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Palladium-Catalyzed Vinylation of Alkyl Vinyl Ethers with Enol Triflates. A Convenient Synthesis of 2-Alkoxy 1,3-Dienes

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Reaction of cyclic or acyclic enol triflates with alkyl vinyl ethers in the presence of a palladium catalyst affords 2-alkoxy 1,3-dienes as the major products. The regioselectivity for α-substitution is high (>90%), and the products can be isolated in synthetically useful yields. Transformation of ketones, via their enol triflates, into α,β-unsaturated methyl ketones is accomplished under mild conditions.

Introduction

Alkoxy dienes have found numerous applications in the synthesis of functionalized cyclohexene derivatives by cycloaddition reactions.[1] Of special interest are regio- and stereocontrolled preparations of natural products[2] and pharmacologically active compounds.[3] Since classical routes to 2-alkoxy 1,3-dienes appear rather toilsome and sometimes unsuitable for the synthesis of more complex members of this class of compounds; more efficient procedures should be valuable.[4]

One of the most important and efficient applications of organotransition metal chemistry is the coupling of two sp^2-hybridized carbons.[7] Consequently, an impressive number of diene syntheses based on such chemistry has been uncovered during the past decades.

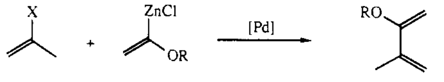
Most of these syntheses rely upon oxidative addition of a low-valent palladium or nickel catalyst to a vinylic halide or trifluoromethanesulfonate[8] (triflate), followed by reaction with a preformed alkenyl metal complex. The latter include derivatives of zinc,[9] tin,[10] boron,[11] zirconium,[12] silicon,[13] aluminum,[14] and magnesium.[15] Although such "cross-couplings" require functionality on both olefinic reactants, this is often justified when the appropriate regio- or stereocontrol cannot be obtained by direct vinylic substitution, the Heck reaction.[16]

Table I. Reaction of Cyclohexenyl Triflate (1) and Cyclohexenyl Iodide (2) with Butyl Vinyl Ether in DMSO at 60 °C[a]

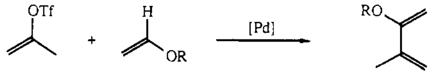
vinylating agent	catalyst	yield,[b] %, of 4 after different rctn times (unchanged 1 or 2): 2 h	5 h	22 h
1	$Pd(PPh_3)_4$	79 (0)	81 (0)	70 (0)
1	$Pd(OAc)_2$	90 (0)	86 (0)	77 (0)
1	$Pd(PPh_3)_4$/LiCl[c]	<5 (79)	<5 (76)	14 (64)
2	$Pd(PPh_3)_4$	9 (77)	18 (68)	36 (43)
2	$Pd(OAc)_2$	6 (94)	10 (90)	19 (81)

[a] The reactions utilized vinylating agent (1 mmol), butyl vinyl ether (5 mmol), triethylamine (2 mmol), and the palladium catalyst (0.03 mmol) in 5 mL of DMSO. [b] GLC yields. [c] Three mmoles of LiCl was added.

In 1983, Negishi[17] and Hegedus[18] introduced a methodology for the preparation of 2-alkoxy 1,3-dienes, based on the palladium-catalyzed coupling of vinyl halides with α-alkoxyethenyl zincs, obtained via lithiation/transmetalation (eq 1). Recently, analogous approaches employing (α-ethoxyvinyl)tributyltin[19] and (α-ethoxyvinyl)trimethylsilane[13] have appeared.



(1)



(2)

We now report the preparation of some 2-alkoxy 1,3-dienes via *direct*, palladium-catalyzed vinylation of simple vinyl ethers[20] with enol triflates (eq 2).

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[1] Diels-Alder reactions of heterosubstituted dienes have been reviewed: (a) Petrzilka, M.; Grayson, J. I. *Synthesis* **1983**, 753. (b) Schmidt, R. R. *Acc. Chem. Res.* **1986**, *19*, 250. For an excellent theoretical survey, see: (c) Kahn, S. D.; Pau, C. F.; Overman, L. E.; Hehre, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 7381.

[2] (a) Desimoni, G.; Tacconi, G.; Barco, A.; Pollini, G. P. *Natural Product Synthesis through Pericyclic Reactions*; ACS Monograph 180; Washington, 1983; Chapter 5. (b) Thomson, R. H. *Naturally Occurring Quinones III*; Chapman and Hall: London, 1987.

[3] For some examples employing 2-alkoxy dienes, see: (a) Pindur, U.; Pfeuffer, L. *Tetrahedron Lett.* **1987**, *28*, 3079. (b) Caine, D.; Harrison, C. H.; VanDerveer, D. G. *Ibid.* **1983**, *24*, 1353. (c) Rao, A. V. R.; Deshpande, V. H.; Reddy, N. L. *Ibid* **1980**, *21*, 2661. (d) Lebouc, A.; Delaunay, J.; Riobê, O. *J. Chem. Res.* M **1980**, 2683.

[4] Classical preparations of 2-alkoxy 1,3-dienes involve O-alkylation of dienolates and pyrolytic dealcoholysis of β-alkoxy acetals, derived from α,β-unsaturated carbonyl compounds.[5] More recently the methylenation of α,β-unsaturated esters has been described.[6] See also ref 1.

[5] Dolby, L. J.; Marshall, K. *Org. Prep. Proced.* **1969**, *1*, 229.

[6] (a) Pine, S. H.; Pettit, R. J.; Geib, G. D.; Cruz, S. G.; Gallego, C. H.; Tijerina, T.; Pine, R. D. *J. Org. Chem.* **1985**, *50*, 1212. (b) Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3270.

[7] For general discussions of these reactions, see: (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, 1987; Chapter 14:4. (b) Negishi, E.; Takahashi, T.; Baba, S.; Van Horn, D. E.; Okukado, N. *J. Am. Chem. Soc.* **1987**, *109*, 2393. (c) Negishi, E.; Takahashi, T.; Akiyoshi, K. In *Catalysis of Organic Reactions*; Rylander, P. N., Greenfield, H., Augustine, R. L., Eds.; Marcel Decker: New York, 1988.

[8] These starting materials were introduced fairly recently and are particularly attractive because of their simple preparation. The applications of triflates in organometallic chemistry were reviewed recently: Scott, W. J.; McMurry, J. E. *Acc. Chem. Res.* **1988**, *21*, 47.

[9] Jabri, N.; Alexakis, A.; Normant, J. F. *Tetrahedron Lett.* **1981**, *22*, 959.

[10] Coupling with halides: (a) Stille, J. K.; Groh, B. L. *J. Am. Chem. Soc.* **1987**, *109*, 813. With triflates: (b) Scott, W. J.; Stille, J. K *J. Am. Chem. Soc.* **1986**, *108*, 3033.

[11] Suzuki, A. *Pure Appl. Chem.* **1985**, *57*, 1749.

[12] Okukado, N.; Van Horn, D. E.; Klima, W. L.; Negishi, E. *Tetrahedron Lett.* **1978**, *19*, 1027.

[13] Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1988**, *53*, 918.

[14] Baba, S.; Negishi, E. *J. Am. Chem. Soc.* **1976**, *98*, 6729.

[15] Dang, H. P.; Linstrumelle, G. *Tetrahedron Lett.* **1978**, *19*, 191.

[16] (a) Heck, R. F. *Pure Appl. Chem.* **1981**, *53*, 2323; (b) *Org. React.* (N. Y.) **1982**, *27*, 345.

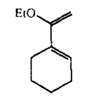
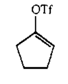
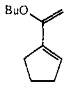
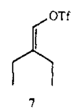
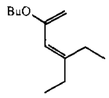
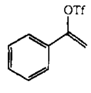
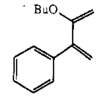
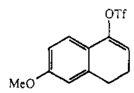
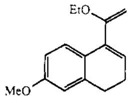
[17] Negishi, E.; Luo, F.-T. *J. Org. Chem.* **1983**, *48*, 1560.

[18] Russel, C. E.; Hegedus, L. S. *J. Am. Chem. Soc.* **1983**, *105*, 943.

[19] Kosugi, M.; Sumiya, T.; Obara, Y.; Suzuki, M.; Sano, H.; Migita, T. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 767.

[20] A recent report from Stilles group demonstrated a palladium-catalyzed vinylation of the enol ether 2,3-dihydro-4*H*-pyran starting from a vinyl triflate. This process furnished a 1,6-diene as a result of double bond migration: Scott, W. J.; Pena, M. R.; Swärd, K.; Stoessel, S. J.; Stille, J. K. *J. Org. Chem.* **1985**, *50*, 2302.

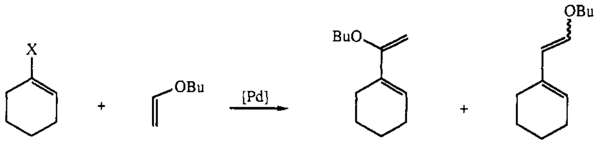
Table II. 2-Alkoxy 1,3-Dienes Prepared by Palladium-Catalyzed Vinylation of Vinyl Ethers with Enol Triflates[a]

enol triflate	vinyl ether	product	yield,[b] %
1	**3a**	4	87; 69;[c] 94[d]
1	**3b**	 10	82
 6	**3a**	 11	48; 37;[c] 65[d]
 7	**3a**	 12	72
 8	**3a**	 13	12
 9	**3b**	 14	56

[a] The triflate was reacted with 5 equiv of vinyl ether in the presence of 1.5 equiv of triethylamine and 0.03 equiv of palladium acetate in DMSO at 60 °C for 3 h. [b] Isolated by chromatography, unless stated. [c] Isolated by distillation. [d] GLC yield.

Results

Initially, cyclohexenyl triflate (**1**) and cyclohexenyl iodide (**2**) were evaluated as potential precursors for the intermediate vinylpalladium species (eq 3). The reactions were performed under traditional Heck reaction conditions, using triethylamine as the base in DMSO.[21]



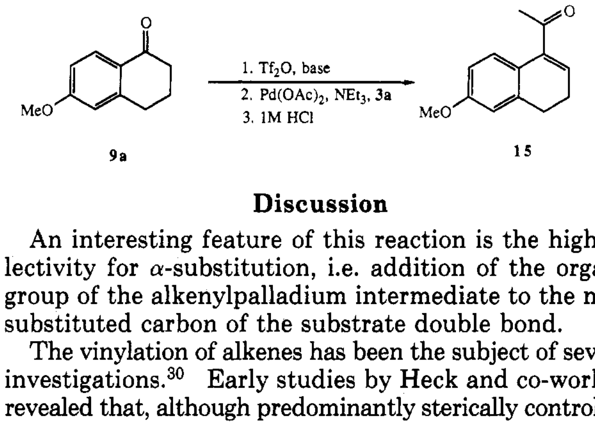
(3)

1: X=OTf
2: X=I
3a
4 major
5 minor

The triflate **1** was found to be superior with respect to both reaction rate[22] and selectivity for alkoxydiene formation[24] (Table I). The vinylation occurred at the oxygen-substituted carbon of the butyl vinyl ether (**3a**), producing the 2-alkoxy diene **4** as the major product. Selectivity was high with both vinylating agents. The observed (GLC) ratio of internally (α) to terminally (β) substituted product (**4**:**5**) was about 20:1. Using 3 mol % of either palladium acetate or tetrakis(triphenylphosphine)palladium as the catalyst precursor, the reaction starting from **1** was complete within 2 h at 60 °C. Prolonged reaction times caused some product decomposition. In the presence of lithium chloride, the reaction was much slower (see below).

The study was next extended to include some other enol triflates. The preparative results are summarized in Table II. The triflates were reacted with excess butyl (**3a**) or ethyl (**3b**) vinyl ether for 3 h at 60 °C in DMSO. In all the cases studied, formation of the α-vinylated product was strongly favored (>90%). After purification by column chromatography, the 2-alkoxy 1,3-dienes could be isolated in moderate to good yields, with the exception of the products of the reaction employing the styryl triflate **8**. This particularly reactive material[25] apparently eliminated triflic acid to give phenylacetylene under the conditions used. Thus, GLC-MS analysis of the reaction mixture in this case revealed the presence of a large amount of 1,3-diphenyl-1-butyn-3-ene,[26] as well as traces of the hydrolysis product acetophenone, in addition to the expected **13**. Attempted vinylation of higher enol ethers[29] was very slow under similar conditions, and at elevated temperatures product decomposition was observed.

The reaction also constitutes an alternative route to α,β-unsaturated methyl ketones, using the vinyl ether as an acyl anion equivalent. This procedure was illustrated by the conversion of the tetralone **9a** into the acetyl derivative **15** in two steps as outlined in eq 4. Thus, hydrolysis of the diene resulting from vinylation with 1 M HCl followed by chromatography provided **15** in 48% overall yield without isolation of the intermediates.



(4)

9a
15

Discussion

An interesting feature of this reaction is the high selectivity for α-substitution, i.e. addition of the organic group of the alkenylpalladium intermediate to the most substituted carbon of the substrate double bond.

The vinylation of alkenes has been the subject of several investigations.[30] Early studies by Heck and co-workers revealed that, although predominantly sterically controlled, these reactions sometimes proceed with unpredictable regio- and stereochemistry[16] and certainly lower selectivity than the analogous arylation reactions. Both the substitution pattern and the electronic properties of the vinylic halide appear to be important in this respect. If an electron-withdrawing substituent is present on one of the carbons of the substrate alkene, however, the vinylic group normally adds to the other. Consequently, vinylations of alkenes such as acrylates and acrylonitriles represent the majority of successful applications of the reaction to date.[31]

Previous reports from this laboratory have dealt with the palladium-catalyzed vinylic substitution of enol ethers

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[21] The use of dimethylformamide or acetonitrile gave a considerably slower reaction.

[22] Although the vinyl iodide showed higher reactivity under phase-transfer conditions,[23] very long reaction times and larger amounts of palladium catalyst were necessary to achieve complete conversion. We have had similar experiences with reactions starting from (*E*)-1-iodohexene.

[23] Jeffery, T. *Tetrahedron Lett.* **1985**, *26*, 2667.

[24] In our hands, reactions employing vinyl iodides produced considerable amounts of homocoupling products despite the use of a large excess of vinyl ether.

[25] Stang, P. J.; Hargrave, R. J.; Dueber, T. E. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1486.

[26] This compound was most probably produced by a palladium-catalyzed reaction of residual **8** with phenylacetylene.[27] The product enyne, which has been reported to be unstable, could not be isolated by chromatography and was identified through a comparison of its mass spectrum with the published data.[28]

[27] Cacchi, S.; Morera, E.; Ortar, G. *Synthesis* **1986**, 320.

[28] Takai, K.; Sato, M.; Oshima, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 108.

[29] The following were studied: butyl (*Z*)-1-propenyl ether, ethyl propenyl ether (*E*/*Z* mixture) and 2,3-dihydro-4*H*-pyran.

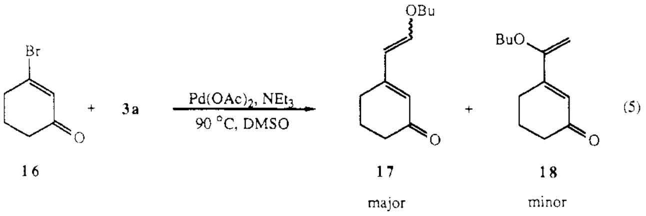
[30] For reviews, see: ref 16 (vinyl halides) and ref 8 (vinyl triflates).

[31] Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic: London, 1985; p 214.

with either aryl or aroyl halides as reagents.[32-37] A critical issue for the utilization of these processes for synthesis has been the regiochemistry. While aromatic acid chlorides furnish β-aroylated products with complete regioselectivity,[32,36] the related arylation reactions invariably give mixtures of regioisomers.[35] High selectivity for α-arylation in acyclic systems has so far been observed only in a few instances.[38] In the present reaction between enol triflates and vinyl ethers, electronic effects apparently dominate, producing primarily the α-substituted product.

During a study[33] of the very similar reaction of vinyl ethers with aryl triflates, an essentially nonregioselective process, we noted that the presence of halide ions in the medium strongly favored the formation of β-products and enhanced the reaction rate. Surprisingly, the presence of lithium chloride in the reaction of cyclohexenyl triflate with butyl vinyl ether suppressed the reaction rate considerably (Table I). No significant effect on the product distribution was observed. This finding, together with the very different regioselectivities encountered, suggests that α-vinylation and β-arylation/aroylation may proceed via different intermediates. Since α-vinylation appears to be logical via a true Heck reaction, an alternative pathway might be considered for the latter reactions.[32,35]

Finally, we were interested to see whether the regioselectivity of vinylation could be altered through selection of a vinylating agent set up for β-attack. Since high selectivity for β-product formation was achieved with use of electron-poor aryl bromides,[35,37] the readily available β-bromocyclohexenone **16** was chosen for this purpose. Indeed, at 90 °C, vinylation of butyl vinyl ether occurred, furnishing the β-vinylated diene **17** as the major product (eq 5). The observed (GLC) ratio of **17** to **18** was 6:1.[39] Similar effects of carbonyl conjugation in the vinylating agent have been reported previously.[16b]



In summary, the regioselective palladium-catalyzed reaction of enol triflates with alkyl vinyl ethers offers an alternative route to 2-alkoxy dienes suitable for cycloaddition reactions. Although only a limited number of examples are provided here, the facile, regiocontrolled preparation of enol triflates,[41] together with the simplicity of the experimental procedure, should give the method some generality. The reaction also constitutes a new method for accomplishing the transformation of ketones, via their enolates, into α,β-unsaturated methyl ketones under comparatively mild conditions.

Experimental Section

Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL 300 spectrometer at 300 and 75.4 MHz, respectively. Chemical shifts are given relative to internal tetramethylsilane. Mass spectra were obtained at 70 eV on a Finnigan 4021 (Data System Incos 2100) GLC–MS instrument. Elemental analyses were obtained from the Microanalytical Laboratory at the University of Lund. Gas chromatographic analyses were performed on a Varian 3700 instrument, equipped with a Supelcowax 10 capillary column (30 m × 0.32 mm) and a flame ionization detector. A Varian 4270 integrator was used for the determination of peak areas. Flash chromatography was performed essentially as described by Still and co-workers.[42]

Materials. Solvents were distilled and stored over molecular sieves until use. Triethylamine was distilled from calcium hydride. Butyl (**3a**) and ethyl (**3b**) vinyl ether were obtained from Fluka AG and were used as received. Palladium salts were obtained from Johnson-Matthey Chemicals. Tetrakis(triphenylphosphine)palladium was prepared by the standard procedure.[43] The enol triflates (**1** and **6–9**) were synthesised from the corresponding ketones by using an excess of triflic anhydride (Janssen) and 2,6-di-*tert*-butylpyridine (Fluka), essentially following the improved procedure of Stang and Treptow.[44] The enol triflates were distilled and stored at −20 °C until use. 3-Bromo-2-cyclohexen-1-one[45] (**16**) and, in low yield, cyclohexenyl iodide[46] (**2**) were prepared by literature methods. Silica gel 60 (E. Merck, 0.040–0.0064 mm) or aluminum oxide (Fluka AG, Type 5016A, pH 9.5) was used for chromatography. Petroleum ether refers to the fraction boiling at 40–60 °C.

Reaction of Cyclohexenyl Triflate and Cyclohexenyl Iodide with Butyl Vinyl Ether. A stock solution was prepared containing naphthalene (internal standard, 2.00 g), triethylamine (4.0 g, 40 mmol), and butyl vinyl ether (10.0 g, 100 mmol) in 100 mL of DMSO. The vinylating agent (**1** or **2**, 1 mmol) was charged in a thin-necked 20-mL Pyrex tube, and 5 mL of the stock solution was added. The appropriate catalyst (see Table I) (0.03 mmol) was introduced, and the tube was closed with a screw cap fitted with a Teflon gasket. After careful mixing, the tube was immersed in an oil bath, maintained at 60 °C. Samples were periodically removed and partitioned between 1 M NaOH and diethyl ether. After GLC–MS analysis of the product distribution, the yield of **4** was determined by hydrolysis (1 M HCl) to 1-acetylcyclohexene, whose response factor was obtained from a commercially obtained sample.

Preparative Reactions. The preparation of 1-(1-butoxyethenyl)cyclohexene illustrates the general procedures employed. The product dienes decomposed slowly at room temperature, but storage over longer periods (months) was possible at −20 °C under argon. Spectral and analytical properties of the other isolated 2-alkoxy 1,3-dienes are compiled below.

1-(1-Butoxyethenyl)cyclohexene (4). Isolation by Chromatography. Butyl vinyl ether (2.5 g, 25 mmol), triethylamine (0.75 g, 7.5 mmol), and cyclohexenyl triflate (1.15 g, 5 mmol) were charged in a thin-necked, 50-mL Pyrex tube. A solution of palladium acetate (34 mg, 0.15 mmol) in 10 mL of DMSO was added, and the tube was closed with a screw cap. The orange mixture was heated to 60–65 °C with stirring on an oil bath. Within 15 min, the solution turned black. After 3 h, GLC analysis showed that the starting **1** had been consumed, and a palladium mirror was observed in the vessel. After cooling, the reaction mixture was poured into 100 mL of ice–water and extracted with three 50-mL portions of petroleum ether. The combined organic layers were washed with 50 mL of 1 M NaOH. Drying ($MgSO_4$) and concentration under reduced pressure afforded the crude product as a yellow oil, which was passed through a column (ϕ

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(32) Andersson, C.-M.; Hallberg, A. *J. Org. Chem.* **1988**, *53*, 4257.

(33) Andersson, C.-M.; Hallberg, A. *J. Org. Chem.* **1988**, *53*, 2112.

(34) Andersson, C.-M.; Hallberg, A. *J. Org. Chem.* **1988**, *53*, 235.

(35) Andersson, C.-M.; Hallberg, A.; Daves, G. D., Jr. *J. Org. Chem.* **1987**, *52*, 3529.

(36) Andersson, C.-M.; Hallberg, A. *Tetrahedron Lett.* **1987**, *28*, 4215.

(37) Hallberg, A.; Westfelt, L.; Andersson, C.-M. *Synth. Commun.* **1985**, *15*, 1131.

(38) (a) Lee, T. D.; Daves, G. D., Jr. *J. Org. Chem.* **1983**, *48*, 399. (b) Hallberg, A.; Westfelt, L.; Holm, B. *Ibid.* **1981**, *46*, 5414.

(39) This ratio could not be accurately determined, due to some product decomposition at the elevated temperature necessary.[40] The isolation of the β-product stereoisomers in 52% yield (see the Experimental Section) still establishes high selectivity. We obtained similar results (β:α = 8:1) by starting from the corresponding iodo derivative.[45]

(40) Facile oxidative cleavage of some enol ethers with atmospheric oxygen is known, see: Taylor, R. *J. Chem. Res. S* **1987**, 178.

(41) Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 85.

(42) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(43) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.

(44) Stang, P. J.; Treptow, W. *Synthesis* **1980**, 283.

(45) Piers, E.; Grierson, J. R.; Lau, C. K.; Nagakura, I. *Can. J. Chem.* **1982**, *60*, 210.

(46) Pross, A.; Sternhell, S. *Aust. J. Chem.* **1970**, *23*, 989.

3 cm) of 50 g basic alumina using 2% triethylamine in petroleum ether as the eluent. Early fractions contained the desired diene 4 (monitored by treatment of TLC spots with an acidic aqueous solution of 2,4-dinitrophenylhydrazine). Evaporation of the solvent gave 0.79 g (87%) of the title compound as a colorless oil. The material thus obtained was >95% pure by capillary GLC analysis.

Isolation by Distillation. Butyl vinyl ether (10 g, 100 mmol), triethylamine (4.0 g, 40 mmol), and cyclohexenyl triflate (4.6 g, 20 mmol) were charged in a 100-mL, thin-necked Pyrex tube. After the addition of a solution of palladium acetate (0.14 g, 0.6 mmol) in 40 mL of DMSO, the tube was closed with a screw cap. After heating to 65 °C for 2 h, the cooled solution was poured into 100 mL of 1 M NaOH and extracted with three 50-mL portions of diethyl ether. The ethereal solution was washed twice with 25 mL of 1 M NaOH and dried over K_2CO_3. After concentration, vacuum distillation over a 15-cm Vigreux column (in the presence of a small amount of solid K_2CO_3) afforded 2.5 g (69%) of the title diene 4: bp 71–73 °C (0.3 mmHg); ^{1}H NMR ($CDCl_3$) δ 6.32 (m, 1 H), 4.15 (d, 1 H, J = 2.1 Hz), 3.98 (d, 1 H, J = 2.1 Hz), 3.72 (t, 2 H, J = 6.4 Hz), 2.15 (m, 4 H), 1.69 (m, 4 H), 1.58 (m, 2 H), 1.47 (m, 2 H), 0.96 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 160.6, 132.1, 124.8, 80.5, 66.9, 31.2, 25.4, 25.1, 22.8, 22.2, 19.5, 13.9; MS, *m/e* (relative intensity) 180 (4), 165 (22), 125 (14), 124 (17), 109 (78), 43 (100). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.8; H, 11.2.

1-(1-Ethoxyethenyl)cyclohexene (10): ^{1}H NMR (CCl_4) δ 6.19 (m, 1 H), 4.00 (d, 1 H, J = 2 Hz), 3.82 (d, 1 H, J = 2 Hz), 3.70 (q, 2 H), 2.10 (m, 4 H), 1.62 (m, 4 H), 1.32 (t, 3 H); ^{13}C NMR (CCl_4) δ 160.2, 131.5, 124.1, 80.0, 61.8, 25.1, 24.8, 22.6, 22.1, 14.5; MS *m/e* (relative intensity) 152 (23), 137 (6), 124 (18), 123 (3), 109 (56), 43 (100). Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 79.3; H, 10.6.

1-(1-Butoxyethenyl)cyclopentene (11): bp 45–7 °C (0.2 mmHg). The material obtained by chromatography in this case contained a high-boiling impurity, which was removed through Kugelrohr distillation (0.8 mmHg, oven temperature 70 °C): ^{1}H NMR (CCl_4) δ 5.96 (s, broad, 1 H), 3.95 (s, broad, 2 H), 3.67 (t, 2 H, J = 6 Hz), 2.41 (t, 4 H, J = 8 Hz), 1.90 (p, 2 H, J = 8 Hz), 1.68 (m, 2 H), 1.47 (m, 2 H), 0.94 (t, 3 H); ^{13}C NMR (CCl_4) δ 157.5, 139.1, 127.1, 82.7, 66.0, 32.7, 32.0, 31.0, 23.0, 19.3, 13.8; MS *m/e* (relative intensity) 166 (8), 151 (23), 111 (35), 110 (14), 95 (91), 43 (100). Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.0; H, 11.0.

2-Butoxy-4-ethyl-1,3-hexadiene (12): ^{1}H NMR (CCl_4) δ 5.44 (s, 1 H), 3.91 (d, 1 H, J = 1.6 Hz), 3.84 (d, 1 H, J = 1.6 Hz), 3.64 (t, 2 H), 2.31 (q, 2 H, J = 7.5 Hz), 2.05 (dq, 2 H, J = 7.5, 1.3 Hz), 1.68 (m, 2 H), 1.46 (m, 2 H), 1.04 (t, 3 H), 0.99 (t, 3 H), 0.96 (t, 3 H); ^{13}C NMR (CCl_4) δ 159.7, 146.7, 119.8, 84.6, 66.3, 31.1, 30.2, 24.6, 19.3, 13.8, 13.5, 12.6; MS *m/e* (relative intensity) 182 (13), 167 (2), 153 (5), 126 (15), 125 (11), 111 (94), 43 (100). Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.4; H, 12.2.

2-Butoxy-3-phenyl-1,3-butadiene (13): ^{1}H NMR ($CDCl_3$) δ 7.3–7.4 (m, 5 H), 5.73 (d, 1 H, J = 2 Hz), 5.23 (s, broad, 1 H), 4.29 (s, broad, 1 H), 4.13 (d, 1 H, J = 2 Hz), 3.82 (t, 2 H), 1.77 (m, 2 H), 1.50 (m, 2 H), 0.99 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 160.3, 145.9, 140.4, 128.7, 127.9, 127.4, 114.7, 87.4, 67.4, 31.2, 19.5, 13.9; MS *m/e* (relative intensity) 202 (11), 187 (2), 159 (7), 146 (40), 145 (39), 131 (43), 118 (58), 117 (63), 41 (100).

4-(1-Ethoxyethenyl)-7-methoxy-1,2-dihydronaphthalene (14): ^{1}H NMR (CCl_4) δ 7.08 (m, 1 H), 6.55 (m, 2 H), 6.02 (t, 1 H, J = 6 Hz), 4.18 (d, 1 H, J = 1.5 Hz), 4.08 (d, 1 H, J = 1.5 Hz), 3.74 (q, 2 H, J = 7 Hz), 3.67 (s, 3 H), 2.63 (t, 2 H, J = 8 Hz), 2.21 (m, 2 H), 1.28 (t, 3 H, J = 7 Hz); ^{13}C NMR (CCl_4) δ 161.0, 158.2, 137.3, 136.1, 126.2, 126.0, 124.7, 113.1, 110.5, 84.4, 62.3, 54.3, 28.3, 22.8, 14.4; MS *m/e* (relative intensity) 230 (18), 215 (1), 201 (6), 199 (3), 186 (16), 173 (11), 159 (19), 43 (100). Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 77.5; H, 7.92.

4-Acetyl-7-methoxy-1,2-dihydronaphthalene (15). To a mixture of 7-methoxy-1,2-dihydronaphthalen-4-yl triflate (1.54 g, 5 mmol), butyl vinyl ether (2.5 g, 25 mmol), and triethylamine (0.75 g, 7.5 mmol) in a thin-necked, 50-mL tube a solution of palladium acetate (34 mg, 0.15 mmol) in 10 mL of DMSO was added. The tube was capped and heated to 65 °C for 3 h with stirring. After cooling, the crude mixture was poured into 100 mL of 1 M HCl and extracted with three 50-mL portions of diethyl ether. The combined ethereal layers were washed with 50 mL of 1 M HCl, saturated $NaHCO_3$, and brine. The organic solution was then treated with active charcoal, dried ($MgSO_4$), and concentrated. Flash chromatography (silica), with a mixture of petroleum ether and diethyl ether (4:1) as the eluent, gave the title substance as a pale yellow oil: 0.49 g (48%); ^{1}H NMR ($CDCl_3$) δ 7.69 (d, 1 H, J = 8 Hz), 6.89 (t, 1 H, J = 5 Hz), 6.73 (m, 2 H), 3.79 (s, 3 H), 2.68 (t, 2 H, J = 8 Hz), 2.42 (s, 3 H), 2.39 (m, 2 H); MS *m/e* (relative intensity) 202 (36), 187 (4), 159 (56), 144 (27), 128 (10), 127 (11), 115 (21). Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.2; H, 6.98. Found: C, 75.9; H, 6.90.

Reaction of 3-Bromo-2-cyclohexen-1-one (16) with Butyl Vinyl Ether. Butyl vinyl ether (1.0 g, 10 mmol), triethylamine (0.3 g, 3 mmol), the vinyl bromide **16** (0.35 g, 2 mmol), and naphthalene (internal standard, 0.20 g) were charged in a thin-necked tube. Palladium acetate (22 mg, 0.1 mmol) dissolved in 4 mL of DMSO was added, and the solution was degassed and purged with argon. The sealed tube was heated to 90 °C with stirring until GLC analysis showed that **16** had been consumed (6 h). GLC–MS analysis of the resulting solution revealed the presence of the isomeric (butoxyethenyl)cyclohexenones in a β:α ratio (17:18) of 6:1 (see Discussion). Also present was a smaller amount of a byproduct, which by its mass spectrum was assigned as 3-carbobutoxy-2-cyclohexene-1-one, probably formed by partial oxidation of the products.[40] The reaction mixture was partitioned between diethyl ether and water, and the organic phase was dried and concentrated. Flash chromatography of the resulting oil (silica; diethyl ether–petroleum ether, 2:1) allowed the isolation of an *E*/*Z* mixture (≈2/1) of 3-(2-butoxyethenyl)-2-cyclohexen-1-one (**17**) as a pale yellow oil: 0.20 g (52%); ^{1}H NMR (CCl_4, *E*/*Z* mixture) δ 6.89 (d, J = 13 Hz, *E*), 6.19 (d, J = 7 Hz, *Z*), 5.86 (s, broad, *Z*), 5.64 (s, broad, *E*), 5.56 (d, J = 13 Hz, *E*), 4.81 (d, J = 7 Hz, *Z*), 3.90 (t, J = 6.5 Hz, *Z*), 3.81 (t, J = 6.5 Hz, *E*), 2.36 (m, *E* + *Z*), 2.33 (m, *E* + *Z*), 1.98 (m, *E* + *Z*), 1.66 (m, *E* + *Z*), 1.43 (m, *E* + *Z*), 0.98 (t, *Z*), 0.96 (t, *E*); MS *m/e* (relative intensity) 194 (58), 138 (77), 137 (22), 120 (16), 119 (100).

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Registry No. **1**, 28075-50-5; **2**, 17497-53-9; **3a**, 111-34-2; **3b**, 109-92-2; **4**, 118716-31-7; **6**, 28075-49-2; **7**, 53282-31-8; **8**, 28143-79-5; **9**, 115375-59-2; **10**, 118716-32-8; **11**, 118716-33-9; **12**, 118716-34-0; **13**, 118716-35-1; **14**, 118716-36-2; **15**, 83669-11-8; **16**, 56671-81-9; (*E*)-**17**, 118716-37-3; (*Z*)-**17**, 118716-38-4; **18**, 118716-39-5; Pd(PPh_3)$_4$, 14221-01-3; Pd(OAc)$_2$, 3375-31-3; LiCl, 7447-41-8.