated to give 121 mg of a slightly yellow liquid. Purification on a radial-layer chromatography (silica gel, methanol–ether 1:9) gave 38 mg (27%) of the desired product identical in all respects with authentic material.[2]

(e) With Diethylsuccinate To Give 7. The dianion was formed by the addition of diethyl succinate (0.17 g, 1.0 mmol) to lithium diisopropylamide (2.2 mmol) in THF (4.0 mL) at −78 °C and stirring for 0.5 h at this temperature. Diene **2** (0.15 g, 1.0 mmol) in HMPA (1.0 mL) was added to the dianion solution and the resulting mixture was stirred at −78 °C for 0.5 h, then at −10 °C for 1 h. The resulting product was poured into aqueous 5% HCl (20 mL) and the aqueous layer was extracted with ether (2 × 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. Chromatography on silica gel (Chromatotron) (hexane–AcOEt, 10:1) afforded 180 mg of **7** in 71% yield as a colorless oil: ^1H NMR (270 MHz, $CDCl_3$, Me_4Si) δ 5.05 (t, 2 H, J = 0.6 Hz, C=CH), 4.80 (d, 2 H, J = 0.6 Hz, C=CH), 4.15 (q, 4 H, J = 7.2 Hz, OCH_2), 2.66–2.86 (m, 4 H, CH_2), 2.29 (t, 2 H, J = 12.0 Hz, CH), 1.26 (t, 6 H, J = 7.2 Hz, CH_3); IR (neat) 3084 (w), 2980 (s), 1730 (s), 1635 (w), 1439 (m), 1368 (m), 1017 (m), 890 (m), 857 (w), 736 (w). Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.75; H, 7.72.

(f) With Acetylacetone To Give 8. To a solution of lithium diisopropylamide (LDA) (2.2 mmol) in 4 mL of THF was added acetylacetone (1.0 mmol, 0.103 mL). After stirring for 30 min, dichloride **2** (1.0 mmol, 0.151 g) dissolved in HMPA and THF (1 mL + 1 mL) was added to the mixture, which was stirred at −78 °C for 1 h and 0 °C for 1 h.

Aqueous isolation (2 N HCl), removal of dried solvent, and chromatographic purification on silica gel (hexane–AcOEt 10:1) gave 0.155 g of product (72%): TLC R_f 0.36 (hexane–AcOEt = 5:1); ^1H NMR (270 MHz, $CDCl_3$, Me_4Si) δ 10.88 (br s, 1 H, enol OH), 5.16–5.43 (5 H, m, $=CH_2$ plus =CH enol), 4.18 (2 H, s, CH_2Cl), 3.52 (s, trace, $COCH_2CO$), 2.33–2.68 (4 H, m, CH_2CH_2), 2.16 (s, trace, $OCCH_3$), 1.98 (3 H, s, CH_3CO, enol).

All attempts to cyclize this material to compound **9** produced intractible mixtures of unidentified products.

(g) With Dimethyl Acetylenedicarboxylate To Give 10. In a 5-mL sealed tube were placed the starting diene **2** (1 mmol, 151 mg) and dimethyl acetylenecarbonylate (1 mmol, 142 mg) followed by the addition of toluene (5 mL). Reaction was carried out at 100 °C for 2 days.

After the reaction was complete, the resulting mixture was concentrated to give colorless oil, which was then chromatographed (silica gel, Et_2O–pentane = 1:2) to give 246 mg (84%) of the pure adduct **10**: mp 67–68 °C; ^1H NMR (270 MHz, $CDCl_3$, Me_4Si) δ 4.14 (s, 4 H, CH_2Cl), 3.80 (s, 6 H, OCH_3), 3.22 (s, 4 H, CH_2); IR (KBr) 3006 (w), 2955 (m), 1719 (s), 1712 (s), 1656 (m), 1436 (s), 1427 (s), 1285 (s), 1265 (s), 1240 (m), 1180 (m), 1145 (m), 1066 (s), 998 (m), 943 (m), 928 (m), 783 (s), 748 (m), 670 (s) cm^{-1}; mass spectrum, m/e (relative intensity) 292 (M^+, 1), 261 (12), 225 (12), 217 (47), 190 (100), 162 (37), 131 (44), 103 (42). Anal. Calcd for $C_{12}H_{14}Cl_2O_4$: C, 49.16; H, 4.81. Found: C, 49.16; H, 4.88.

(h) With Maleic Anhydride To Give 11. In a 5-mL sealed tube were placed the diene **2** (2 mmol, 302 mg) and maleic anhydride (2 mmol, 196 mg) followed by the addition of THF (5 mL). The colorless homogeneous solution was stirred at 100 °C for 24 h.

The resulting solution was concentrated to give 680 mg of a damp white solid, NMR of which showed that their still remained about 5% of the starting diene. Recrystallization from 15 mL of a mixture of acetone–ether = 1:4 gave 139 mg of a white crystal (1.36 mmol, 68%). From the mother liquor 29 mg (0.12 mmol, 6%) was obtained: mp 116–116.5 °C; ^1H NMR (360 MHz, $CDCl_3$, Me_4Si) δ 4.22 (d, 2 H, J = 11.7 Hz), 4.02 (d, 2 H, J = 11.7 Hz), 3.48 (m, 2 H), 2.79 (d, 2 H, J = 15.4 Hz), 2.52 (d, 2 H, J = 15.3 Hz); IR (KBr) 3044 (w), 2972 (w), 2948 (w), 1842 (s), 1767 (s), 1653 (w), 1470 (m), 1443 (m), 1436 (m), 1425 (m), 1354 (m), 1314 (s), 1270 (s), 1230 (s), 1199 (s), 1150 (s), 1093 (ns), 1026 (s), 952 s), 942 (s), 906 (s), 900 (s), 818 (m), 725 (m), 714 (s), 702 (ns), 673 (s), 657 (s), 644 (s) cm^{-1}; mass spectrum, m/e (relative intensity) 213 (1), 212 (5), 178 (13), 105 (65), 91 (100), 36 (65). Anal. Calcd for $C_{10}H_{10}Cl_2O_3$: C, 48.22; H, 4.05. Found: C, 48.37; H, 4.09.

(i) Reaction of 3 with Maleic Anhydride To Give 12. In a 5-mL sealed tube were placed 1,1-dicarbomethoxy-3,4-dimethylenecyclopentane (**3**) (0.58 mmol, 122 mg) and maleic anhydride (0.58 mmol, 67 mg) followed by addition of THF (5 mL). The reaction was carried out at 80 °C for 3 h.

After the reaction was complete, THF was removed by evaporation. Product was purified by recrystallization (acetone–ether = 1:3, reflux to 15 °C) to give 63% of the desired adduct: mp 123.5–124 °C; ^1H NMR (270 MHz, $CDCl_3$, Me_4Si) δ 3.47 (s, 6 H, OCH_3), 3.39 (m, 2 H), 3.00 (s, 4 H, CH_2), 2.47 (br, 4 H); IR (KBr) 3004 (w), 2958 (w), 2906 (w), 2848 (w), 1856 (m), 1780 (s), 1757 (s), 1737 (s), 1448 (m), 1436 (m), 1356 (w), 1260 (s), 1203 (s), 1152 (m), 1120 (m), 1071 (s), 1050 (m), 996 (m), 967 (m), 957 (m), 940 (m), 912 (s), 891 ns), 723 (w); mass spectrum, m/e (relative intensity) 308 (M^+, 14), 277 (5), 249 (12), 248 (44), 221 (37), 220 (100), 176 (26e, 175 (64), 117 (97), 116 (44), 115 (82), 91 (38), 59 (33), 44 (42). Anal. Calcd for $C_{15}H_{16}O_7$: C, 58.44; H, 5.23. Found: C, 58.27; H, 5.23.

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Registry No. **2**, 19869-24-0; **3**, 87185-05-5; **4**, 87185-07-7; **5**, 87185-08-8; **6**, 87185-09-9; **7**, 96151-85-8; **8**, 96151-86-9; **10**, 96151-87-0; **11**, 96151-88-1; **12**, 96151-89-2; A, 96151-90-5; B, 96151-91-6; $BrCH{=}C(Cl)CH_2C(CH_2C(CH_2Cl){=}CHBr){=}CHBr$, 96151-92-7; $CH_2{=}C(CH_2Br)C(CH_2Br){=}CH_2$, 18214-55-6; $PdCl_2(CH_3CN)_2$, 14592-56-4; $CuCl_2$, 7447-39-4; $CuBr_2$, 7789-45-9; $CH_2{=}C{=}CH_2$, 463-49-0; $CH_2{=}C{=}CHPh$, 2327-99-3; $CH_2{=}C{=}CHBr$, 10024-18-7; $CH_3(CH_2)_5CH{=}C{=}CH_2$, 22433-33-6; $MeO_2CCH_2CO_2Me$, 108-59-8; $PhSO_2CH_2CN$, 7605-28-9; $BuNH_2$, 109-73-9; MeNHNHMe·2HCl, 306-37-6; $CO_2Et(CH_2)_2CO_2Et$, 123-25-1; $AcCH_2Ac$, 123-54-6; $CO_2Me{\equiv}CCO_2Me$, 762-42-5; maleic anhydride, 108-31-6.