Synthesis of Polyether Exomethylene Paracyclophanes via an Intramolecular Pd-Catalyzed Bis-Enyne Benzannulation Protocol

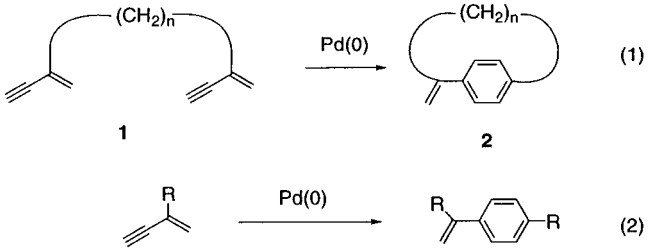
Douglas Weibel,† Vladimir Gevorgyan, and Yoshinori Yamamoto*

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-77, Japan

Received September 23, 1997

Several novel crownlike exomethylene paracyclophanes were efficiently synthesized via an intramolecular palladium-catalyzed benzannulation of conjugated bis-enynes. A method for the efficient synthesis of bis-enynes **8**, bearing an oligo(oxyethylene) linkage, was developed by utilizing a two-step procedure from commercially available and inexpensive ethylene glycols. A remarkable complete reversal of reactivity of ambident dilithiated nucleophile **4** toward triflate **7** in the presence of 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) was found.

The pioneering synthesis of cyclophane was reported by Pellegrin in 1899.[1] Extensive studies on cyclophanes, however, began only in the early 1950s after Brown[2] and Cram[3] reported the first direct syntheses of [2.2] paracyclophane. Since then, substantial attention has been paid to this class of compounds, arising from their display of intriguing chemical, physicochemical, and biological properties. Systematic studies of the preparation of cyclophanes, and investigations of properties displayed by various types of cyclophanes, have been described in hundreds of papers and fully documented in a number of excellent reviews.[4] Ether cyclophanes are a common representative of naturally occurring phanes[5] and are therefore of practical interest. Additionally, polyether-containing cyclophanes possess a crown ether-like motif, capable of exhibiting interesting ionophore properties[6] and subsequently acting as important subjects for host−guest chemistry.[7] Although several synthetic methods for the preparation of ether cyclophanes have been developed during last three decades,[8] most of these methods are cumbersome and allow the target compounds to be obtained in very low overall yields.[8] We have recently reported an efficient synthetic route for constructing a variety of exomethylene paracyclophanes **2** (eq 1)[9] via an intramolecular version of a palladium-catalyzed dimerization of conjugated enynes (eq 2).[10] Encouraged by the successful synthesis of carbacyclophanes **2** (eq 1) and motivated by the importance of heteroatom-containing cyclophanes as mentioned above,



we attempted to apply the benzannulation methodology[9] to the preparation of practically important ether paracyclophanes[5−7] possessing an exomethylene group adjacent to a benzene ring.[11]

We now wish to report the first efficient synthesis of ether- and polyether exomethylene paracyclophanes via a palladium-catalyzed intramolecular bis-enyne benzannulation protocol.

Results and Discussion

Synthesis of Ether and Polyether Bis-Enynes. Bis-enyne **5** was chosen as a substrate for a model study on the synthesis of ether cyclophanes via the benzannulation methodology. Ether bis-enyne **5** was efficiently prepared, as were similar all-carbon analogues,[9] by exhaustive alkylation of commercially available 4-chlorobutyl ether (**3**) with 2 equiv of dilithiated 2-methyl-1-buten-3-yne[12] **4** (Scheme 1).

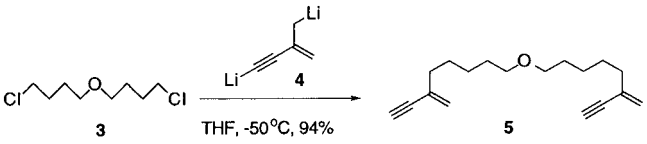
In contrast to the alkylation of **3**, alkylation of poly(ethylene glycol) derivatives **6**, bearing an alkoxy group

† Present address: Cornell University, Baker Labs, Ithaca, NY 14853.

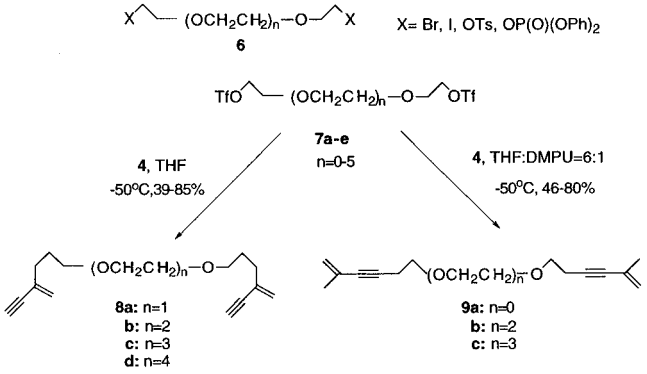
(1) Pellegrin, M. M. *Rec. Trav. Chim. Pays-Bas* **1899**, *18*, 457.
(2) Brown, C. J.; Farthing, A. C. *Nature* **1949**, *915*, 915.
(3) Cram, D. J.; Steinberg, H. *J. Am. Chem. Soc.* **1951**, *73*, 5691.
(4) For recent reviews see: (a) *Topics Current Chemistry* 172; Weber, E., Ed.; Springer-Verlag: Berlin, 1994. (b) *Cyclophane Chemistry*; Vögtle, F., Ed.; Willey: Chichester, 1993. (c) F. Diederich, *Cyclophanes*; Royal Society of Chemistry: Cambridge, 1991.
(5) See for example: (a) Toyota, M.; Kinugawa, T.; Asakawa, Y. *Phytochemistry* **1994**, *37*, 859. (b) Fukuyama, Y.; Asakawa, Y. *Phytochemistry* **1991**, *30*, 4061. (c) Hashimoto, T.; Kanayama, S.; Kan, Y.; Tori, M.; Asakawa, Y. *Chem. Lett.* **1996**, 741. (d) Hashimoto, T.; Yoshida, T.; Kan, Y.; Takaoka, S.; Tori, M.; Asakawa, Y. *Tetrahedron Lett.* **1994**, *35*, 909. (e) Suzuki, Y.; Nishiyama, S.; Yamamura, S. *Tetrahedron Lett.* **1989**, *30*, 6043. (f) Sutherland, I. O. In *Cyclophanes*, Keehn, P. M., Rosenfeld, S. M., Eds.; Vol. II, p 602, Academic Press: New York, 1983. See also ref 4b, p 431.
(6) See for example: (a) Heleson, R. C.; Timko, J. M.; Cram, D. J. *J. Am. Chem. Soc.* **1974**, *96*, 7380. (b) Heleson, R. C.; Tarnowski, T. L.; Timko, J. M.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 6411. (c) Allwood, B. L.; Spencer, N.; Shahriari-Zavarech, H.; Stoddart, J. F. Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1061. (d) Frensch, K.; Vögtle, F. *J. Org. Chem.* **1979**, *44*, 884. (e) Jarvi, E. T.; Whitlock, Jr. H. W. *J. Am. Chem. Soc.* **1980**, *102*, 657.
(7) For reviews see: (a) ref 4b p 447. (b) ref 4a p 87.
(8) For reviews see: (a) ref 4. See also for example: (b) Iyoda, M.; Sakaitani, M.; Otsuka, H.; Oda, M. *Tetrahedron Lett.* **1985**, *26*, 4777. (c) Shea, K. L.; Burke, L. D.; Doedens, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 5305. (d) See ref 6d.
(9) Saito, S.; Tsuboya, N.; Yamamoto, Y. *J. Org. Chem.* **1997**, *62*, 5042.
(10) Saito, S.; Salter, M. M.; Gevorgyan, V.; Tsuboya, N.; Tando, K.; Yamamoto, Y. *J. Am. Chem. Soc.* **1996**, *118*, 3970.
(11) Ether cyclophanes having a vinyl group adjacent to a benzene ring are useful substrates for the synthesis of cyclobutane-linked crownophanes via a [2 + 2] photocycloaddition reaction. See: Inokuma, S.; Yamamoto, T.; Nishimura, J. *Tetrahedron Lett.* **1990**, *31*, 97.
(12) Klusener, P. A. A.; Kulik, W.; Brandsma, L. *J. Org. Chem.* **1987**, *52*, 5261.

S0022-3263(97)01770-2 CCC: $15.00
Published on Web 01/23/1998

Scheme 1



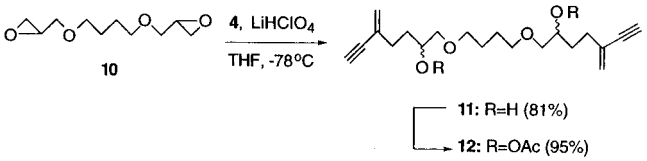
Scheme 2



β to the leaving group, proved extremely difficult.[13] Thus, halogen (Br, I), phosphate and tosyloxy derivatives **6** failed to undergo alkylation with **4** under the previously mentioned reaction conditions.[9] After considerable investigation, only triflate was found to be an acceptable leaving group for this displacement reaction, which led to concerns regarding the instability of bis-triflate intermediates.[14] Bis-triflates **7a**−**e** were consequently prepared according to standard procedures and immediately submitted to alkylation with **4** (Scheme 2). Polyether bis-triflates **7a**−**e** selectively reacted with the alkyllithium moiety of ambident nucleophile **4** under typical reaction conditions [9] to afford polyether bis-enynes **8a**−**d** in moderate to good chemical yield (Scheme 2, for details see Experimental Section). It worth noting that the addition of DMPU to the reaction mixture as a cosolvent, prior to the addition of nucleophile, dramatically changed the mode of alkylation (Scheme 2). Although it is known that DMPU enhances the nucleophilicity of acetylides,[15] we were surprised to find that it could cause a complete reversal of reactivity between sp^3- and sp-anions in ambident nucleophile **4**, in favor of the acetylide moiety. Thus, only bis-enyne **9** was produced in the presence of DMPU, and no traces of **8** were detected under these reaction conditions (Scheme 2) by GLC and NMR analysis of the crude reaction mixtures.

In contrast to unreactive **6**, diglycidyl ether **10**, which also formally possesses an alkoxy moiety β to a leaving group, reacted with **4** in a regioselective manner,[16] affording the diastereomeric diols **11** in good chemical yield (Scheme 3). Consequent acylation of **11** using standard procedures afforded diacetoxy bis-enyne **12** in high yield (Scheme 3).

Scheme 3



Scheme 4

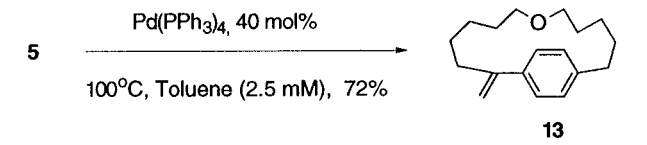
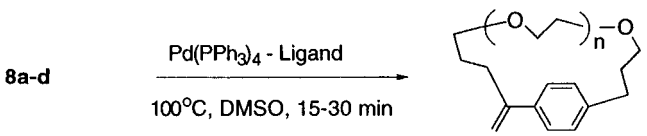


Table 1



bis-enyne	$Pd(PPh_3)_4$ (mol %)	ligand (mol %)	concn (mM)	product, yield (%)
8a $n = 1$	4	PPh_3, 50	20	**14a**, 34
8b $n = 2$	5	PPh_3, 40	15	**14b**, 100
8c $n = 3$	4	P(*o*-Tol)$_3$, 12	7	**14c**, >95 (NMR)
8d $n = 4$	10	P(*o*-Tol)$_3$, 30	5	**14d**, 50 (NMR)

Intramolecular Benzannulation of Ether and Polyether Bis-Enynes. Preliminary investigations of the intramolecular benzannulation of ether bis-enyne **5** were carried out under high-dilution (2.5 mM) in the presence of 40 mol % of $Pd(PPh_3)_4$,[9] affording exomethylene ether paracyclophane **13** in 72% yield (Scheme 4).

We next examined the benzannulation of polyether bis-enynes **8a**−**d** (Table 1). Unsatisfied with reaction conditions requiring high dilutions and excessively large amounts of palladium catalyst,[9] we initiated an investigation for a more synthetically useful procedure. After brief experimental optimizations, we found that bis-enynes **8a**−**d** in DMSO (5−20 mM) at 100 °C in the presence of a combined catalyst system, $Pd(PPh_3)_4$ (4−10 mol %)−additional phosphine ligand (12−50 mol %),[17] smoothly underwent intramolecular benzannulation to afford exomethylene paracyclophanes **14a**−**d** in satisfactory to quantitative yields (Table 1). Although the reasons for moderate yield of **14a** are not clearly understood, cyclophanes **14b** and **14c** bearing three and four oxygen atoms, respectively, at the polyether chain were obtained in quantitative yields (Table 1). The largest cyclophane synthesized, **14d**, containing a total of twenty atoms in the bridging chain (excluding exocyclic olefin) was obtained in 50% yield.

The remarkably high yield of **14b** and **14c** deserves special note. Fully optimized conditions for cyclization of the closest carbon analogues **1** (n = 12, 14)[9] required 40 mol % of Pd catalyst and high dilution (2.5 mM) to afford exomethylene paracyclophanes **2** in 71% yield (eq 1).[9] Such high dilution conditions were absolutely necessary to avoid formation of dimers and oligomers.[9] In

(13) It is generally accepted that alkylation of substrates bearing a β-alkoxy functionality is difficult due to the electron-withdrawing nature of the β-oxygen. For a review see: Streitwieser, A. *Solvolytic Displacement Reactions*; McGraw-Hill: New York, 1962; pp 16−18.

(14) Direct nucleophilic alkylation at the carbon center of triflates bearing a β-oxygen atom has been reported. For a review on alkylations with organocuprate reagents see for example: (a) Lipshutz, B. H. *Synthesis* **1987**, 325. For alkylations with Grignard reagents see: (b) Kotsuki, H.; Kadota, I.; Ochi, M. *Tetrahedron Lett.* **1989**, *30*, 1281.

(15) Kotsuki, H.; Kadota, I.; Ochi, M. *Tetrahedron Lett.* **1990**, *31*, 4609.

(16) For regeoselective epoxide ring openings with acetylides in the presence of metal salts, see: Chini, M.; Crotti, P.; Favero, L.; Macchia, F. *Tetrahedron Lett.* **1991**, *32*, 6617.

(17) During the course of our studies on the palladium-catalyzed *homo*-benzannulation of conjugated enynes, we have found that addition of 3−10 equiv of phosphine ligand vs Pd allows a significant decrease in the amount of palladium catalyst used. Gevorgyan, V.; Tando, K.; Uchiyama, N.; Yamamoto, Y. Unpublished results.

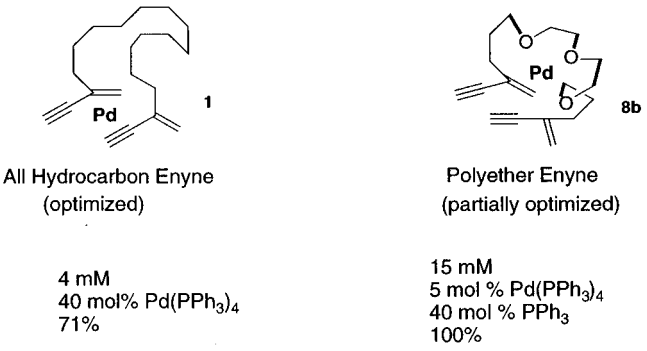


Figure 1.

Scheme 5

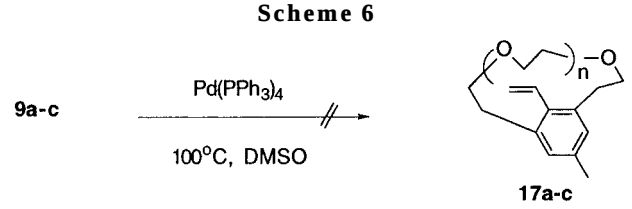
contrast, polyether bis-enynes **8b**,**c** cyclize in the presence of 4−5 mol % (10−8-fold decrease) of Pd catalyst and under relatively concentrated conditions (15−7 mM vs 2.5 mM for **1**[9]), producing the corresponding polyether cyclophanes **14b**,**c** quantitatively (Table 1). It is worth noting that no traces of dimers or higher oligomers were detected in these cases, suggesting perfect intramolecular control. Taken together, the above observation may be explained by the following proposal: a host/guest relationship between palladium and **8b**, and **8c**, bearing 3 and 4 oxygen atoms, respectively, could be responsible for the observed perfect intramolecular control of cyclization (Figure 1).[18]

Benzannulation of unprotected diol **11** appeared to be reasonably unfacile. All attempts to perform this reaction with small amounts of Pd catalyst failed, perhaps due to a strong affinity of Pd for the hydroxy groups of **11**.[19] Subsequently, cyclic diol **15** was obtained in 44% yield by employing 40 mol % of palladium catalyst (Scheme 5). In contrast to **11**, acetoxy-protected bis-enyne **12** smoothly underwent benzannulation in the presence of 10 mol % of $Pd(PPh_3)_4$, affording **16** in nearly quantitative yield (Scheme 5). Conversely, bis-enyne **9**, possessing 2,4-disubstituted enyne units,[20] remained untouched under all reaction conditions examined, with no trace of metacyclophane **17** detected by GC-MS analysis of reaction mixtures (Scheme 6).

Conclusion

An efficient method for the synthesis of polyether exomethylene paracyclophanes *via* a palladium catalyzed *homo*-benzannulation of polyether bis-enynes was developed. The efficient preparation of polyether bis-enynes in two steps from commercially available, inexpensive ethylene glycols has been demonstrated. The remarkable reversal of reactivity of ambident dilithiated nucleophile **4** toward triflate **7** in the presence of DMPU has been discovered.

Scheme 6



Experimental Section

General Information. All solvents were purified and dried according to standard procedures. Reactions were performed under an argon atmosphere in oven-dried glassware unless otherwise noted. Ether bis-enynes were prepared by reaction of dilithiated 2-methyl-1-buten-3-yne[12] with the corresponding chlorobutyl ether (**3**), bis-triflate (**7a**−**e**), and bis-epoxide (**10**). Diacetyl bis-enyne **12** was prepared from diol **11** according to standard procedures. 4-Chlorobutyl ether (**3**) was purchased from TCI. All other commercially available reagents were purchased from Aldrich.

Synthesis of 3. Bis-enyne **3** was prepared in 94% yield from 4-chlorobutyl ether and dilithiated 2-methyl-1-buten-3-yne,[12] according to published procedures for the preparation of alkyl bis-enynes.[9]

Synthesis of Bis-Enynes 8a−d (General Procedure). A mixture of the corresponding ethylene glycol (6.0 mmol), pyridine (12.3 mmol), and CH_2Cl_2 (5 mL) was added slowly (over 30 min) via addition funnel to a stirred solution of triflic anhydride (12.3 mmol) at 0 °C in CH_2Cl_2 (5 mL). After addition, the reaction mixture was immediately filtered through a short column (silica gel) and concentrated at 0 °C under reduced pressure. Before all of the solvent was completely removed, the pink-colored solution was flushed with argon, transferred to the addition funnel for the alkylation, and immediately added dropwise at −80 °C to a concurrently prepared aliquot of dilithiated 2-methyl-1-buten-3-yne[12] (12.9 mmol) in THF (20 mL). The temperature was allowed to rise to 0 °C over approximately 1 h, at which time no starting material was detected by GLC analysis. The reaction mixture was cooled to −40 °C and quenched by the dropwise addition of saturated NH_4Cl (12 mL). After warming to room temperature, the solvent was removed *in vacuo* and the residual yellow oil was extracted with ether−water. The aqueous phase was back extracted with 4 portions of ether and the ethereal portions were combined, washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the crude oil by column chromatography (silica gel, eluent: hexanes−ethyl acetate) gave polyether bis-enyne **8a**−**d** in 39−85% isolated yields.

Synthesis of 11. Bis-enyne **11** was prepared in 89% yield in the same manner as **8a**−**d**, except 1,4-butanediol diglycidyl ether (**10**) was alkylated instead of bis-triflate.

5: ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm) 5.42 (s, 2H), 5.31 (s, 2H), 3.40 (t, 4H, J = 6.9 Hz), 2.88 (s, 2H), 2.17 (t, 4H, J = 7.7 Hz), 1.63−1.33 (m, 12H). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ(ppm) 130.8, 122.7, 84.2, 76.6, 70.8, 36.9, 29.5, 27.8, 25.5. IR (neat) 1621 (cm^{-1}). HRMS (EI) m/z calcd for $C_{18}H_{26}O$ 258.1984, found 258.1962.

8a: ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm) 5.44 (s, 2H), 5.33 (s, 2H), 3.58 (s, 4H), 3.50 (t, 4H, J = 7.4 Hz), 2.90 (s, 2H), 2.25 (t, 4H, J = 7.4 Hz), 1.83 (m, 4H). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ(ppm) 130.1, 123.0, 83.9, 77.0, 70.2, 70.1, 33.4, 27.8. IR (neat) 2086, 1608, 912 (cm^{-1}). HRMS (EI) m/z calcd for $C_{16}H_{22}O_2$ 246.3495, found 246.1630.

(18) A template-directed effect of alkali metal salts in the ruthenium-catalyzed ring-closure metathesis has been recently demonstrated, see: Marsella, M. J.; Maynard, H. D.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1101.

(19) It is worth noting that in the intermolecular mode of the palladium-catalyzed *homo*-benzannulation of conjugated enynes, the palladium catalyst tolerates the presence of a hydroxy group. See: refs 10, 17.

(20) It was also found that 2,4-disubstituted enynes do not undergo intermolecular *homo*-benzannulation under the mentioned reaction conditions. Gevorgyan, V.; Sadayori, N.; Yamamoto, Y. *Tetrahedron Lett.* **1997**, *38*, 8603.

9a: ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm) 5.22 (s, 2H), 5.16 (s, 2H), 3.62 (t, 4H, J = 7.2 Hz), 2.59 (t, 4H, J = 7.2 Hz), 1.88 (s, 6H). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ(ppm) 127.0, 120.9, 85.5, 82.8, 69.2, 23.6, 20.6. IR (neat) 2230, 1614, 894 (cm^{-1}). HRMS (EI) m/z calcd for $C_{14}H_{18}O$ 202.2963, found 202.1351.

11: ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm) 5.36 (s, 2H), 5.28 (s, 2H), 3.72 (broad s, 2H), 3.49−3.36 (m, 6H), 3.21 (t, 2H, J = 6.2 Hz), 2.83 (s, 2H), 2.61 (broad s, 2H), 2.36−2.12 (m, 4H), 1.64−1.55 (m, 8H). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ(ppm) 130.1, 123.2, 83.8, 77.4, 75.1, 71.1, 69.3, 33.0, 31.3, 26.4. IR (neat) 3445, 1611, 910 (cm^{-1}).

12: ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm) 5.42 (s, 2H), 5.30 (s, 2H), 4.98 (m, 2H), 3.52 (m, 8H), 3.01 (s, 2H), 2.21 (m, 4H), 2.07 (s, 6H), 1.85 (m, 4H), 1.61 (s, 4H). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ(ppm) 170.5, 129.6, 123.1, 83.5, 77.4, 77.3, 77.0, 76.6, 32.7, 29.2, 26.1, 21.0. IR (neat) 1738, 1612 (cm^{-1}). HRMS (EI) m/z calcd for $C_{24}H_{34}O_6$ 418.2357, found 418.2346.

Intermolecular Benzannulation of Bis-Enyne 8a−d (General Procedure). Bis-enyne **8a−d** was added in one portion to a stirred solution of $Pd(PPh_3)_4$ and additive PPh_3 (or *o*-Tol_3P) in DMSO at 100 °C under the conditions indicated in Table 1. After completion of the reaction (monitored by GLC analysis), the reaction mixture was cooled to room temperature, poured into water, and extracted with ether. The aqueous phase was back extracted with ether (four portions), and ethereal phases were combined, washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. Purification of crude products by column chromatography (silica gel, eluent: hexanes−ethyl acetate) provided ether paracyclophanes **14a−d** in 34−100% yields (see Table 1).

13: ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm) 7.23 (d, 2H, J = 8.1 Hz), 7.09 (d, 2H, J = 8.1 Hz), 5.10 (s, 1H), 4.99 (s, 1H), 3.13 (t, 2H, J = 5.7 Hz), 3.02 (t, 2H, J = 5.7 Hz), 2.65 (t, 2H, J = 6.0 Hz), 2.55 (t, 2H, J = 6.0 Hz), 1.49 (m, 2H), 1.39 (m, 2H), 1.22 (m, 6H), 1.10 (q, 2H, J = 6.0 Hz). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ(ppm) 151.2, 141.2, 140.5, 128.8, 127.1, 111.6, 70.3, 69.2, 36.4, 35.1, 30.3, 30.2, 30.0, 29.7, 28.9, 26.8, 22.6. IR (neat) 1602, 903 (cm^{-1}). HRMS (EI) m/z calcd for $C_{18}H_{26}O$ 258.1983, found 258.1976.

14a: ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm) 7.21 (d, 2H, J = 7.9 Hz), 7.16 (d, 2H, J = 7.9 Hz), 5.11 (s, 1H), 5.03 (s, 1H), 3.39 (t, 2H, J = 4.6 Hz), 3.17 (t, 2H, J = 4.2 Hz), 3.00 (t, 2H, J = 4.3 Hz), 2.88 (t, 2H, J = 6.4 Hz), 2.73 (t, 2H, J = 6.1 Hz), 2.54 (t, 2H, J = 5.9 Hz), 1.94−1.87 (m, 2H), 1.72−1.64 (m, 2H). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ(ppm) 151.6, 141.1, 140.7, 128.4, 127.1, 111.5, 71.4, 70.5, 70.3, 69.5, 35.2, 33.2, 31.0, 30.7. IR (neat) 1637, 901 (cm^{-1}). HRMS (EI) m/z calcd for $C_{16}H_{22}O_2$ 246.3495, found 246.1619.

15: ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm) 7.21 (d, 2H, J = 7.6 Hz), 7.09 (d, 2H, J = 7.6 Hz), 5.10 (s, 1H), 5.02 (s, 1H), 3.52 (broad s, 2H), 3.30−3.11 (m, 8H), 2.84 (m, 2H), 2.64 (m, 2H), 2.53 (m, 2H), 1.58−1.30 (m, 8H). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ(ppm) 149.2, 140.7, 138.3, 132.2, 128.4, 112.5, 74.7, 74.5, 71.2, 69.7, 33.4, 32.5, 32.3, 31.1. IR (neat) 3427, 901 (cm^{-1}). HRMS (EI) m/z calcd for $C_{20}H_{30}O_4$ 334.4558, found 334.2137.

16: ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm) 7.32 (d, 2H, J = 8.2 Hz), 7.17 (d, 2H, J = 8.2 Hz), 5.29 (s, 1H), 5.11 (s, 1H), 4.95−4.80 (m, 2H), 3.50−3.00 (several m, 8H), 2.83 (m, 2H), 2.63 (m, 2H), 2.08 (distorted s, 6H), 1.68−1.31 (several m, 8H). ^{13}C NMR (67.9 MHz, $CDCl_3$) δ(ppm) 170.7, 147.7, 140.6, 140.4, 138.1, 128.7, 128.6, 126.6, 113.0, 112.9, 72.5, 72.1, 72.0, 71.2, 71.1, 70.9, 32.0, 31.8, 31.1, 29.7, 29.6, 26.5, 26.4, 26.3, 21.3, 21.2. IR (neat) 1738, 1655, 1628, 899 (cm^{-1}). MS (EI) m/z 418 (M^+, 21), 170 (100).

Acknowledgment. We are grateful to Dr. Isao Kadota for valuable advice. D.W. gratefully acknowledges Fulbright/JUSEC for financial support.

Supporting Information Available: The characterization data of compounds **8b−d**, **14b−d**, ^{1}H NMR spectra of compounds **5**, **8a−d**, **9a**, **11−13**, **14a−14d**, and ^{13}C NMR spectra of compounds **15**, **16** (17 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.

JO9717705