presence of $Eu(hfc)_3$ gave ee 56 ± 5%. Calculation with $[\alpha]^{20}_{D\,max}$ +15.7 ± 0.3° gave ee 52 ± 4%.

The same reaction was conducted on (*R*)-11 (228 mg, 1.02 mmol) ($[\alpha]^{20}_D$ −4.97 ± 0.34° (*c* 1.65, EtOH), 33 ± 5% ee) and gave 211 mg (70% yield) of 4: $[\alpha]^{20}_D$ −4.37 ± 0.28° (*c* 2.15, toluene). Examination of the ^1H NMR spectrum in the presence of $Eu(hfc)_3$ gave ee 30 ± 5%. Calculation with $[\alpha]^{20}_{D\,max}$ −15.7 ± 0.3° gave ee 28 ± 3%.

Stereoselective Cyclization of (2-Bromophenyl)- and (2-Iodophenyl)alkynes Catalyzed by Palladium(0) Complexes

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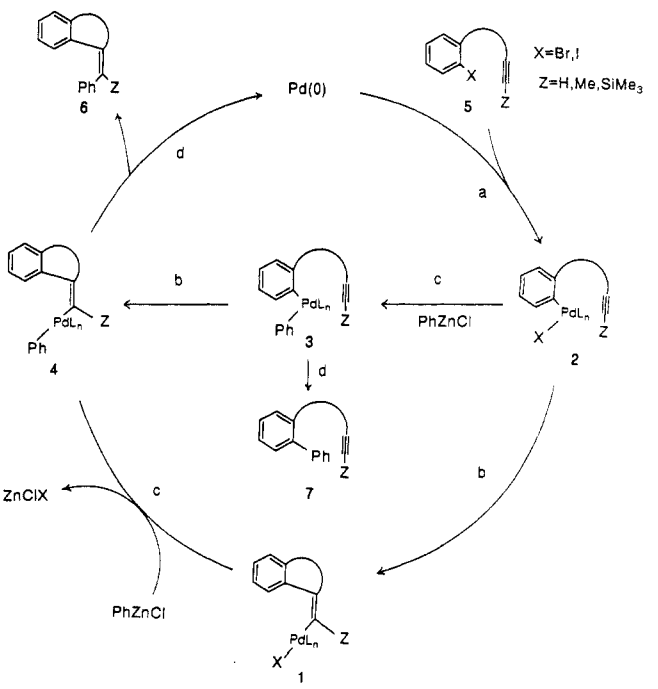
The Pd(II)-intermediate generated by intramolecular arylation of alkynes can be further cross-coupled with phenylzinc chloride to recycle the Pd(0) catalyst and give stereodefined exocyclic indans and tetralins. For example, (*Z*)-1-benzylideneindan can be obtained in 60% yield from 4-(2-iodophenyl)-1-butyne and phenylzinc chloride in the presence of 5 mol % of $Pd(PPh_3)_4$ in THF at room temperature. The alkynyl group can be terminal or internal. Several features and the mechanism of the process are discussed.

The usefulness of the highly regio- and stereoselective coupling involving the Pd-catalyzed arylation or alkenylation of olefins (Heck reaction) has been widely recognized by synthetic chemists.[1] Although particular attention has been paid to the Pd-catalyzed intramolecular arylation of alkenes to form cyclic or heterocyclic compounds,[2] the number of papers reporting the potential utility of the Pd-catalyzed intramolecular arylation of alkynes is still very small.[3] One obvious reason is that the Pd-catalyzed intramolecular arylation of alkynes was limited by the lack of a β-hydride elimination pathway for the Pd(II) intermediate to recycle Pd(0) complexes. It is also well documented that the coupling of organic electrophiles with organometallic reagents catalyzed by a Pd(0) complex (for example, vinyl halide and phenylzinc chloride in the presence of Pd(0) catalyst)[4] involves a Pd(II) intermediate after the oxidative addition step. Thus, we intended to use the alkenylpalladium(II) intermediate 1 generated by the arylation of alkynes for further cross-coupling reactions. The objectives of this investigation were (1) to explore the applications of Pd-catalyzed arylation of alkynes, (2) to demonstrate the generality of the cross-coupling reaction by using palladium as the catalyst, and (3) to synthesize stereodefined exocyclic indanes and tetralins (Scheme I).

Scheme I. Proposed Mechanism for the Cyclization and Coupling Reaction of Aryl Halides 5 with Phenylzinc Chloride in the Presence of Pd(0) Catalyst[a]



[a] (a) Oxidative addition; (b) cis-carbopalladation; (c) transmetalation; (d) reductive elimination.

Results and Discussion

Two requirements must be met for the successful execution of this catalytic process. (1) Either the intramolecular cis-carbopalladation of **2** must be faster than the

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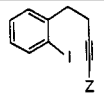
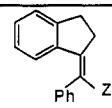
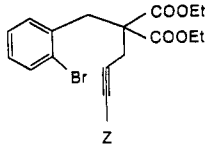
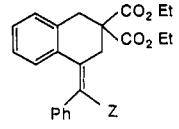
Table I. Pd-Catalyzed Intramolecular Carbopalladation and Cross-Coupling Reaction

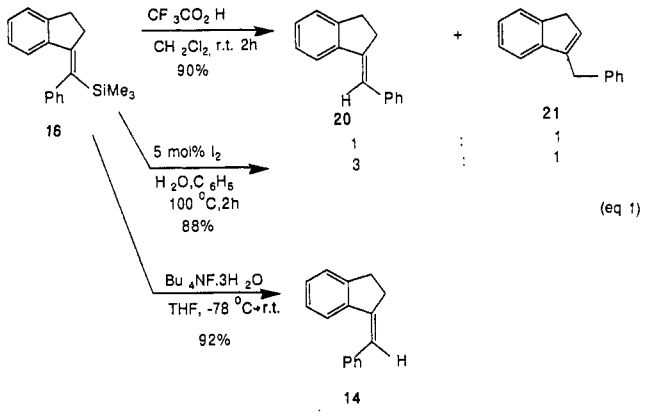
substrate	cyclized product	yield,[a] %
		
8, Z = H	14	60
9, Z = Me	15	68
10, Z = $SiMe_3$	16	46[b]
		
11, Z = H	17	51
12, Z = Me	18	55
13, Z = $SiMe_3$	19	43[b]

[a] Isolated yield of purified product. [b] Compounds **10** and **13** were 36 and 48% recovered.

transmetalation of the intermediate **2** with phenylzinc chloride or the intramolecular cis-carbopalladation of **3** must be faster than the reductive elimination of **3**. (2) When Z is equal to a methyl group, the β-elimination of **1** and **4** must be slower than transmetalation and reductive elimination.

The reaction of phenylzinc chloride with **5** in the presence of 5 mol % of $Pd(PPh_3)_4$ in THF at room temperature gave cyclized products **6** in 43–68% yields (Table I). The uncyclized products **7** were isolated in only 10–12% yields. The need for the $Pd(PPh_3)_4$ catalyst has been established in all cases by running control experiments in its absence. When a stoichiometric amount of $Pd(PPh_3)_4$ was used, only the cyclized and cross-coupled products **6** were obtained in 40–72% yields. Using dimethylformamide instead of THF as the solvent to run the reaction at room temperature[2c,5] gave both cyclized and uncyclized products in good yields at about 1:1 ratio. Using 5 mol % $Pd(dba)_2$ in the reaction gave very low yields of both cyclized and uncyclized products.

These examples demonstrate several features of the Pd-catalyzed intramolecular arylation of alkynes and cross-coupling reactions. The intramolecular cis-carbopalladation process via the arylpalladium(II) species (**2** or **3**) with alkynes to form a new five- or six-membered ring at room temperature is faster than the competitive processes. The reductive elimination of **3** is probably circumvented by the rapid complexation of Pd(II) with the proximate triple bond. The results using stoichiometric amounts of Pd indeed show that the cis-carbopalladation of **2** is faster than the transmetalation process, and the products are derived exclusively from the intermediate **1**. The reaction is not resricted to aryl iodides. Aryl bromides **11–13** are cyclized and cross-coupled with pheylzinc chloride by the palladium catalyst to give **17–19** in 43–55% yield. The absence of allenes under these conditions suggests that when Z is equal to a methyl group, the β-elimination of **1** or **4** to give allenes is relatively slow. Probably the orbital overlap between Pd and the hydrogen on methyl group is unfavorable when Pd is on an sp^2 carbon.[6] When Z is trimethylsilyl, the lower yields of cyclized products indicate that steric effects play a role to some extent in the cyclization processes. The nondetectable amount of regioisomers, stereoisomers, and double-bond migration isomers based on ^1H, ^{13}C, and ^1H 2D NOESY NMR spectroscopy clearly indicate that the cyclization and cross-coupling processes are highly regio- and stereoselective. Attempts to desilylate compound **16** by using trifluoroacetic acid in methylene chloride or with catalytic amounts of iodine and water in benzene at 100 °C[7] gave compounds **20** and **21** as shown in eq 1. However, compound **16** was desilylated stereospecifically to **14** by treatment with a solution of tetrabutylammonium fluoride in THF at −78 °C for 2 h, thus, verifying the identity and stereochemistry of **16**. Unlike radical cyclization reactions,[8] five- and six-membered rings are accessible in this reaction.



(eq 1)

We believe there are several aspects of this process that merit emphasis. Since the cyclization and coupling take place simultaneously, the process is quick and operationally simple. The formation of tri- or tetra-substituted alkylidene indans and tetralins of defined stereochemistry is a major advantage of this method. In contrast, the conventional methods to prepare benzylideneindan give the *E* isomer of **14** in low yields.[9]

Experimental Section

Melting points and boiling points are uncorrected. ^1H and ^{13}C NMR spectra were obtained at 200 and 50 MHz, respectively. Precoated silica gel 60F-254 on aluminum plates made by EM Chemical Co. were used for thin-layer chromatography. Purification by column chromatography was carried out with EM Reagents silica gel 60 (70–230 mesh ASTM). High-pressure liquid chromatography (HPLC) separation were performed at a flow rate of 3 mL/min by use of two Chemco Pak 10 × 250 columns packed with Chemcosorb 5-ODS-H. GLC analyses were performed on a 3.2 m × 3.1 mm column packed with SE-30 (5% on Chromosorb W). All reactions involving organometallics were carried out in oven-dried (120 °C) or flame-dried glassware equipped with a side arm, a reflux condenser, gas outlet adapter, and a mercury bubbler for the purpose of maintaining an inert atmosphere. The purity of all title compounds was judged to be ≥95% by HPLC and ^1H NMR as well as ^{13}C NMR spectral analyses. Tetrakis(triphenylphosphine)palladium[10] and bis(dibenzylideneacetone)palladium[11] were prepared by published procedures. Zinc chloride was dried before being used at 100 °C at 1 mm for 3 h. Tetrahydrofuran (THF) and diethyl ether were

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(6) This slow β-elimination has also been observed previously.[3a]

(7) Yamakawa, K.; Nishitani, K.; Tominaga, T. *Tetrahedron Lett.* **1975**, 2829.

(8) For a review, see: Giese, B. *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*; Pergamon Press: New York, 1986.

(9) For example: (a) Irradiation of 2-vinylstilbene absorbed on silica gel gave (*E*)-1-benzylideneindan, but no *Z* form in 8.7% yield: Tol, A. J. W.; Laarhoven, W. H. *J. Org. Chem.* **1986**, *51*, 1663. (b) The Wittig reaction of benzylidenetriphenylphosphorane and 1-indanone gave 1-benzylideneindan in 3–9.1% yield: Witschard, G.; Griffin, C. E. *J. Org. Chem.* **1964**, *29*, 2335.

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distilled from sodium benzophenone ketyl immediately prior to use. Dimethylformamide from Aldrich was dried and distilled from CaH_2 under reduced pressure.

1-(3-Butynyl)-2-iodobenzene (8). Allenylmagnesium bromide[12] (10.5 mL of 4.0 N in diethyl ether) was added to a solution of 2-iodobenzyl bromide[13] (11.88 g, 40 mmol) in 50 mL of THF at 0 °C. The reaction mixture was warmed to room temperature, and stirring was continued for 3 h. The reaction was quenched at 0 °C with water (100 mL), and the solution was extracted with diethyl ether (50 mL × 3). The combined organic layers were washed with water (30 mL × 2) and brine (30 mL × 2), dried ($MgSO_4$), and concentrated. Distillation of the remaining liquid gave 8.80 g (86%) of 8: bp 100–102 °C (5 mm); IR (neat) 3300 (s), 2120 (w), 1435 (s), 1010 (s), 745 (s), 640 (s) cm^{-1}. ^1H NMR ($CDCl_3$, TMS) δ 1.99 (t, J = 2.6 Hz, 1 H), 2.49 (dt, J = 2.6, 7.5 Hz, 2 H), 2.96 (t, J = 7.5 Hz, 2 H), 6.87–6.96 (m, 1 H), 7.26–7.30 (m, 2 H), 7.81 (d, J = 7.7 Hz, 1 H) ppm; ^{13}C NMR ($CDCl_3$, TMS) δ 18.97, 39.50, 69.11, 83.02, 100.14, 128.14, 129.66, 139.36, 142.52 ppm; MS m/z 256 (M^+), 217, 129, 90; HRMS calcd for $C_{10}H_9I$ 255.9749, found 255.9756.

1-(3-Pentynyl)-2-iodobenzene (9). A solution of lithium diisopropylamide (LDA), prepared from diisopropylamine (1.06 g, 10.5 mmol) and n-BuLi (5 mL of 2.1 N in hexane) in 10 mL of THF at 0 °C, was added dropwise over 15 min to 8 (2.56 g, 10 mmol) in 10 mL of THF at 0 °C. After 30 min of stirring, methyl iodide (2.13 g, 15 mmol) was added. The solution was warmed to room temperature and stirred for 3 h. The product was isolated and purified as described for 8 to give 2.05 g (76%) of 9: bp 132–134 °C (3 mm); IR (neat) 1465 (s), 1450 (s), 1435 (s), 1010 (s), 750 (s) cm^{-1}; ^1H NMR ($CDCl_3$, TMS) δ 1.78 (t, J = 2.5 Hz, 3 H), 2.37–2.46 (m, 2 H), 2.91 (t, J = 7.2 Hz, 2 H), 6.85–6.94 (m, 1 H), 7.26–7.29 (m, 2 H), 7.80 (dt, J = 0.8, 7.9 Hz, 1 H) ppm; ^{13}C NMR ($CDCl_3$, TMS) δ 3.40, 19.40, 40.16, 76.38, 77.82, 100.25, 127.92, 128.06, 129.53, 139.29, 143.13 ppm; HRMS calcd for $C_{11}H_{11}I$ 269.9906, found 269.9881.

1-[4-(Trimethylsilyl)-3-butynyl]-2-iodobenzene (10). The compound was prepared in 64% yield (2.10 g) by a procedure similar to that for the preparation of 9 using 2.56 g (10 mmol) of 8, 10.5 mmol of LDA, and 1.63 g (15 mmol) of trimethylsilyl chloride: bp 135–137 °C (3 mm); IR (neat) 2180 (m), 1010 (m), 840 (s), 760 (m), 748 (m) cm^{-1}; ^1H NMR ($CDCl_3$, TMS) δ 0.14 (s, 9 H), 2.52 (t, J = 7.5 Hz, 2 H), 2.94 (t, J = 7.5 Hz, 2 H), 6.8–6.9 (m, 1 H), 7.2–7.3 (m, 2 H), 7.81 (d, J = 7.7 Hz, 1 H) ppm; ^{13}C NMR ($CDCl_3$, TMS) δ 0.02, 20.48, 39.64, 85.58, 100.21, 105.77, 128.07, 129.99, 139.32, 142.76 ppm; MS m/z 328 (M^+), 313, 217, 201, 185, 143; HRMS calcd for $C_{13}H_{17}ISi$ 328.0144, found 328.0143.

Diethyl 2-[(2-Bromophenyl)methyl]-2-(2-propynyl)-propanedioate (11). Diethyl 2-(2-bromobenzyl)malonate[14] (9.02 g, 27.4 mmol) was added to a solution of sodium ethoxide in ethyl alcohol, prepared from sodium (0.63 g, 27.4 mmol) and 30 mL of absolute alcohol at 25 °C, at ambient temperature. The reaction mixture was stirred for 1.5 h, and then freshly distilled propargyl bromide (3.33 g, 28 mmol) was added. The reaction mixture was stirred for another 12 h at 25 °C, followed by the workup procedures as described for 8. Purification by column chromatography (20% EtOAc in hexanes as eluant) gave 7.93 g (79%) of 11 as a colorless liquid: IR (neat) 1735 (br s), 1015 (m), 755 (m) cm^{-1}; ^1H NMR ($CDCl_3$, TMS) δ 1.23 (t, J = 7.2 Hz, 6 H), 2.14 (t, J = 2.7 Hz, 1 H), 2.78 (d, J = 2.7 Hz, 2 H), 3.61 (s, 2 H), 4.1–4.3 (m, 4 H), 7.0–7.6 (m, 4 H) ppm; ^{13}C NMR ($CDCl_3$, TMS) δ 13.77 23.03, 36.48, 57.40, 61.71, 72.12, 79.40, 125.63, 127.10, 128.56, 131.95, 132.98, 135.52, 169.52 ppm; MS m/z 365 (M^+ – H), 287 (M^+ – Br). Anal. Calcd for $C_{17}H_{19}BrO_4$: C, 55.60; H, 5.22. Found: C, 55.57; H, 5.24.

Diethyl 2-[(2-Bromophenyl)methyl]-2-(2-butynyl)-propanedioate (12). The compound was prepared in 72% yield (1.98 g) as a colorless liquid by a procedure similar to that for the preparation of 11 using 2.37 g (7.2 mmol) of diethyl 2-(2-bromobenzyl)malonate, 7.2 mmol of sodium ethoxide in 10 mL of absolute alcohol, and 1.01 g (7.6 mmol) of 1-bromo-2-butyne:[15] IR 1740 (br s), 1280 (s), 1240 (s), 1200 (s), 1065 (s), 1050 (s) cm^{-1}; ^1H NMR ($CDCl_3$, TMS) δ 1.23 (t, J = 7.1 Hz, 6 H), 1.81 (t, J = 2.5 Hz, 3 H), 2.71 (q, J = 2.5 Hz, 2 H), 3.59 (s, 2 H), 4.1–4.3 (m, 4 H), 7.0–7.6 (m, 4 H) ppm; ^{13}C NMR ($CDCl_3$, TMS) δ 3.48, 13.77, 23.33, 36.43, 57.65, 61.51, 73.92, 79.54, 125.62, 127.00, 128.40, 131.98, 132.90, 135.80, 169.88 ppm; MS m/z 381 (M^+ + H), 301 (M^+ – Br), 281; HRMS calcd for $C_{18}H_{22}BrO_4$ (M^+ + H) 381.0701, found 381.0690.

Diethyl 2-[(2-Bromophenyl)methyl]-2-[3-(trimethylsilyl)-2-propynyl]propanedioate (13). The compound was prepared in 68% yield (1.55 g) as a colorless liquid by a procedure similar to that for the preparation of 11 using 1.71 g (5.2 mmol) of diethyl 2-(2-bromobenzyl)malonate, 5.2 mmol of sodium ethoxide in 10 mL of absolute alcohol, and 1.03 g (5.4 mmol) of 3-bromo-1-(trimethylsilyl)-1-propyne:[16] IR (neat) 2180 (m), 1730 (s), 1250 (s), 1185 (s), 1030 (s), 840 (s), 760 (s) cm^{-1}; ^1H NMR ($CDCl_3$, TMS) δ 0.16 (s, 9 H), 1.24 (t, J = 7.2 Hz, 6 H), 2.78 (s, 2 H), 3.60 (s, 2 H), 4.3–4.4 (m, 4 H), 7.0–7.6 (m, 4 H) ppm; ^{13}C NMR ($CDCl_3$, TMS) δ –0.13, 13.83, 24.34, 36.54, 57.64, 61.64, 88.96, 101.97, 125.70, 127.09, 128.50, 131.97, 132.98, 135.73, 169.58 ppm; MS m/z 423 (M^+ – 15), 360, 359, 223, 179, 171, 169, 103; HRMS calcd for $C_{20}H_{27}O_4Si$ (M^+ – Br) 359.1678, found 359.1685.

(Z)-2,3-Dihydro-1-(1-phenylmethylidene)indene (14). A Representative Procedure for Pd-Catalyzed Intramolecular Cross-Coupling Reaction. To a mixture of 8 (1.28 g, 5 mmol) in 10 mL of THF were sequentially added $Pd(PPh_3)_4$ (0.29 g, 0.25 mmol) in 3 mL of THF and phenylzinc chloride solution, prepared from phenylmagnesium bromide (10 mL of 1.5 N in THF) and zinc chloride solution (12.5 mL of 1.2 N in THF), over 2 h. The reaction mixture was then stirred at room temperature for another 8 h. The reaction mixture was worked up as described for 8, and the product was purified by column chromatography (20% EtOAc in hexanes as eluant) to give 14 as a colorless liquid in 60% yield (0.62 g): IR (neat) 1640 (w), 750 (s), 720 (m), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$, TMS) δ 2.8–3.0 (m, 4 H), 6.60 (br s, 1 H), 7.22 (t, J = 8.2 Hz, 1 H), 7.1–7.4 (m, 8 H) ppm; ^{13}C NMR ($CDCl_3$, TMS) δ 30.03, 34.01, 121.39, 124.19, 125.18, 125.60, 126.52, 127.98, 128.26, 128.38, 138.25, 139.49, 143.22, 148.63 ppm; MS m/z 206 (M^+), 178, 165, 128, 115, 101, 91; HRMS calcd for $C_{16}H_{14}$ 206.1096, found 206.1099.

(Z)-2,3-Dihydro-1-(1-methyl-1-phenylmethylidene)indene (15): 68% yield; colorless oil; IR (neat) 1600 (w), 1460 (m), 1440 (m), 755 (s), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$, TMS) δ 2.12 (t, J = 1.4 Hz, 3 H), 2.81–2.90 (m, 2 H), 3.01 (dd, J = 5.5, 10 Hz, 2 H), 6.29 (d, J = 7.9 Hz, 1 H), 6.76 (dt, J = 0.6, 7.9 Hz, 1 H), 7.01 (dt, J = 1.0, 7.4 Hz, 1 H), 7.1–7.4 (m, 6 H) ppm; ^{13}C NMR ($CDCl_3$, TMS) δ 23.87, 29.71, 30.67, 123.96, 124.82, 125.48, 126.52, 127.95, 128.75, 129.77, 137.36, 144.47, 147.35 ppm; MS m/z 220 (M^+), 205, 178, 165, 129, 105; HRMS calcd for $C_{17}H_{16}$ 220.1252, found 220.1248.

(E)-2,3-Dihydro-1-[1-(trimethylsilyl)-1-phenylmethylidene]indene (16): 46% yield; mp 47–48 °C; IR (neat) 1605 (m), 1246 (s), 885 (s), 846 (s), 833 (s), 756 (s), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$, TMS) δ 0.11 (s, 9 H), 2.9–3.0 (m, 4 H), 6.10 (d, J = 8.0 Hz, 1 H), 6.74 (t, J = 7.6 Hz, 1 H), 6.97–7.34 (m, 7 H) ppm; ^{13}C NMR ($CDCl_3$, TMS) δ –0.22, 30.25, 32.43, 124.96, 125.27, 125.61, 127.53, 127.65, 128.64, 136.22, 141.15, 144.78, 147.68, 151.18 ppm; MS m/z 278 (M^+), 263, 245, 219, 185, 135; HRMS calcd for $C_{19}H_{22}Si$ 278.1491, found 278.1484.

(Z)-Diethyl 1,2,3,4-tetrahydro-1-(1-phenylmethylidene)-naphthalene-3,3-dicarboxylate (17): 51% yield; colorless oil; IR (neat) 1735 (s), 1240 (m), 1180 (m), 1060 (m), 765 (m), 700 (m) cm^{-1}; ^1H NMR ($CDCl_3$, TMS) δ 1.22 (t, J = 7.1 Hz, 6 H), 3.02 (d, J = 1.3 Hz, 2 H), 3.37 (s, 2 H), 4.1–4.3 (m, 4 H), 6.51 (br s, 1 H), 6.8–7.2 (m, 9 H) ppm; ^{13}C NMR ($CDCl_3$, TMS) δ 14.02, 34.97, 39.85, 55.03, 61.52, 124.88, 126.65, 127.61, 127.69, 128.15, 128.54, 128.86, 132.98, 133.60, 135.18, 137.83, 170.79 ppm; MS m/z 364 (M^+), 290, 261, 217, 149; HRMS calcd for $C_{23}H_{24}O_4$ 364.1675, found 364.1679. Anal. Calcd for $C_{23}H_{24}O_4$: C, 75.80; H, 6.64. Found: C, 75.78; H, 6.63.

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(Z)-Diethyl 1,2,3,4-tetrahydro-1-(1-methyl-1-phenylmethylidene)naphthalene-3,3-dicarboxylate (18): 55% yield; colorless oil; IR (neat) 1730 (br s), 1270 (s), 1240 (s), 1220 (s), 1180 (s), 760 (s), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$, TMS) δ 1.22 (t, J = 7.1 Hz, 6 H), 2.20 (s, 3 H), 3.12 (s, 2 H), 3.30 (s, 2 H), 4.1–4.2 (m, 4 H), 6.52 (d, J = 7.6 Hz, 1 H), 6.67 (t, J = 7.6 Hz, 1 H), 6.9–7.2 (m, 7 H) ppm; ^{13}C NMR ($CDCl_3$, TMS) δ 14.07, 22.38, 34.34, 35.59, 55.21, 61.53, 124.87, 126.27, 126.38, 127.15, 128.11, 128.22, 128.73, 129.03, 130.23, 134.66, 136.08, 144.90, 171.20 ppm; MS m/z 378 (M^+), 304, 231, 217, 216, 215, 105, 103; HRMS calcd for $C_{24}H_{26}O_4$ 378.1831, found 378.1844.

(E)-Diethyl 1,2,3,4-tetrahydro-1-[1-(trimethylsilyl)-1-phenylmethylidene]naphthalene-3,3-dicarboxylate (19): 43% yield; colorless oil; IR (neat) 1736 (br s), 1259 (s), 837 (s), 760 (m), 703 (m) cm^{-1}; ^1H NMR ($CDCl_3$, TMS) δ −0.17 (s, 9 H), 1.09 (t, J = 7.1 Hz, 6 H), 2.77 (s, 2 H), 3.16 (s, 2 H), 3.9–4.1 (m, 4 H), 6.90–6.98 (m, 2 H), 7.1–7.5 (m, 7 H) ppm; ^{13}C NMR ($CDCl_3$, TMS) δ 0.79, 13.85, 35.59, 36.40, 54.74, 61.36, 125.20, 125.99, 127.37, 127.55, 127.94, 135.52, 139.45, 142.82, 144.27, 144.66, 171.28 ppm; MS m/z 436 (M^+), 421, 363, 333, 273, 245, 205, 178, 164, 149, 119, 107, 91; HRMS calcd for $C_{26}H_{32}O_4Si$ 436.2070, found 436.2048. Anal. Calcd for $C_{26}H_{32}O_4Si$: C, 71.52; H, 7.39. Found: C, 71.50; H, 7.43.

(E)-2,3-Dihydro-1-(1-phenylmethylidene)indene (20):[17,18] mp 71–72 °C (lit.[18] mp 71–72 °C); ^1H NMR ($CDCl_3$, TMS) δ 3.10 (s, 4 H), 6.96 (s, 1 H), 7.18–7.65 (m, 9 H) ppm; ^{13}C NMR ($CDCl_3$, TMS) δ 30.57, 30.75, 118.88, 120.67, 125.13, 126.10, 126.47, 128.02, 128.29, 138.10, 142.43, 143.97, 145.66 ppm; MS m/z 206 (M^+), 205, 204.

3-(Phenylmethyl)indene (21):[19] ^1H NMR ($CDCl_3$, TMS) δ 3.35–3.36 (m, 2 H), 3.89–3.92 (m, 2 H), 6.12–6.14 (m, 1 H), 7.18–7.46 (m, 9 H) ppm; ^1H NMR ($CDCl_3$, TMS) δ 34.36, 37.61, 119.23, 123.62, 124.49, 125.90, 126.00, 128.25, 128.83, 129.89, 139.25, 143.36, 144.44, 145.01 ppm; MS m/z 206 (M^+), 205.

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Registry No. 8, 119826-66-3; 9, 120417-24-5; 10, 127530-86-3; 11, 127619-92-5; 12, 127619-93-6; 13, 127619-94-7; 14, 127619-95-8; 15, 127619-96-9; 16, 127619-97-0; 17, 127619-98-1; 18, 127619-99-2; 19, 127620-00-2; 20, 16275-02-8; 21, 22495-71-2; $Pd(PPh_3)_4$, 14221-01-3; allenylmagnesium bromide, 18295-60-8; 2-iodobenzyl bromide, 40400-13-3; diethyl 2-(2-bromobenzyl)malonate, 66192-11-8; propargyl bromide, 106-96-7; 1-bromo-2-butyne, 3355-28-0; 3-bromo-1-(trimethylsilyl)-1-propyne, 38002-45-8; phenylzinc chloride, 28557-00-8.

Supplementary Material Available: ^1H and ^{13}C NMR spectra for compounds 8–10, 12, 13–16, and 18 (21 pages). Ordering information is given on any current masthead page.

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Lewis Acid Promoted Ring-Opening Allylation of Epichlorohydrin with Allylic Silanes and Stannanes To Afford 1-Chloro-5-alken-2-ols. A Short Synthesis of (S)-(−)-Ipsenol

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Epichlorohydrin (1) was allylated in good yields with representative allylic silanes (2, 5, 7, 9) and stannanes (12, 18) in the presence of appropriate Lewis acids. The reaction proceeds with ring opening at the unsubstituted site in 1 and with allylic inversion in the allylating agents to give 1-chloro-5-alken-2-ols cleanly. A short synthesis of (S)-(−)-ipsenol (29) from 1 and an (allenylmethyl)silane (26) demonstrates the utility of this method in organic synthesis.

Allylation of oxiranes is generally carried out under basic conditions by utilizing allyllithium or allylmagnesium reagents in the presence or absence of a copper(I) catalyst.[1] However, if these transformations can also be achieved under nonbasic or weakly acidic conditions, as has been realized in the allylation of aldehydes and ketones with allylic silanes[2] and stannanes,[3] the scope of utilizing oxiranes as synthetic intermediates will be further extended.

In the literature, however, only two such reactions are described.[4,5] In one report,[4] it is stated that allylative ring opening of ethylene oxide can be performed smoothly with allylsilanes under the influence of $TiCl_4$. Introduction of a methyl substituent (i.e., propylene oxide), however, results in the formation of mixtures of products, and it is suggested that rapid isomerization of the oxirane might be at least in part the cause for the problem.[6]

In the second report,[5] the successful allylation of alkenyloxiranes with allyltin reagents in the presence of $BF_3{\cdot}OEt_2$ is described. The allylative ring opening takes place at the site of the alkenyl substitution. Therefore,

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