1-alkenes in the presence of platinum catalysts to afford high yields of tetraalkylsilanes, but the procedure requires a high ratio of Pt/R_3SiH ($\sim 10^{-3}$ mol/mol). Lower ratios of platinum to silane can be used, but the catalyst will require frequent activation with air. At a platinum/silane ratio of 1.3×10^{-3} (mol/mol, 40 °C), Millan et al.[17] reacted triethylsilane with 1-hexene to yield 75% of triethylhexylsilane in less than 40 min.

Green et al.[12] reported new diplatinum catalysts which are active for hydrosilylation at room temperature and more resistant to deactivation than chloroplatinic acid. Whether these catalysts will be effective with monoalkylsilanes is not known.

Recent work indicated that reduction of platinum complexes or platinum metal to Pt(0) does not necessarily result in catalyst deactivation, but depending on the colloidal nature of Pt(0), it can actually become a more active catalyst for hydrosilylation reaction.[18]

Conclusion. Platinum catalysts are widely used in hydrosilylation of alkenes. The reaction requires only a small amount of catalyst and is ideally suited for halogen- or alkoxy-activated silanes and electron-rich alkenes. With relatively unactivated monoalkyl-, dialkyl-, and trialkylsilanes and 1-alkenes, the reaction affords only low yields of hydrosilylation products and is accompanied by side reactions and catalyst deactivation. It was discovered that treatment of platinum catalyst with oxygen restored its hydrosilylation activity and allowed all simple alkylsilanes to be converted to tetraalkylsilanes. In many of the runs, the unreacted alkenes were isomerized up to ~25%, mostly during the later stage of hydrosilylation. The isomerization appears to be promoted by Pt(0) complexes[12] and efforts must be made to maintain the catalyst in the active form by reactivation.

Experimental Section

All reactions, unless otherwise indicated, were carried out at atmospheric pressure in standard laboratory glassware under nitrogen. Chromatographic analyses were performed on a Hewlett-Packard 5880A (FID) chromatograph, using a 25-m, 2% OV-101, fused silica capillary column, programmed from 50 to 300 °C at 8 deg/min. The ^1H NMR spectra were recorded on a Varian T-60 spectrometer, usually in carbon tetrachloride or acetone-d_6. The chemical shifts are in δ units (ppm) relative to Me_4Si (s = singlet, d = doublet, t = triplet, m = multiplet). The IR spectra were recorded on a Perkin-Elmer Model 597 spectrometer. GC/MS data were obtained on a Finnigan 4510 system with an electron impact source at 70 eV. All platinum catalysts were obtained from commercial sources. The following procedure is representative of the reaction of silanes with 1-alkenes (see footnotes of Tables II and III for details).

Reaction of *n*-Hexylsilane with 1-Octene. A 100-mL, three-necked, round-bottomed flask, fitted with a condenser connected to a nitrogen source, a stirrer, thermometer, and a serum cap, was charged with 1-octene (10.0 g, 89 mmol), *n*-hexylsilane (1.4 g, 12.1 mmol), and chloroplatinic acid hexahydrate (0.004 g, 7.7×10^{-3} mmol). After being purged with nitrogen (15 min), the mixture was heated to 95 °C. After 1 h, the reaction stopped at about 50% silane conversion. The mixture was cooled to 25 °C, and compressed air was bubbled vigorously through the mixture for 1 min. The mixture was again heated to 95 °C (under N_2) for 1 h. Analysis (GLC) showed that silane completely reacted to give hexyltrioctylsilane: bp 180–185 °C (~0.5 mmHg) (73%); NMR δ 1.32 (s, 44 H, CH_2), 0.92 (distorted t, 12 H, CH_3), 0.47 (br m, 8 H, CH_2Si); mass spectrum, *m/e* (relative intensity) 452 (0) [P^+], 367 (10) [$(P - C_6H_{13})^+$], 339 (35) [$(P - C_8H_{17})^+$], 256 (14), 255 (61) [$(C_8H_{17})_2SiH^+$], 228 (15), 227 (78) [$(C_8H_{17})(C_6H_{13})SiH^+$], 143 (100), 115 (40), 113 (28), 101 (15), 99 (79), 87 (17), 85 (58), 83 (15), 73 (36), 71 (28), 59 (34), 43 (21), 32 (21), 28 (72); IR (absence of Si–O, Si–H bonds).

Registry No. $C_6H_{13}Si(C_8)_3$, 109528-78-1; Et_3SiH, 617-86-7; $RhCl(PPh_3)_2$, 14694-95-2; $MeSi(C_8)_3$, 3510-72-3; $Et_3Si(C_8)$, 10175-53-8; $Si(C_8)_4$, 3429-74-1; $C_6H_{13}Si(C_{10})H_2$, 109528-79-2; $C_6H_{13}Si(C_{10})_2H$, 109552-35-4; $C_6H_{13}Si(C_8)H_2$, 109528-80-5; $C_6H_{13}Si(C_8)_2H$, 109528-81-6; $C_6H_{13}Si(C_8)_2(C_{10})$, 109528-82-7; $C_6H_{13}Si(C_8)(C_{10})_2$, 109528-83-8; $C_6H_{13}Si(C_{10})_3$, 109528-84-9; $MeSi(C_{10})H_2$, 109528-85-0; $MeSi(C_8)_2(C_{10})$, 83094-48-8; $MeSi(C_8)(C_{10})_2$, 83584-71-8; $MeSi(C_{10})_3$, 18769-78-3; $C_6H_{13}SiH_3$, 1072-14-6; $MeSi(C_8)_2H$, 51502-63-7; $HSi(C_8)_3$, 18765-09-8; Pt, 7440-06-4; $PtCl_2(PPh_3)_2$, 10199-34-5; $PtCl_2(CH_3CN)_2$, 13869-38-0; PtO_2, 11129-89-8; $MeSi(C_8)H_2$, 80204-10-0; F, 111-66-0; G, 872-05-9; chloroplatinic acid hexahydrate, 18497-13-7.

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Stereoselective (*E*)-Olefin Formation by Wittig-Type Olefination of Aldehydes with Allylic Tributylphosphorus Ylides Derived from Allylic Nitro Compounds

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The Wittig reaction has been widely recognized as a practical method for olefination of aldehydes and ketones.[1] Concurrently, much attention has been paid on the mechanistic details of this reaction to account for the stereochemical results strongly depending on the type of ylides and the reaction conditions.[1,2]

Allylic triphenylphosphorus ylides, available from allylic halides, triphenylphosphine (PPh_3), and base, have been used as valuable reagents to produce conjugated dienes and polyenes by reacting with saturated and conjugated aldehydes, respectively.[1] Recently it has been revealed that allylic alcohols and their derivatives react directly with PPh_3 through the mediation of palladium(0) complex to afford allylic phosphorus ylides or phosphonium salts, which are subsequently utilized for olefination of aldehydes.[3] These reactions apparently involve the intermediary of π-allylpalladium complexes which are formed by the oxidative addition of allylic substrates to a palladium(0) complex, followed by the attack of PPh_3 on the π-allyl complexes.[4] In these olefination reactions, no appreciable stereoselectivity with respect to a newly formed double bond was observed, as is usual with allylic triphenylphosphorus ylides.[1a,3] To our knowledge, little is known about the stereochemistry of the Wittig reactions effected with allylic trialkylphosphorus ylides.[1]

Here we report that allylic nitro compounds, prepared from nitromethane and ketones,[5] undergo the Pd(0)-cat-

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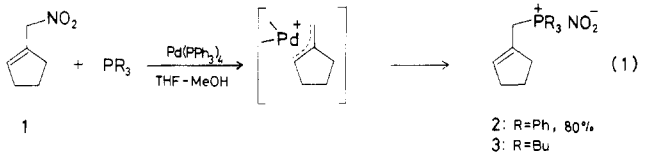
Table I. Olefination of Benzaldehyde with Allylic Phosphorus Ylide Derived from 1 (eq 2)[a]

run	solvent	base	R^1	yield of 4,[b] %	E/Z[c]
1	THF-MeOH[d]	*n*-BuLi	Ph	63	45/55
2		*n*-BuLi	*n*-Bu	82	$E > 95$
3		*t*-BuOK	*n*-Bu	83	$E > 95$
4		CH_3ONa	*n*-Bu	65	$E > 95$
5	MeOH	*t*-BuOK	*n*-Bu	16	$E > 95$
6	THF	*n*-BuLi	*n*-Bu	0	
7		*t*-BuOK	*n*-Bu	0	
8	DMF	*t*-BuOK	*n*-Bu	0	

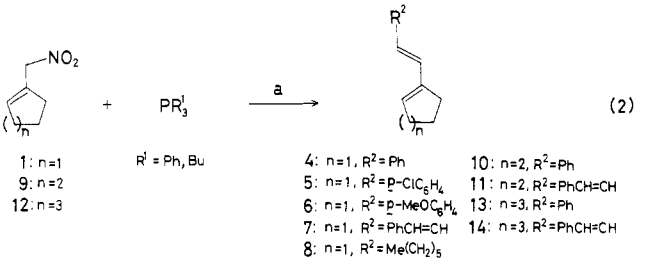
[a] See general procedure A in the Experimental Section. [b] Isolated yield. [c] Determined by GLPC and ^1H NMR. [d] 1/1.

alyzed allylic substitution by tri-*n*-butylphosphine (PBu_3) to generate allylic tributylphosphonium nitrite, which can be utilized for the highly stereoselective olefination of aldehydes.

Allylic nitro compounds are excellent substrates for Pd(0)-catalyzed allylic substitution by several nucleophiles.[6] First, the preparation of allylic phosphonium salts from allylic nitro compounds and PPh_3 was attempted. 1-Nitromethylcyclopentene (1) (1.5 mmol) was allowed to react with PPh_3 (1.0 mmol) in the presence of $Pd(PPh_3)_4$ (0.03 mmol) in THF–MeOH (1:1 v/v) at 65 °C for 24 h. The solvent was removed in vacuo, and the residue was successively washed with THF and benzene to afford white powder, which was analytically pure and characterized as the allylic phosphonium nitrite **2** (80% yield) (eq 1).



Next, we performed the one-pot Wittig–olefination reaction starting from **1** and PPh_3 without isolation of **2**. The resultant solution of **2** in THF–MeOH was treated with *n*-BuLi at −40 °C and allowed to react with benzaldehyde at room temperature (eq 2). The desired product **4** was obtained in 63% yield, showing no stereoselectivity (E/Z = 45/55) as expected (entry 1 in Table I).



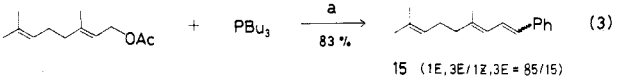
(a) (i) 3 mol % $Pd(PPh_3)_4$, 65 °C, 24 h; (ii) *n*-BuLi at −40 °C or *t*-BuOK at 25 °C; 25 °C, 2 h; (iii) R^2CHO, −40 or 25 °C; 25 °C, 24 h (65 °C, 1 h).

In order to induce the *E* stereoselectivity, we examined the potential of the tributylphosphonium salt **3**, because it was reported that in the Wittig reactions effected with nonstabilized and benzylic (semistabilized) phosphorus ylides, (*E*)-alkenes are preferentially formed by changing arylphosphines to alkylphosphines.[1a,f,7] As a consequence, such variation was quite effective for the olefination with the semistabilized allylic phosphorus ylide, drastically improving not only the stereoselectivity ($E > 95\%$) but also the yield (82%) of **4**,[8] even when $Pd(PPh_3)_4$ was employed as the catalyst (entry 2 in Table I).[9] The absence of lithium salt did not practically affect the stereochemistry, i.e., when *t*-BuOK was employed as a base to generate ylides, both the yield and the stereoselectivity were comparable to those with *n*-BuLi (entries 2 and 3 in Table I). This result is in good accord with a general tendency that the stereochemistry of the Wittig reactions effected with semistabilized benzylic phosphorus ylides and nonstabilized tributylphosphorus ylides is little affected by the presence of dissolved lithium salts.[1a,2] Attempts to prepare the allylic phosphonate from **1** and triethyl phosphite (the Arbuzov reaction) were unsuccessful under any reaction condition.

In the one-pot procedure of eq 2, the choice of solvent was a crucial factor, particularly in the process for the formation of phosphonium salts. Although MeOH, THF, acetonitrile, and DMF were not suitable solvents, the use of the mixed solvent of MeOH and THF led to the remarkable improvement in the yield of the product **4** as shown in Table I.

Under the optimum conditions described (see general procedure B in the Experimental Section), various conjugated olefins could be prepared in a highly regio- and stereoselective fashion from allylic nitro compounds and aldehydes as summarized in Table II.[10] In all cases, the employment of an excess amount (1.5–2.0 equiv) of allylic nitro compound and PBu_3 increased the yields of the products. The initial olefin geometry in the allylic nitro compound **15** was retained during the reaction (entry 10). Although this one-pot olefination method cannot be extended to aliphatic saturated aldehydes due to their aldol condensation, olefination of *n*-heptanal with roughly purified **3** and *n*-BuLi proceeded smoothly to give **8** in 82% yield with high stereoselectivity (entry 5 in Table II). The cyclic allylic nitro compounds larger than 1-nitromethylcycloheptene (**12**) failed to react with PBu_3 as well as PPh_3 due to the steric hindrance encountered in the attack of the phosphine on the π-allyl Pd intermediate.

The present method is applicable to allylic acetates. For example, starting from geranyl acetate and PBu_3, the 1*E*,3*E*-isomer was desirably produced (1*E*,3*E*/1*Z*,3*E* = 85/15) (eq 3), in contrast to the predominant formation of the 1*Z*,3*E*-isomer (1*E*,3*E*/1*Z*,3*E* = 30/70) observed when PPh_3 was used.[3b]



(a) (i) 3 mol % $Pd(PPh_3)_4$; THF–MeOH, 65 °C, 24 h; (ii) *n*-BuLi at −40 °C; 25 °C, 2 h; (iii) PhCHO, −40 °C; 25 °C, 24 h.

Thus, the present results indicate that allylic nitro compounds can be converted to allylic phosphonium salts by the catalysis of Pd(0) complex and that olefination of

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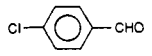
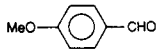
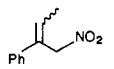
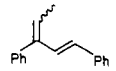
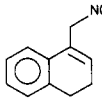
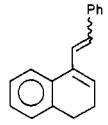
(8) Although prolonged heating (24 h) was required for the formation of **3** compared with that of **2** (3 h), **4** was obtained in a better yield (entries 1–3 in Table II).

(9) Utilization of bis(dibenzylideneacetone)palladium(0) [$Pd(dba)_2$] having no PPh_3 ligand as a catalyst resulted in comparably high stereoselectivity but in the slight decrease in the yield (71%) of the product **4**.

(10) When PPh_3 was employed in place of PBu_3 for the formation of phosphonium salts, a mixture of *E* and *Z* products with respect to the newly formed double bond was obtained in all cases.

Table II. Olefination of Aldehydes with Allylic Tributylphosphorus Ylides Derived from Allylic Nitro Compounds (eq 2)[a]

run	nitro compd (equiv)	aldehyde (1.0 equiv)	product[b]	yield,[c] %
1	**1** (1.5)	PhCHO	**4** ($E > 95$)	83 (55)[d]
2	**1** (1.5)		**5** ($E > 95$)	70
3	**1** (1.5)		**6** ($E > 95$)	40
4	**1** (1.5)	(*E*)-PhCH=CHCHO	**7** ($E,E > 95$)	61
5	**1** (1.0)	$Me(CH_2)_5CHO$	**8** ($E/Z = 93/7$)	82[e]
6	**9** (2.0)	PhCHO	**10** ($E > 95$)	87 (38)[f]
7	**9** (2.0)	(*E*)-PhCH=CHCHO	**11** ($E,E > 95$)	67
8	**12** (1.5)	PhCHO	**13** ($E > 95$)	81
9	**12** (1.5)	(*E*)-PhCH=CHCHO	**14** ($E,E > 95$)	55[e]
10	 (1.5) **15** ($Z/E = 63/37$)	PhCHO	 **16** ($1E,3E/1E,3Z = 64/36$)	61
11	 (1.5) **17**	PhCHO	 **18** ($E/Z = 92/8$)	82

[a] General procedure B. [b] The stereochemistry was assigned by GLPC and ^1H NMR. [c] Isolated yield. [d] One equivalent of **1** and PBu_3 was used. [e] Phosphonium salt **3** was prepared from **1** (1.5 equiv) and PBu_3 (1.0 equiv), roughly purified, and used for olefination (see Experimental Section). [f] One equivalent of **9** and PBu_3 was used.

aldehydes with allylic tributylpyhosphorus ylides derived from the phosphonium salts gives the highly stereoselective *E* products.

Experimental Section

Melting points were taken with a Meihoh Sharp melting point apparatus and are uncorrected. Spectral data were recorded on the following instruments: NMR, JEOL FX-90Q (90 MHz) or Varian XL-300 (300 MHz); IR, Shimadzu IR-27G; GC mass spectra, Hitachi M-80B. GLC analyses were performed on a Shimadzu GC-3BT chromatograph using a column packed with Silicone SE30 (3 mm × 2 m). Column chromatography was carried out with Merck silica gel 60 (less than 230 mesh) under moderate pressure (3 atm). Elemental analyses were performed by the Kyoto University Microanalytical Laboratories. All reactions were run under argon. Solvents were dried by using standard methods. Commercial reagents were purified by recrystallization or distillation. Allylic nitro compounds were synthesized from ketones and nitromethane by published procedure.[5] $Pd(PPh_3)_4$ was prepared by published procedure.[11]

Preparation of Triphenyl (1-Cyclopentenylmethyl)phosphonium Nitrite (2). A mixture of PPh_3 (262 mg, 1.0 mmol), $Pd(PPh_3)_4$ (35 mg, 0.03 mmol), and **1** (190 mg, 1.5 mmol) in a mixed solvent of THF (4 mL) and MeOH (4 mL) was stirred at 65 °C for 24 h. The reaction mixture was filtered, and the filtrate was concentrated under reduced pressure. The residure was successively washed with THF (10 mL) and benzene (10 mL). Removal of the solvent in vacuo gave 310 mg (80%) of **2**: mp 163–170 °C; IR (KBr) 1586, 1486, 1439 cm^{-1}; ^1H NMR (90 MHz, D_2O–TSP) δ 8.02–7.48 (m, 15 H), 5.56 (br, 1 H), 4.27 (d, J = 15.4 Hz, 2 H), 2.44–1.50 (br m, 6 H). Anal ($C_{24}H_{24}NO_2P$) C, H, N.

General Procedure A for the Olefination of Benzaldehyde with 1 (Table I). (*E*)-1-Styrylcyclopentene (4). A mixture of PBu_3 (303 mg, 1.5 mmol) or PPh_3 (393 mg, 1.5 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol), and **1** (190 mg, 1.5 mmol) in the stated solvent (7.0 mL) was stirred at 65 °C for 24 h. To the reaction mixture was added either *n*-BuLi (1.5 mmol, hexane solution) at −40 °C or *t*-BuOK (168 mg, 1.5 mmol) at 25 °C. [MeONa (81 mg, 1.5 mmol) was added at 25 °C.] The mixture was stirred at 25 °C for 2 h, and a solution of benzaldehyde (106 mg, 1.0 mmol) in the solvent (1.0 mL) was added. After being stirred at 25 °C for 24 h and at 65 °C for 1 h, the reaction mixture was diluted with ether (50 mL), washed with brine (3 × 25 mL), dried over $MgSO_4$, and concentrated in vacuo. The crude product could be purified by column chromatography (hexane). The isomer ratio was determined by GLC.

4: mp 36–40 °C; IR (neat) 1600, 1490, 1445, 956 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.50–7.18 (m, 5 H), 6.99 (d, J = 15.4 Hz, 1 H), 6.38 (d, J = 15.4 Hz, 1 H), 5.85 (br, 1 H), 2.72–2.30 (br m, 4 H), 2.20–1.79 (m, 2 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 142.8, 137.9, 131.9, 128.8, 128.5, 127.1, 126.3, 125.9, 33.1, 31.3, 23.3; mass spectrum, m/e (relative intensity) 170.0 (p, 88), 155.0 (32), 142.1 (100), 141.0 (98), 128.0 (35). Anal ($C_{13}H_{14}$) C, H.

General Procedure B for the Olefination of Aldehydes with Allylic Tributylphosphorus Ylides Derived from Allylic Nitro Compounds (Table II). A mixture of PBu_3 (1.5 or 2.0 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol), and the allylic nitro compound (1.5 or 2.0 mmol) in THF–MeOH (1:1 v/v, 7 mL) was stirred at 65 °C for 24 h. At 25 °C *t*-BuOK (1.5 or 2.0 mmol) was added, and the mixture was stirred for 2 h. A solution of the aryl aldehyde (1 mmol) in THF–MeOH (1 mL) was added at 25 °C, while that of cinnamaldehyde (132 mg, 1.0 mmol) in the same solvent (1 mL) was added at −40 °C. The reaction mixture was stirred at 25 °C for 24 h [additional heating was carried out at 65 °C for 1 h in the olefination of aryl aldehydes], diluted with ether (50 mL), washed with water (2 × 25 mL), dried over $MgSO_4$, and concentrated in vacuo. The crude products could be purified by column chromatography (hexane). The isomer ratio was determined by GLC.

(*E*)-1-(4-Chlorostyryl)cyclopentene (5): mp 73–77 °C; IR (CCl_4) 1632, 1492, 960 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.39–7.15 (br, 4 H), 6.96 (d, J = 16.0 Hz, 1 H), 6.31 (d, J = 16.0 Hz, 1 H), 5.82 (br, 1 H), 2.66–2.27 (br m, 4 H), 2.12–1.80 (m, 2 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 142.6, 136.4, 132.7, 130.3, 128.7, 127.8, 127.4, 126.4, 33.1, 31.2, 23.2; mass spectrum, m/e (relative intensity) 204.2 (p, 63), 175.0 (58), 169.1 (100), 153.1 (20), 141.1 (97), 138.0 (11), 128.0 (23), 125.1 (18), 115.1 (21).

(*E*)-1-(4-Methoxystyryl)cyclopentene (6): mp 90–95 °C; IR (CCl_4) 1607, 1509, 1463, 955 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.34 (d, J = 8.5 Hz, 2 H), 6.88 (d, J = 16.8 Hz, 1 H), 6.83 (d, J = 8.5 Hz, 2 H), 6.34 (d, J = 16.8 Hz, 1 H), 5.79 (br, 1 H), 3.80 (s, 3 H), 2.67–2.29 (br m, 4 H), 2.13–1.80 (m, 2 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 159.0, 142.9, 130.7, 128.2, 127.9, 124.0, 114.1, 55.3, 33.0, 31.3, 23.2; mass spectrum, m/e (relative intensity) 200.1 (p, 100), 185.2 (15), 171.2 (87), 169.2 (37), 158.1 (19), 144.1 (11), 141.1

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(33), 128.1 (33), 121.1 (29), 115.1 (32).

(*E,E*)-1-Phenyl-4-(1-cyclopentenyl)-1,3-butadiene (7): mp 36–40 °C; IR ($CHCl_3$) 1596, 1491, 1447, 983 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.42–7.17 (m, 5 H), 6.85 (dd, J = 10.6, 15.5 Hz, 1 H), 6.58 (d, J = 15.1 Hz, 1 H), 6.56 (d, J = 15.5 Hz, 1 H), 6.27 (dd, J = 10.6, 15.1 Hz, 1 H), 5.80 (br, 1 H), 2.53–2.42 (br m, 4 H), 1.96 (tt, J = 7.4, 8.1 Hz, 2 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 143.0, 137.7, 132.0, 131.8, 130,2, 129.8, 129.6, 128.7, 127.3, 126.3, 33.2, 31.3, 23.3; mass spectrum, m/e (relative intensity) 196.2 (p, 100), 181.1 (14), 168.1 (65), 167.1 (62), 153.1 (31), 147.2 (12), 141.1 (25), 128.0 (33), 115.1 (24), 105.1 (32), 103.1 (21), 92.1 (42), 91.1 (56). Anal ($C_{15}H_{16}$) C, H.

(*E*)-1-Styrylcyclohexene (10): IR (neat) 1598, 1494, 1447, 958 cm^{-1}; ^1H NMR (90 MHz, DCl_3) δ 7.48–6.96 (m, 5 H), 6.76 (d, J = 15.4 Hz, 1 H), 6.39 (d, J = 15.4 Hz, 1 H), 5.86 (br, 1 H), 2.40–1.92 (br m, 4 H), 1.88–1.50 (br, 4 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 138.2, 136.0, 132.7, 130.8, 128.6, 126.9, 126.2, 124.8, 26.3, 24.7, 22.7; mass spectrum, m/e (relative intensity) 184.0 (p, 43), 169.1 (18), 156.0 (30), 155.1 (41), 142.1 (67), 141.1 (100), 129.0 (41), 128.0 (64), 115.1 (46), 104.0 (20), 91.1 (59).

(*E,E*)-1-Phenyl-4-(1-cyclohexenyl)-1,3-butadiene (11): mp 63–69 °C; IR ($CHCl_3$) 1596, 1490, 1445, 983 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.42–7.16 (m, 5 H), 6.84 (dd, J = 8.5, 15.5 Hz, 1 H), 6.53 (d, J = 15.5 Hz, 1 H), 6.36 (d, J = 15.3 Hz, 1 H), 6.29 (dd, J = 8.5, 15.3 Hz, 1 H), 5.83 (br, 1 H), 2.40–1.92 (br m, 4 H), 1.84–1.38 (br m, 4 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 136.8, 136.0, 135.1, 130.0, 129.6, 128.9, 127.5, 126.1, 125.1, 124.5, 25.1, 23.6, 21.5; mass spectrum, m/e (relative intensity) 210.1 (p, 66), 182.2 (13), 168.1 (30), 167.1 (54), 165.1 (14), 154.1 (14), 128.1 (19), 119.1 (24), 115.1 (24) 91.1 (100).

(*E*)-1-Styrylcycloheptene (13): IR (neat) 1598, 1495, 1445, 958 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.50–7.00 (m, 5 H), 6.76 (d, J = 15.8 Hz, 1 H), 6.42 (d, J = 15.8 Hz, 1 H), 6.01 (t, J = 6.9 Hz, 1 H), 2.56–2.00 (br m, 4 H), 1.96–1.38 (br m, 6 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 143.1, 138.3, 135.4, 133.5, 128.6, 126.8, 126.3, 124.8, 32.2, 28.9, 27.5, 26.9, 26.4; mass spectrum, m/e (relative intensity) 198.1 (p, 68), 185.1 (13), 155.1 (77), 142.1 (83), 141.1 (100), 129.0 (41), 128.0 (78), 117.1 (20), 115.1 (61), 105.0 (16), 91.1 (66).

(*E,E*)-1-Phenyl-4-(1-cycloheptenyl)-1,3-butadiene (14): mp 58–63 °C; IR ($CHCl_3$) 1590, 1494, 1447, 985 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.44–7.05 (m, 5 H), 6.85 (dd, J = 9.8, 15.4 Hz, 1 H), 6.51 (d, J = 15.4 Hz, 1 H), 6.42 (d, J = 15.1 Hz, 1 H), 6.33 (dd, J = 9.8, 15.1 Hz, 1 H), 5.95 (t, J = 5.9 Hz, 1 H), 2.50–2.12 (br m, 4 H), 1.98–1.40 (br m, 6 H); mass spectrum, m/e (relative intensity) 224.1 (p, 58), 181.1 (24), 169.8 (23), 167.1 (35), 154.1 (15), 141.0 (13), 133.0 (23), 128.0 (21), 115.1 (24), 105.1 (14), 91.1 (100).

(1*E*,3*E*)- and (1*E*,3*Z*)-1,3-diphenyl-1,3-pentadiene (16): 1*E*,3*E*/1*E*,3*Z* = 64/36; IR (neat) 1599, 1492, 1443, 961, 700 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.52–7.08 (m, 10 H), 7.00 (d, J = 15.4 Hz, 1 H), 6.40 (d, J = 15.4 Hz, 1 H), 5.69 (q, J = 7.2 Hz, 1 H) [5.82 (q, J = 7.0 Hz, 1 H) for the 1*E*,3*Z*-isomer], 1.98 (d, J = 7.2 Hz, 3 H) [1.62 (d, J = 7.0 Hz, 3 H) for the 1*E*,3*Z*-isomer]; mass spectrum, m/e (relative intensity) 220.1 (p, 60), 205.2 (100), 203.1 (24), 142.1 (19), 129.0 (20), 115.1 (34), 91.1 (31) for the 1*E*,3*E*-isomer, m/e (relative intensity) 220.1 (p, 70), 205.2 (100), 204.2 (18), 142.0 (13), 129.1 (18), 115.1 (39) for the 1*E*,3*Z*-isomer.

(*E*)- and (*Z*)-1-styryl-3,4-dihydronaphthalene (18): *E*/*Z* = 92/8; IR (neat) 1600, 1496, 1488, 1449, 962 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.54–7.12 (br m, 9 H), 7.07 (d, J = 17.0 Hz, 1 H), 6.78 (d, J = 17.0 Hz, 1 H), 6.31 (t, J = 5.1 Hz, 1 H), 2.73 (t, J = 7.7 Hz, 2 H), 2.36 (dt, J = 5.1, 7.7 Hz, 2 H) for the *E*-isomer, δ 7.48–7.10 (br m, 9 H), 6.65 (d, J = 11.6 Hz, 1 H), 6.32 (d, J = 11.6 Hz, 1 H), 5.96 (t, J = 4.6 Hz, 1 H), 2.81 (t, J = 7.7 Hz, 2 H), 2.28 (dt, J = 4.6, 7.7 Hz, 2 H) for the *Z*-isomer; ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 137.8, 136.8, 136.2, 134.4, 130.0, 128.7, 128.3, 127.7, 127.4, 127.1, 126.7, 126.4, 124.1, 28.3, 23.5 for the *E*-isomer; mass spectrum, m/e (relative intensity) 232.2 (p, 100), 229.2 (11), 217.1 (45), 215.1 (26), 202.1 (24), 189.1 (13), 152.1 (21), 141.1 (40), 128.0 (62), 115.1 (39), 91.1 (31) for the *E*-isomer, m/e (relative intensity) 232.2 (p, 100), 229.2 (8), 217.1 (40), 215.1 (30), 202.1 (25), 153.1 (18), 141.1 (26), 128.1 (38), 115.1 (30) for the *Z*-isomer.

Preparation of (*E*)-1-(1-Octenyl)cyclopentene (8) (entry 5 in Table II). A mixture of PBu_3 (1.0 mmol), $Pd(PPh_3)_4$ (35 mg, 0.03 mmol), and 1 (1.5 mmol) in THF–MeOH (1:1 v/v, 8 mL) was stirred at 65 °C for 24 h. The solvent was removed in vacuo. The oily residue was washed with ether (3 × 10 mL). After removal of ether in vacuo, THF (7 mL) was added. At −40 °C *n*-BuLi (1.0 mmol) was added, the mixture was stirred at 25 °C for 2 h, and a solution of *n*-heptanal (114 mg, 1.0 mmol) in THF (1 mL) was added at −78 °C. The reaction mixture was slowly allowed to warm to 25 °C over 2 h, stirred for 24 h, diluted with ether (50 mL), washed with water (2 × 25 mL), dried over $MgSO_4$, and concentrated in vacuo. Column chromatography of the crude product gave 146 mg (82%) of *8*: *E*/*Z* = 93/7; IR (neat) 959 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 6.26 (d, J = 15.4 Hz, 1 H), 5.56 (br, 1 H), 5.53 (dt, J = 15.4, 6.7 Hz, 1 H), 2.33 (m, 4 H), 2.23–1.76 (br m, 4 H), 1.55–1.13 (br m, 8 H), 0.88 (t, J = 5.3 Hz, 3 H) for the *E*-isomer; ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 142.8, 131.3, 128.0, 127.0, 32.9, 32.7, 31.9, 31.5, 29.6, 29.0, 23.2, 22.6, 14.1 for the *E*-isomer; mass spectrum, m/e (relative intensity) 178.2 (p, 23), 135.1 (7), 121.1 (15), 107.2 (24), 94.1 (51), 91.2 (31), 79.1 (100) for the *E*-isomer, m/e (relative intensity) 178.2 (p, 22), 135.2 (5), 121.1 (26), 107.2 (24), 94.1 (35), 91.2 (30), 79.1 (100) for the *Z*-isomer.

(1*E*,3*E*)-4,8-Dimethyl-1-phenyl-1,3,7-nonatriene (15):[3c] ^1H NMR (90 MHz, $CDCl_3$) δ 7.52–7.11 (m, 5 H), 7.02 (dd, J = 15.4, 11.0 Hz, 1 H), 6.44 (d, J = 15.4 Hz, 1 H), 6.00 (d, J = 11.0 Hz, 1 H), 5.12 (br, 1 H), 2.13 (m, 4 H), 1.85 (s, 3 H), 1.69 (s, 3 H), 1.62 (s, 3 H).

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Registry No. **1**, 2562-42-7; **2**, 109432-80-6; **3**, 109432-82-8; (*E*)-**4**, 109432-85-1; (*Z*)-**4**, 109432-86-2; (*E*)-**5**, 109432-87-3; (*E*)-**6**, 109432-88-4; (*E,E*)-**7**, 109432-89-5; (*E*)-**8**, 109432-83-9; (*Z*)-**8**, 109432-84-0; **9**, 5330-61-0; (*E*)-**10**, 68826-53-9; (*E,E*)-**11**, 109432-90-8; (*E*)-**13**, 109432-91-9; (*E,E*)-**14**, 109432-92-0; (*E,E*)-**15**, 53598-04-2; (*Z,E*)-**15**, 53163-68-1; (*E,E*)-**16**, 109432-93-1; (*E,Z*)-**16**, 69366-38-7; **17**, 104489-04-5; **12**, 52315-51-2; (*E*)-**18**, 109432-94-2; (*Z*)-**18**, 109432-95-3; $Pd(PPh_3)_4$, 14221-01-3; PPh_3, 603-35-0; PBu_3, 998-40-3; PhCHO, 100-52-7; $Me(CH_2)_5CHO$, 124-13-0; *p*-ClC_6H_4CHO, 104-88-1; *p*-$MeOC_6H_4CHO$, 123-11-5; (*E*)-PhCH=CHCHO, 14371-10-9; (*Z*)-$NO_2CH_2CH(Ph)$=CHMe, 104488-93-9; (*E*)-$NO_2CH_2CH(Ph)$=CHMe, 104488-92-8; Me_2C=$CH(CH_2)_2C$(Me)=$CHCH_2OAc$, 105-87-3.

Ultrasound in Organic Synthesis. 12.[1] In Situ Generation and Uses of Butyllithium Reagents in Several Synthetic Reactions

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Butyllithium reagents—primary, secondary, tertiary—are among the most useful organometallics in organic synthesis, as strong bases, as precursors to various lithiated reactive intermediates or other organometallics, and as initiators of several types of reactions including polymerization.[2] Many of these reactions are under stereo- and regiocontrol by complex-induced proximity effects.[3] Due to their reactivity toward etheral solvents, butyllithium reagents are commercially available as hydrocarbon solutions. Standardization is generally necessary before use,

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