Palladium-Assisted Alkylation of Olefins. 2. By Benzyl-, Phenyl-, and Cyano-Stabilized Carbanions

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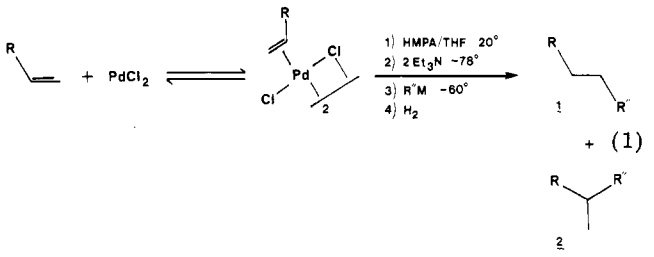
Phenyllithium and benzylmagnesium chloride alkylate (1-hexene)palladium(II) complexes in modest yield to produce 1-phenylhexane or 1-phenylheptane, respectively, after a reductive isolation. *N*-Vinylacetamide reacts with benzylmagnesium chloride in the presence of palladium(II) chloride to produce *N*-acetylamphetamine in good yield. Nitrile-stabilized carbanions alkylate palladium(II)-coordinated olefins in fair to good yields. Stabilized phosphorus ylides react with the same complexes to form relatively stable organopalladium intermediates which produce aryl (from the phosphine group) olefins upon thermal decomposition.

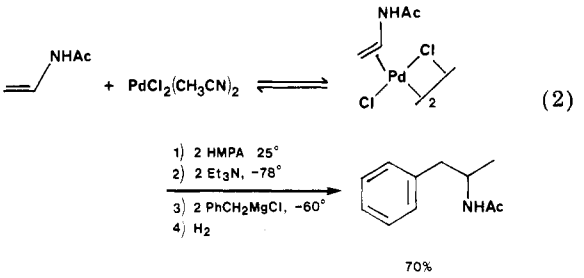
Introduction

The palladium-assisted alkylation of olefins has recently been reported (eq 1).[1] Stabilized carbanions (pK_a = 10–17) reacted with (olefin)palladium(II) complexes in the presence of 2 equiv of triethylamine to result in the alkylation of the olefin predominantly at the 2-position. With the addition of hexamethylphosphoramide (HMPA) to the reaction medium, less stabilized carbanions (pK_a = 30) also alkylated olefins in reasonable yield, the regiochemistry of the process being strongly dependent on the nature of the olefins. In this paper we report the extension of the process to benzylmagnesium chloride, phenyllithium, and nitrile-stabilized carbanions.

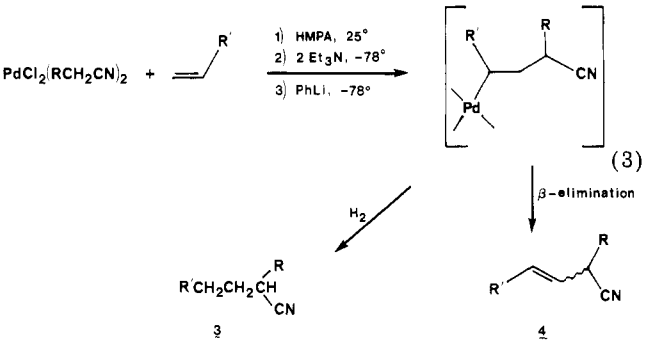


Results and Discussion

As the basicity of the carbanion increases, the palladium-assisted alkylation of olefins becomes increasingly sensitive to reaction conditions. This is seen in the reaction of benzylmagnesium halide with (olefin)palladium(II) complexes. Reaction with the palladium(II)–olefin complex of 1-hexene prepared from the acetonitrile complex of palladium chloride, $PdCl_2(CH_3CN)_2$ gave a 3:1 mixture of regioisomer (23% overall yield) resulting from the alkylation of the 2-position of the olefin (1-phenyl-2-methylhexane) and the terminal position of the olefin (1-phenylheptane), respectively. In contrast, the same reaction using the benzonitrile complex of palladium chloride, $PdCl_2(PhCN)_2$, as a source of palladium(II) produced 1-phenylheptane as the sole product (30% yield). This indicated that the regiochemistry of alkylation was sensitive to the nature of the nitrile ligand, in spite of the presence of a large excess of HMPA and 2 equiv of triethylamine. These disappointingly low yields were obtained after a significant effort to optimize the conditions for this conversion and may be indicative of the inherent limits of this reaction. The electron-rich olefin, *N*-vinylacetamide, reacted with benzylmagnesium chloride in considerably better yield (70%), producing *N*-acetylamphetamine (eq 2).



Phenyllithium reacted with the (1-hexene)palladium(II) complex prepared from $PdCl_2(PhCN)_2$ to give low (15–20%) yields of 1-phenylhexane after a reductive product isolation step. When the reaction was repeated by using $PdCl_2(CH_3CN)_2$ as the source of palladium(II), the major product was 1-cyanoheptane, from the alkylation of 1-hexene by the acetonitrile anion, apparently generated in situ by deprotonation of acetonitrile by phenyllithium. This provides a general procedure for the alkylation of olefins by cyano-stabilized carbanions (eq 3). The results are summarized in Table I.



The highest yields (~75%) of alkylation by the acetonitrile anion were obtained by externally generating the nitrile anion (*n*-BuLi, 0 °C) and by adding it at −78 °C to the standard olefin/$PdCl_2(CH_3CN)_2$/Et_3N/HMPA mixture. Comparable yields with other nitriles were obtained by starting with the preformed palladium complex of the particular nitrile to be introduced.[3] Slightly lower yields (10–15%) were obtained by using the benzonitrile complex

(1) L. S. Hegedus, R. E. Williams, M. A. McGuire, and T. Hayashi, *J. Am. Chem. Soc.*, **102**, 4973 (1980), and references therein.
(2) L. S. Hegedus and W. H. Darlington, *J. Am. Chem. Soc.*, **102**, 4980 (1980), and references therein.
(3) These nitrile complexes are easily formed by dissolving commercial $PdCl_2$ in the desired nitrile, followed by precipitation of the complex with pentane. See: J. Tsuji, "Organic Synthesis with Palladium Compounds", Springer-Verlag, Berlin, 1980, p 2.

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Table I. Palladium-Assisted Alkylation of Olefins by Nitrile-Stabilized Carbanions (Eq 3)

olefin	nitrile	isolatn	products	% yield[a]
1-hexene	CH_3CN	H_2	3, R′ = *n*-Bu, R = H	65
1-octene	CH_3CN	H_2	3, R′ = *n*-hex, R = H	70[b]
1-octene	CH_3CN	β eliminatn	4, R′ = *n*-hex, R = H	69[d]
1-octene	CH_3CH_2CN	H_2	3, R′ = *n*-hex, R = Me	71[b]
1-octene	CH_3CH_2CN	β eliminatn	4, R′ = *n*-hex, R = Me	66[c,d]
1-hexene	$PhCH_2CN$	H_2	3, R′ = *n*-Bu, R = Ph	50
1-hexene	$PhCH_2CN$	β eliminatn	4, R′ = *n*-Bu, R = Ph	45[d]

[a] Yields are for isolated, purified products. [b] In addition to the nitrile product, 10–15% of the alkylated benzene, from attack of the olefin by phenyllithium, was obtained. [c] In addition to the nitrile product, 10–15% of the alkenylated benzene, from attack of the olefin by phenyllithium, was obtained. [d] The product is a mixture of olefin regioisomers.

$PdCl_2(PhCN)_2$ as a source of palladium(II) and adding 2 equiv of the desired nitrile having α protons to the reaction solution prior to the addition of the olefin. Formation of stable (cyanoalkyl)palladium complexes by attack of the carbanion on the palladium[4] was not observed, regardless of the procedure followed. The unique ability of phenyllithium to deprotonate carbanion precursors in the *presence* of (olefin)palladium(II) comlexes is currently being explored for use in the *intramolecular* alkylation of olefins.

This alkylation reaction was regiospecific, alkylation always occurring at the less substituted terminus of the olefin. This is typical for reactions of nonstabilized carbanions.[1] Acetonitrile, propionitrile, and phenylacetonitrile anions reacted in fair to good yield with the straight-chain olefins, 1-hexene and 1-octene. A reductive isolation procedure (1 atm of H_2, 0 °C) produced the expected saturated nitrile product. Allowing the reaction to warm to 25 °C in the absence of hydrogen permitted a β-hydride elimination to ensue. The resulting product was a mixture of positional olefin isomers, from a palladium-catalyzed olefin isomerization process.[2] These mixtures of olefins were easily reduced to their saturated analogues by exposure to hydrogen in the presence of a palladium catalyst.

Finally, the reaction of the stabilized ylide Ph_3PCHCO_2Et with the palladium (II) complex of 1-hexene was briefly examined. This ylide is known to alkylate $[CpFe(CO)_2(olefin)]^+$ species cleanly,[5] and similar chemistry was anticipated for (olefin)palladium(II) complexes. However, reaction of the palladium(II) complex of 1-hexene with the ester-stabilized ylide under standard alkylation conditions led to the production of a relatively stable palladium species which did not decompose in solution at room temperature. Heating the solution to 50 °C for several hours resulted in the slow deposition of metallic palladium. The sole indentifiable organic product from this reaction was 1-phenyl-1-hexene (30% yield). The phenyl group was shown to have come from the triphenylphosphine by using the ylide prepared from tri-*p*-tolylphosphine. From this reaction, 1-(4-methylphenyl)-1-hexene was isolated in 20% yield. These observations suggest that the stabilized phosphorus ylides attacked the palladium, forming a relatively stable ylide complex rather than attacking the coordinated olefin. A number of stable isolable palladium complexes of phosphorus[6-10] and sulfur ylides are known,[11-13] and most are formed by the direct reaction of the ylide with a halopalladium(II) complex. The incorporation of aryl groups from phosphines, observed in the thermal decomposition of the palladium species formed above, is likely to have occcurred by oxidative addition of a phosphine aryl group to a zerovalent palladium species, followed by insertion of hexene into the arylpalladium(II) complex and β-hydride elimination. Oxidative addition of arylphosphines to both palladium(0) and nickel(0) complexes is a well-known process.[14] The ensuing insertion elimination steps are equivalent to the well-established Heck arylation of olefins.[15]

Experimental Section

All melting points are uncorrected. Infrared spectra were recorded on either a Beckman 4200 or a Beckman Acculab-3 spectrophotometer. ^1H NMR spectra were recorded on either a Varian Model EM360 or a Varian Model T-60 spectrometer using Me_4Si as an internal standard and are reported in δ. All isolations were accomplished by medium-pressure liquid chromatography using a Michel–Miller column (37 mm × 350 mm) packed with Merck Silica Gel-60 (230–400 mesh). All products were detected with an ISCO Model UA-5 Absorbance/Flouresscence Monitor at a wavelength of 254 nm. Analyses were performed by Midwest Microanalytical Labs, Indianapolis, IN.

Materials. All solvents were freshly distilled and stored under an argon atmosphere. Immediately before use they were degassed and saturated with argon. Tetrahydrofuran (THF) (Fisher, Spectra Grade) was refluxed over Na wire with benzophenone and distilled at atmospheric pressure under a N_2 atmosphere. Hexamethylphosphoramide (Aldrich, 99%) was purified by stirring with CaH_2 for 24 h and distilled from CaH_2 under reduced pressure (2–4 mm). Triethylamine was purified by stirring with CaH_2 and distilling from CaH_2 at atmospheric pressure under N_2. Benzylmagnesium chloride was purchased from Alfa as a 1.1 M solution in THF. Phenyllithium was prepared by a known procedure[16a] and was used as ~0.70 M solution in Et_2O. Phoshorus ylides were prepared by standard procedures.[16b] $PdCl_2(RCN)_2$ complexes were prepared by rapidly stirring $PdCl_2$ with the appropriate nitrile, using the nitrile as solvent, for 3 days, followed by filtration to yield the complex as a powdery solid.[3]

General Procedure for the Alkylation of Olefins with Unstabilized Anions. The $PdCl_2(RCN)_2$ (1 equiv) was trans-

(4) For stable cyanoalkylpalladium(II) complexes see: K. Hiraki, M. Onishi, and H. Matsuo, *J. Organomet. Chem.*, **185**, 111 (1980); K. Hiraki, T. Masumoto, Y. Frichita, and Y. Zegi, *Bull, Chem. Soc. Jpn.*, **54**, 1044 (1981).
(5) P. Lennon, A. M. Rosan, and M. Rosenblum, *J. Am. Chem. Soc.*, **99**, 8426 (1977).
(6) K. Itoh, H. Nishiyama, T. Ohnishi, and Y. Ishii, *J. Organomet. Chem.*, **76**, 401 (1974).
(7) H. Nishigama, K. Itoh, and Y. Ishii, *J. Organomet. Chem.*, **87**, 129 (1975).
(8) P. Bravo, G. Fronza, and C. Ticozzi, *J. Organomet. Chem.*, 111, 361 (1976).
(9) S. A. Dias, A. W. Downs, and W. R. McWhinnie, *J. Chem. Soc. Dalton Trans.*, 162 (1975).
(10) H. Koezuka, G-E. Matsubayashi, and T. Tanaka, *Inorg. Chem.*, **15**, 417 (1976).
(11) H. Koezuka, G-E. Matsubayashi, and T. Tanaka, *Inorg. Chem.*, **13**, 443 (1974).
(12) P. Bravo, G. Fronza, C. Ticozzi, and G. Gaudieno, *J. Organomet. Chem.*, **74**, 143 (1974).
(13) P. Bravo, G. Fronza, and C. Ticozzi, *J. Organomet. Chem.*, **124**, C80 (1976).
(14) D. R. Fahey and J. E. Mahan, *J. Am. Chem. Soc.*, **98**, 4499 (1976).
(15) R. F. Heck, *Pure Appl. Chem.*, **50**, 691 (1978).
(16) a) Organic Syntheses, Vol. 3, p 757; (b) U. Schöllkopf, *Angew. Chem.*, **71**, 260 (1959).

ferred to a 100-mL side-arm flask fitted with a stopcock, stir bar, and serum cap. The flask was alternately evacuated and filled with argon (four cycles) on a vacuum line. The flask was then fitted with an argon-filled balloon. THF (40 mL/mmol of complex) was added via syringe to yield a light amber, heterogeneous suspension. The olefin (2–4 equiv) was added all at once, and stirring was continued until the mixture was light, clear, and homogeneous (~15 min). HMPA (2–20 equiv) was added all at once via syringe. After 3 min the slightly darkened solution was cooled to −78 °C, and stirring was continued for 10 min. Triethylamine (2 equiv) was added over a 20-min period via syringe, and stirring was continued for an additional 0.25–1 h. During this time, the solution was allowed to come to the required temperature for addition of the anion. The anion (1–2 equiv) was either added all at once in solid form or added via cooled syringe in THF (3 mL/mmol of anion). The anion solution was generally kept at −78 °C regardless of the temperature of the reaction solution. After 15 min, either the cold bath was removed and the reaction was warmed to room temperature and stirred for 4–8 h to yield the β-elimination product or the flask was flushed with H_2, fitted with an H_2 balloon, stirred at −60 °C for 15 min and then allowed to come to room temperature and stir for 4–8 h to yield the reduced product.

General Isolation Procedure. The black heterogeneous mixture was filtered through a medium-sintered glass filter funnel or through celite filter cell to yield a colorless to light yellow solution. The solvent was removed in vacuo, and the resulting yellow oil was taken up in Et_2O (100 mL/mmol of complex) and washed three times with H_2O (50 mL/mmol of complex) and once with brine. The solution was dried over $MgSO_4$ and filtered to yield a colorless to yellow solution. The solvent was removed in vacuo to yield a yellow to red oil which was then purified by medium-pressure liquid chromatography. All variations on this general procedure are noted for each compound.

Preparation of *N*-Acetylamphetamine. $PdCl_2(CH_3CN)_2$ (65 mg, 0.25 mmol) and *N*-vinylacetamide (42 mg, 0.5 mmol) were combined in the usual manner. HMPA (90 mg, 0.5 mmol) was added, and a slight lightening in color was noted. The reaction then proceeded normally. Fifteen minutes after the addition of triethylamine, the dry-ice was removed from the cold bath and the temperature was allowed to rise to −60 °C (ca. 0.5 h), at which time benzylmagnesium chloride (0.5 mmol) in THF (2 mL) at −78 °C was added over 0.25-h. The reaction mixture was stirred for an additional 0.5 h at −60 °C. The flask was then flushed with H_2, and the reaction was allowed to come to room temperature. After being stirred for 8 h, the solution was filtered and the solvent removed under vacuum. The product was isolated by MPLC (1:1 $EtOAc/CH_2Cl_2$) as a white crystalline solid (89–91 °C; 32 mg, 70%) which was identical with authentic material:[17] NMR ($CDCl_3$) δ 1.13 (d, J = 6 Hz, 3, CH_3), 1.94 (s, 3, $COCH_3$), 2.78 (d, J = 6 Hz, 2, Ar=CH_2), 4.33 (m, 1, CH), 5.35 (b s, 1, NHCO), 7.27 (s, 5, Ar); IR (neat) 3270 (s, NH), 3060, 3020, 2960, 2940 (m, Ar), 1640 (s, CO), 1550 (s, Ar), 1540 (m, Ar), 740 (m, Ar—CH_2), 700 (s, $ArCH_2$) cm^1.

Preparation of 1-Phenylheptane. $PdCl_2(PhCN)_2$ (191 mg, 0.5 mmol) was combined with 1-hexene (168 mg, 2 mmol) in the usual manner. HMPA (1.8 g, 10 mmol) was added all at once, and a distinct darkening was noticed. The reaction mixture was kept at −78 °C for the addition of the anion. Benzylmagnesium chloride (1 mmol) in THF (3 mL) at −78 °C was added via cooled syringe. The reaction mixture turned a muddy red color. The reaction proceeded by the standard reductive pathway. The product was isolated by MPLC (hexane) as a homogeneous (by GLPC) colorless oil (25 mg, 30%) and had ^1H NMR and infrared spectra identical with those of authentic material.[18]

Preparation of 1-Phenylhexane from $PdCl_2(PhCN)_2$ and 1-Hexane. $PdCl_2(PhCN)_2$ (191 mg, 0.5 mmol) and 1-hexene (168 mg, 2 mmol) were combined in the usual manner. HMPA (1.8 g, 10 mmol) was added all at once. The reaction proceeded in the usual manner. The reaction was kept at −78 °C, and phenyllithium (1 mmol) in THF (3 mL) was added all at once. The reaction became a dark brown color. The temperature of the reaction was bought to −60 °C (ca. 0.5 h), and the flask was flushed with H_2. The reaction was stirred an additional 0.25 h at −60 °C. The cold bath was removed. After the mixture was stirred for 8 h at room temperature, usual workup and MPLC isolation (hexane) produced the desired product as a homogeneous (by GLPC) colorless oil (12 mg, 15%) which had ^1H NMR and infrared spectra identical with those of authentic material.[19]

Preparation of Octanenitrile by the in Situ Generation of the Acetonitrile Anion with Phenyllithium. $PdCl_2(CH_3CN)_2$ (130 mg, 0.5 mmol) and 1-hexene (168 mg, 2 mmol) were combined in the usual manner. After the solution became homogeneous, it was stirred for an additional 5 min. Acetonitrile (61.5 mg, 1.5 mmol) was added all at once. After 5 min, HMPA (1.8 g, 10 mmol) was added. The reaction solution was immediately cooled to −78 °C. The reaction then proceeded in the usual manner. The solution was allowed to come to −60 °C, and phenyllithium (1 mmol) in THF (3 mL) was added at −78 °C via cooled syringe. The reaction mixture which turned dark but within 5 min was a bright yellow-red, was stirred at −60 °C for an additional 10 min and was then flushed with H_2. The cold bath was removed and the reaction solution was stirred at room temperature for 4 h. Standard workup and MPLC isolation (10:1 hexane/ether) yielded octanenitrile as a clear, colorless oil (38 mg, 68%) along with 1-phenylhexane (13.5 mg, 14%). Each compound had ^1H NMR and infrared spectra identical with those of authentic material.[20]

Preparation of Decanenitrile by the in Situ Generation of the Acetonitrile Anion by Phenyllithium. $PdCl_2(CH_3CN)_2$ (130 mg, 0.5 mmol) and 1-octene (226 mg, 2 mmol) were combined in the usual manner. The reaction proceeds precisely the same as in the preparation of octanenitrile. MPLC isolation (10:1 hexane/ether) yielded the product as a yellow oil (54 mg, 70%)[21] along with 1-phenyloctane[22] (14 mg, 15%). Each compound had ^1H NMR and infrared spectra identical with those of authentic materials: NMR ($CDCl_3$) δ 0.87 (t, J = 4 Hz, 3, CH_3), 1.28 (m, 14, CH_2), 2.32 (t, J = 6 Hz, 2, CH_2CN); IR (neat) 2950, 2920, 2845, 2235, 1465, 1420, 1375, 1255 cm^{-1}.

Preparation of Decenenitriles through the in Situ Generation of the Acetonitrile Anion by Phenyllithium. The reaction was performed exactly the same as in the decanenitrile case, except in this case the reaction mixture was allowed to warm to room temperature under an argon atmosphere. Standard workup and MPLC (10:1 hexane/ether) isolation yielded a mixture of decenenitriles as a yellow odoriferous oil (52 mg, 69%; which, when reduced by H_2 with Pd/C catalyst, yielded decanenitrile as the only product). A mixture of 1-phenyloctenes (12.5 mg, 13%) also was isolated as a colorless oil which, when reduced (H_2, Pd/C), gave 1-phenyloctane. Decene nitrile: NMR ($CDCl_3$) δ 0.90 (t, J = 4 Hz, 3, CH_3), 1.30 (m, 6, CH_2), 2.05 (m, 4, =$CHCH_2$), 2.26 (d, J = 1 Hz, 2), 5.43 (m, 2, olefinic); IR (neat) 3010 (w), 2940, 2910, 2840 (s), 2230 (w, CN), 2205 (w, CH=CHCN), 1650, 1600, 1460, 1440 cm^{-1}. 1-Phenyloctenes: NMR ($CDCl_3$) δ 0.92 (t, J = 4 Hz, CH_3), 1.28 (m, 7, CH_2), 2.15 (m, 2, =$CHCH_2$), 2.55 (t, J = 7 Hz, 2, Ar—CH_2), 3.20 (d, J = 4 Hz, 0.5, $ArCH_2C$=), 5.30 (m, 1, olefin), 6.18 (m, 1, olefin), 7.1 (d, J = 5 Hz, 5, Ar); IR (neat) 3080, 3060, 3020, 2950, 2920, 2850, 1600, 1495, 1455, 1370, 965, 740, 695 cm^{-1}.

Preparation of 2-Cyanodecane. $PdCl_2(CH_3CH_2CN)_2$ (144 mg, 0.5 mmol) and 1-octene (226 mg, 2 mmol) were combined in the usual manner. After the solution became homogeneous (ca. 10 min), propionitrile (82.5 mg, 1.5 mmol) was added all at once. After an additional 10 min, HMPA (1.8 g, 10 mmol) was added all at once. The reaction then proceeded precisely as in the case of octanenitrile. H_2 reduction, standard work up, and MPLC (10:1 hexane/ether) isolation yielded 2-cyanodecane (59 mg, 71%) and 1-phenyloctane (9.5 mg, 10%) as colorless oils. The nitrile was identical with material synthesized by the method of Sperber:[25]

(17) R. T. Coutts, G. R. Jones, A. Benderly, and A. L. C. Mak, *J. Chromatogr. Sci.*, 17, 350 (1979).
(18) The Aldrich Library of NMR Spectra, IV, 2d, IR 421F
(19) Reference 18, IV, 2c, IR 421C
(20) Reference 18, III, 154D, IR 375E
(21) B. Bogdanovic and J. B. Koster, *Justus Liebigs Ann. Chem.*, 4, 692 (1975).
(22) Sadtler NMR Spectra, 3881M, IR 32043
(23) S. Murahashi, M. Yamamura, K. Yanagisawa, and K. Kondo, *J. Org. Chem.*, 44, 14 (1979).
(24) E. Negishi and S. Baba, *J. Chem. Soc., Chem. Commun.*, 597 (1976).

NMR ($CDCl_3$) δ 0.91 (t, J = 4 Hz, 3, CH_3), 1.35 (m, 14 CH_2), 1.37 (d, J = 7 Hz, 3, H_3CCHCN), 2.69 (m, 1, CH); IR (Neat) 2960, 2930, 2850, 2235 (m, CN), 1460, 1450, 1370, 1260 cm^{-1}.

Preparation of 2-Cyanodecene. This reaction was done in the same manner as 2-cyanodecane, except that the reaction solution was allowed to warm under an argon atmosphere and stirred for 8 h at room temperature. Standard workup, MPLC (10:1 hexane/ether) isolation yielded a mixture of 2-cyanodecenes (54 mg, 66%) along with 1-phenyloctene (9.2 mg, 10%) each as a colorless oil. When each mixture was reduced (H_2, Pd/C) 2-cyanodecane and 1-phenyloctane were obtained as the only products, respectively: NMR ($CDCl_3$) δ 0.90 (t, J = 5 Hz, CH_3), 1.25 (d, J = 1 Hz, CH_3), 1.32 (m, CH_2), 2.01 (m, CH_2C=), 2.22 (m, H_2CC=), 2.68 (m, H_2CCHCN), 5.35 (m, 1.4 olefin); IR (neat) 2950, 2920, 2850, 2237 (m, CN), 2215 (m, CN), 1630, 1615, 1595, 1455, 1380, 960, 790, 760 cm^{-1}.

Preparation of 2-Phenyloctanenitrile. $PdCl_2(PhCN)_2$ (191 mg, 0.5 mmol) and 1-hexene (168 mg, 2 mmol) were combined in the usual manner. When the solution became homogeneous (ca. 10 min) phenylacetonitrile (175 mg, 1.5 mmol) was added all at once. HMPA (1.8 g, 10 mmol) was added after 10 min, and the reaction mixture was cooled to −78 °C. The reaction proceeded as in the case of octanenitrile. When phenyllithium was added, a bright purple color was noted which eventually faded to deep red. H_2 reduction, standard workup, and MPLC (10:1 hexane/ether) isolation yielded 2-phenyloctanenitrile (50 mg, 50%) as a colorless oil which was identical with material prepared by an alternate synthesis:[26] NMR ($CDCl_3$) δ 0.89 (t, J = 5 Hz, 3 CH_3), 1.32 (m, 10, CH_2), 3.66 (t, J = 7 Hz, 1, NCCHAr), 7.17 (s, 5, Ar); IR (neat) 3055, 3020, 2945, 2920, 2850, 2225 (w, CN), 1595, 1490, 1460, 1450, 1370, 1270, 750, 690 cm^{-1}.

Preparation of 2-Phenyloctenenitriles. The preparation was exactly the same as the preparation of 2-phenyloctanenitrile except that the reaction mixture was allowed to warm under an argon atmosphere. Standard workup and MPLC isolation (10:1 hexane/ether) yielded a mixture of 2-phenyloctenenitriles (44.5 mg, 45%) which when reduced with (H_2/Pd/C) yielded 2-phenyloctanenitrile as the only product: NMR ($CDCl_3$) δ 0.93 (t, J = 5 Hz, 3, CH_3), 1.30 (m, 6, CH_2), 2.39 (m, 1, CH_2C=), 3.60 (t, J = 7 Hz, 0.4, NCCHAr), 5.25 (m, 0.6, olefin), 7.04 (d, m, 0.7), 7.13 (s, 5, Ar); IR (neat) 3060, 3020, 2960, 2940, 2850, 2250 (w, CN), 2200 (w, CN), 1670 (w), 1595, 1485, 1445 (m), 1370 (w), 1260 (m), 1140, 1060 (m), 750, 690 (s) cm^{-1}.

Preparation of Decanenitrile by the Extended Generation of the Acetonitrile Anion. $PdCl_2(CH_3CN)_2$ (260 mg, 1 mmol) and 1-octene (500 mg, 4 mmol) were combined in the usual manner. HMPA (3.6 g, 20 mmol) was added all at once. The reaction was then run in the standard manner. The acetonitrile anion was generated with butyllithium at 0 °C and then after 1 h cooled to −78 °C. The reaction solution was allowed to warm to −60 °C, and the anion was added via cooled syringe. The solution immediately turned a deep red color. Stirring continued at −60 °C for 0.5 h at which time the reaction solution was flushed with H_2. The solution was stirred at −60 °C for an additional 0.25 h, whereupon the cold bath was removed and stirred was continued at room temperature for 8 h. Standard workup yielded decanenitrile (109 mg, 75%) as a colorless oil.

Preparation of (*E*)-1-Phenylhexene from (Carboxyethylmethylene)triphenylphosphorane. $PdCl_2(CH_3CN)_2$ (65 mg, 0.25 mmol) and 1-hexene (84 mg, 1 mmol) were combined in the usual manner. HMPA (90 mg, 0.5 mmol) was added all at once. The reaction proceeded in the usual manner. The temperature of the reaction solution was allowed to warm to −60 °C where upon (carboxyethylmethylene)triphenylphosphorane (87 mg, 0.25 mmol) was added as a solid. The solution immediately turned bright yellow and homogeneous. The cold bath was removed and was replaced with a 50 °C bath. The reaction mixture was heated for 4 h at 50 °C. The dark yellow suspension was filtered. The solvent was removed under vacuum to yield a bright yellow solid which was crushed and extracted with hexane (100 mL). The solvent was removed; MPLC isolation (hexane) yielded (*E*)-1-phenylhexene (12 mg, 30%) which was identical with material synthesized by an alternate procedure:[23] NMR ($CDCl_3$) δ 0.92 (t, J = 5 Hz, 3, CH_3), 1.30 (m, 4, CH_2), 2.10 (m, 2, =CCH_2), 6.13 (m, 2, ArCH=CH), 7.12 (m, 5, Ar); IR (neat) 3080, 3050, 3020, 2950, 2850, 1620, 1495 (m), 1455, 1370, 1260 cm^{-1}.

Preparation of (*E*)-1-*p*-Tolylhexene from (Carboxyethylmethylene)tri-*p*-tolylphosphorane and 1-Hexene. The reaction was run exactly as in the 1-phenylhexene case except that the *p*-tolyl ylide (92.25 mg, 0.25 mmol) was used. The same workup was used to yield 1-*p*-tolylhexene (13.5 mg, 30%) as a colorless liquid. This compound corresonds in all ways to the compound prepared by the method of Negishi:[24] NMR ($CDCl_3$) δ 0.92 (t, J = 5 Hz, 3, CH_3), 1.30 (m, 4, CH_2), 2.15 (m, 2, =$CHCH_2$), 2.32 (s, 3, $ArCH_3$), 6.1 (m, 2, ArCH=CH), 7.15 (m, 4, Ar); IR (neat) 3000, 2990, 2900, 2840, 1630, 1505(m), 1450, 1360, 1290, 960, 790 cm^{-1}.

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Registry No. 3 (R′ = *n*-Bu, R = H), 124-12-9; **3** (R′ = *n*-hex, R = H), 1975-78-6; **3** (R′ = *n*-hex, R = Me), 69300-15-8; **3** (R′ = *n*-Bu, R = Ph), 5558-35-0; **4** (R′ = *n*-hex, R = H), 78020-34-5; **4** (R′ = *n*-hex, R = Me), 82323-10-2; **4** (R′ = *n*-Bu, R = Ph), 82323-11-3; $PdCl_2(CH_3CN)_2$, 14592-56-4; $PdCl_2(PhCN)_2$, 14220-64-5; $PdCl_2(CH_3CH_2CN)_2$, 27928-79-6; *N*-acetylamphetamine, 14383-60-9; *N*-vinylacetamide, 5202-78-8; benzyl chloride, 100-44-7; 1-phenylheptane, 1078-71-3; 1-hexene, 592-41-6; phenyllithium, 591-51-5; acetonitrile, 75-05-8; 1-octene, 111-66-0; 1-phenyloctane, 2189-60-8; 1-phenyloctene, 82323-12-4; propionitrite, 107-12-0; phenylacetonitrile, 140-29-4; (*E*)-1-phenylhexene, 6111-82-6; (carboxyethylmethylene)triphenylphosphorane, 1099-45-2; (*E*)-1-*p*-tolylhexene, 61153-37-5; (carboxyethylmethylene)tri-*p*-tolylphosphorane, 77610-02-7.

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