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Direct Synthesis of Terminal Alkynes *via* Pd-Catalyzed Cross Coupling of Aryl and Alkenyl Halides with Ethynylmetals Containing Zn, Mg, and Sn. Critical Comparison of Countercations

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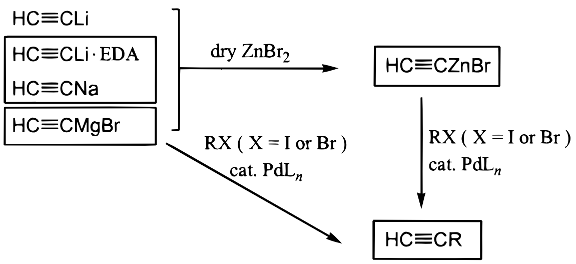
Several Pd-catalyzed cross-coupling procedures for the synthesis of alkynes were reported in the mid 1970s.[1−5] Of these, the Sonogashira protocol[3] involving the treatment of terminal alkynes with organic halides and an amine base, *e.g.*, Et_2NH, in the presence of catalytic quantities of a Pd−phosphine complex and CuI has been most widely used presumably due to generally favorable results and operational simplicity associated with it. One of its serious limitations, however, is its reported inability[3] to provide a direct route to terminal alkynes. We have indeed confirmed this by running the reaction of PhI with an excess of acetylene in the presence of 5 mol % each of $Pd(PPh_3)_4$ and CuI, which gave PhC≡CPh in 40% yield along with only a 20% yield of the desired PhC≡CH. Thus, a selective synthesis of terminal alkynes by this method requires an indirect route involving protection and deprotection of the ethynyl group.[3b,6] We earlier reported a few examples of a direct synthesis of terminal alkynes *via* Pd-catalyzed cross coupling of HC≡CZnCl with organic halides,[4] using mainly a cylinder of acetylene as the source of the ethynyl group. In view of the growing significance of the Pd-catalyzed synthesis of alkynes, we sought practically convenient, direct, and chemoselective routes to terminal alkynes, and we herein report that HC≡CZnBr (or Cl) generated *in situ* from commercially available HC≡CMgBr (or Cl) and HC≡CNa can readily cross couple with a variety of aryl and alkenyl iodides (and bromides in some cases) in the presence of a Pd−phosphine catalyst, e.g., $Pd(PPh_3)_4$, to produce directly and selectively the corresponding terminal alkynes in high yields (Scheme 1). We further present a critical comparison of countercations including Zn, Mg, Sn, and B.

Scheme 1



In our earlier studies[4,5] we reported the first set of examples of the successful use of alkynylmetals containing Mg, Zn, B, Al, and Sn in the Pd-catalyzed alkyne synthesis. On the other hand, alkynyllithiums were generally unsatisfactory,[7] even though alkynylsodiums were reported to be satisfactory.[1] In the current study, we first screened Li, Na, Mg, Zn, B, and Sn with respect to the Pd-catalyzed direct ethynylation of phenyl iodide. The experimental results summarized in Table 1 indicate the following. Ethynylmetals containing Mg, Zn, and Sn provide phenylacetylene in nearly quantitative yields, although the reaction of ethynyltributyltin was substantially slower than the other two. Ethynylsodium is not a satisfactory reagent under the comparable conditions. The total failure observed with lithium ethynyltriethylborate generated *in situ* from ethynyllithium and Et_3B was quite puzzling in view of our earlier favorable results observed with lithium 1-heptynyltributylborate.[5] Using the same batch of Et_3B, we ran two parallel reactions of $LiBEt_3(C{\equiv}CH)$ and $LiBEt_3(C{\equiv}CHex\text{-}n)$ with PhI in the presence of 5 mol % of $Pd(PPh_3)_4$ and obtained PhC≡CH and PhC≡CHex-*n* in <5 and 80% yields, respectively. Although no further insight into the reaction of $LiBEt_3(C{\equiv}CH)$ is available at this time, we tentatively conclude that ethynyltrialkylborates are not suitable reagents for the synthesis of terminal alkynes. Ethynylzinc derivatives are readily generated *in situ* by treatment of ethynyllithium (which *in turn* may be generated by treatment of acetylene with *n*-BuLi[8]) or, more conveniently, commercially available ethynylmagnesium bromide, the corresponding chloride, or ethynylsodium in xylene/mineral oil with dry $ZnBr_2$ or $ZnCl_2$. The use of PhBr in place of PhI did not lead to the formation of PhC≡CH under otherwise the same conditions. The use of $Cl_2Pd(PPh_3)_2$ did not offer any advantage over $Pd(PPh_3)_4$.

Although Mg, Zn, and Sn are comparably satisfactory in the ethynyl−phenyl coupling (Table 1), further delineation of the scope of the Pd-catalyzed ethynyl−aryl coupling revealed some critical limitations associated with Mg and Sn (Table 2). Ethynylmagnesium bromide appears to be as satisfactory as ethynylzinc bromide in cases where substituents do not readily react with HC≡CMgBr and/or sterically interfere with the desired cross coupling. However, at least two kinds of limitations associated with HC≡CMgBr should be noted. The reactions of *p*-nitrophenyl iodide and methyl *p*-iodobenzoate clearly reveal expected chemoselectivity problems associated with Mg. A more subtle limitation associated with Mg is competitive formation of diarylethynes, which must arise *via* H−Mg exchange. There appear to be at least two contributing factors: (i) higher ionicity of the C−Mg bond relative to the C−Zn bond rendering the former more prone to H−Mg exchange and (ii) slower cross coupling rates observed with Grignard reagents relative to the corresponding organozincs. Although not yet clearly demonstrated, one may additionally expect that the formation of a terminal alkyne having a higher acidity than the starting acetylene would also favor the formation of ArC≡CAr. Since $HC{\equiv}CSnBu_3$ is more

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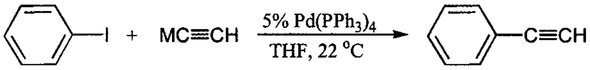
Table 1. Pd-Catalyzed Cross Coupling of Phenyl Iodide with Ethynylmetals



M of $MC\equiv CH$	Reaction time, h	Product yield,[a] %
Li	1	≤3
Na	1	4
MgCl	1	96[b]
ZnBr[c]	1	95
ZnBr[d]	1	98
$SnBu_3$[e]	24	96
BBu_3Li[f]	1	<2
BBu_3Na[g]	1	<2

[a] By NMR or GLC. [b] Diphenylacetylene was formed in 2% yield. [c] Generated *in situ* from $HC\equiv CNa$ and $ZnBr_2$. [d] Generated *in situ* from $HC\equiv CMgCl$ and $ZnBr_2$. [e] Generated *in situ* from $HC\equiv CMgCl$ and $ClSnBu_3$. [f] Generated *in situ* from $HC\equiv CLi$ and $B(Bu\text{-}n)_3$. [g] Generated *in situ* from $HC\equiv CNa$ and $B(Bu\text{-}n)_3$.

expensive than $HC\equiv CMgBr$ or $HC\equiv CZnBr$ and since its use requires more cumbersome isolation and purification procedures, there generally is little incentive for using $HC\equiv CSnBu_3$. Its significantly lower reactivity relative to $HC\equiv CZnBr$, as demonstrated in the reaction of mesityl iodide, is yet another limitation associated with Sn.

Finally, the scope of the Pd-catalyzed ethynyl–alkenyl coupling was investigated. As the results summarized in Table 3 indicate, di-, tri-, and even tetrasubstituted alkenyl iodides can be successfully employed. In all cases, both the starting alkenyl iodides and the products were ≥98% stereoisomerically pure. In the absence of chemoselectivity problems, $HC\equiv CMgBr$ appears to be almost as satisfactory as $HC\equiv CZnBr$, although the superior reactivity of the latter is seen in the reaction of (*E*)-4-iodo-5-methyl-4-octene. At least in one case, a successful use of $HC\equiv CSnBu_3$ for the enyne synthesis was demonstrated. Once again, however, there does not appear to be any need or incentive for the reagent.

In conclusion, direct synthesis of terminal alkynes without protection–deprotection can be achieved by the Pd-catalyzed coupling of aryl or alkenyl iodides with ethynylmetals containing Mg, Zn, or Sn. The reaction of $HC\equiv CSnBu_3$ is generally slower and lower yielding in some difficult cases. It is further handicapped by its higher cost and cumbersome isolation and purification procedures. In cases where no significant difficulties exist, the use of commercially available $HC\equiv CMgBr$ should be considered because of its commercial availability, relative low cost, and operational simplicity. In more demanding cases, where $HC\equiv CMgBr$ is unsatisfactory as exemplified above, the use of $HC\equiv CZnBr$ can provide some distinct advantages over that of $HC\equiv CMgBr$.

Experimental Section

General Procedures. Manipulations involving organometallics were carried out under a dry Ar atmosphere. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$. NMR yields were determined by using dibromomethane or mesitylene as an internal reference. GLC analysis was performed with a column packed with SE-30 Chromosorb W using a TC detector. All chemicals obtained from commercial sources were used as received unless otherwise mentioned. THF was distilled from sodium benzophenone ketyl. DMF was freshly distilled and dried over 4A molecular sieve. $ZnBr_2$ was flame-dried under vacuum. $HC\equiv CMgBr$, $HC\equiv CMgCl$, $HC\equiv CNa$, and $HC\equiv CLi\cdot EDA$ were obtained from Aldrich. $HC\equiv CSnBu_3$ was prepared by the reaction $HC\equiv CMgBr$ (or Cl) with $ClSnBu_3$ in THF. $HC\equiv CB(Bu\text{-}n)_3Na$(or Li) was prepared by the reaction of $B(Bu\text{-}n)_3$ with $HC\equiv CNa$ (or Li) in THF. $Pd(PPh_3)_4$,[9] $PdCl_3(PPh_2)_2$,[10] (*E*)-1-iodo-1-octene,[11] (*E*)-4-iodo-4-octene,[12] and (*E*)-1-iodo-2-methyl-1-octene[13] were prepared as reported in the literature. Iodomesitylene was prepared from bromomesitylene by lithiation followed by iodinolysis. All other aryl iodides were obtained from commercial sources.

(*E*)-4-Iodo-5-methyl-4-octene. This compound was prepared as reported previously[13] except for the reaction temperature of 22 °C. When the reaction was carried out at 50 °C for 6 h, as specified earlier,[13] a mixture of the *E*- and *Z*-isomers resulted. The procedure used in this study is as follows. To a suspension of Cl_2ZrCp_2 (2.92 g, 10 mmol) in 1,2-dichloromethane (25 mL) was added Me_3Al (1.44 g, 1.92 mL, 20 mmol) (pyrophoric!) under argon at 22 °C. All Cl_2ZrCp_2 dissolved within 10–15 min to give a lemon-yellow solution. To this was added 1.10 g (1.47 mL, 10 mmol) of 4-octyne. After the solution was stirred for 6 h at 22 °C, 3.05 g (12 mmol) of iodine dissolved in 15 mL of THF was added at 0 °C. After the iodine color faded, the reaction mixture was quenched with water–ether, and the organic layer was separated, washed with aqueous $Na_2S_2O_3$, dried over $MgSO_4$, filtered, and distilled to give 2.01 g (82%) of (*E*)-4-iodo-5-methyl-4-octene: ^1H NMR ($CDCl_3$, Me_4Si) δ 0.90 (t, $J = 7.4$ Hz, 6 H), 1.4–1.7 (m, 4 H), 1.91 (s, 3 H), 2.1–2.3 (m, 2 H), 2.50 (t, $J = 7.4$ Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.96, 13.84, 21.53, 23.01, 29.75, 35.68, 42.93, 104.76, 139.99 ppm; stereoisomer purity >98%.

Pd-Catalyzed Cross Coupling of Aryl Iodides with Ethynylmetals. (a) Reaction of 2-Iodo-*p*-xylene with Ethynylzinc Bromide. Representative Procedure for the Use of Ethynylzinc Bromide. To a flame-dried 50-mL flask equipped with a magnetic stirring bar were sequentially added under an Ar atmosphere $HC\equiv CZnBr$, 2-iodo-*p*-xylene (464 mg, 2 mmol), and $Pd(PPh_3)_4$ (115 mg, 0.1 mmol). A solution of $HC\equiv CZnBr$ was prepared by the reaction of $HC\equiv CMgBr$ (3 mmol, 6 mL of 0.5 M solution in THF) with dry $ZnBr_2$ (675 mg, 3 mmol) dissolved in 5 mL of THF. The course of reaction was monitored by gas chromatography, and the reaction was complete in 3 h at 22 °C. The reaction mixture was quenched with aqueous NaCl, extracted with Et_2O, dried over $MgSO_4$, and concentrated *in vacuo*. Column chromatography on silica gel afforded 2-ethynyl-*p*-xylene[14] (220 mg, 85%): ^1H NMR ($CDCl_3$, Me_4Si) δ 2.26 (s, 3 H), 2.39 (s, 3 H), 3.22 (s, 1 H), 6.9–7.3 (m, 3 H) ppm; ^{13}C NMR ($CDCl_3$, Me_4Si) δ 20.02, 20.64, 80.47, 82.70, 121.63, 129.30, 129.59, 132.92, 134.94, 137.58 ppm. **(b) Reaction of 2-Iodo-*p*-xylene with Ethynylmagnesium Bromide.** This reaction was carried out in the same manner as above except that $HC\equiv CMgBr$ was used and that the reaction time was 48 h. **(c) Reaction of 2-Iodo-*p*-xylene with Ethynyltributyltin.** This reaction was carried out in the same manner as above except that $HC\equiv Csn(Bu\text{-}n)_3$ was used and that the reaction time was 24 h.

The reaction conditions for the other cases are shown in Table 2.

4-Ethynyltoluene:[15] ^1H NMR ($CDCl_3$, Me_4Si) δ 2.36 (s, 3 H), 3.04 (s, 1 H), 7.13 (d, $J = 8$ Hz, 2 H), 7.40 (d, $J = 8$ Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, Me_4Si) δ 21.49, 76.44, 83.83, 118.99, 129.05, 132.00, 138.94 ppm.

1-Ethynyl-4-fluorobenzene:[15] ^1H NMR ($CDCl_3$, Me_4Si) δ 3.04 (s, 1 H), 6.9–7.1 (m, 2 H), 7.4–7.6 (m, 2 H) ppm; ^{13}C NMR

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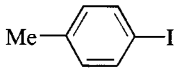
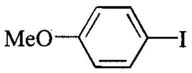
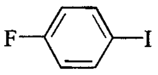
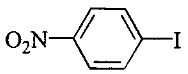
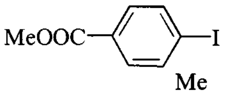
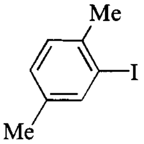
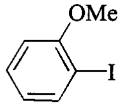
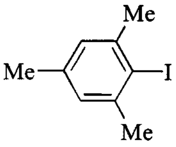
Table 2. Critical Comparison of Mg, Zn, and Sn in the Pd-Catalyzed Cross Coupling of Aryl Iodides with Ethynylmetals[a]

$$ArI + MC\equiv CH \xrightarrow{5\% Pd(PPh_3)_4} ArC\equiv CH$$

ArI	M of $MC\equiv CH$	Solvent	Temp. °C	Time h	Product Yield,[b)] % $ArC\equiv CH$	$ArC\equiv CAr$	ArI %
	MgBr	THF	22	1	92(86)	c)	0
	MgBr	THF	22	1	95	c)	0
	ZnBr[d)]	THF	22	1	95	c)	0
	MgBr	THF	22	1	97(72)	c)	0
	ZnBr[d)]	THF	22	1	94	c)	0
	MgBr	THF	0	12	0	c)	c)
	ZnBr[d)]	THF	0	3	93(89)	c)	0
	ZnBr[d)]	THF	22	1	92(86)	c)	0
	MgBr	THF	22	48	60(56)	24	14
	ZnBr[d)]	THF	22	3	92(85)	4	0
	$SnBu_3$[e)]	THF	22	24	73	6	15
	MgBr	THF	22	20	51	36	c)
	ZnBr[d)]	THF	22	2	77	trace	c)
	MgBr	DMF	60	48	28	12	66
	MgBr	THF/DMF[f)]	60	24	1	c)	95
	ZnBr[d)]	THF/DMF[f)]	60	18	74(68)	10	c)
	$SnBu_3$[e)]	THF/DMF[f)]	60	24	3	c)	95
	$SnBu_3$[e)]	THF/DMF[f)]	60	72	36	8	52

[a] 1.5 equiv of $HC\equiv CMgBr$ relative to ArI was used in each case. [b] By NMR or GLC. The numbers in parentheses are isolated yields. [c] Not determined or detected. [d] Generated *in situ* from $HC\equiv CMgBr$ and dry $ZnBr_2$. [e] Generated *in situ* from $HC\equiv CMgBr$ and $ClSn(Bu\text{-}n)_3$. [f] 3 equiv of DMF relative to ArI was added.

($CDCl_3$, Me_4Si) δ 76.93, 82.56, 115.59 (d, $J = 89$ Hz), 118.13 (d, $J = 13$ Hz), 134.03 (d, $J = 34$ Hz), 162.73 (d, $J = 995$ Hz) ppm.

4-Ethynyl-1-nitrobenzene:[16] in this case, the reaction temperature was 0 °C; ^1H NMR ($CDCl_3$, Me_4Si) δ 3.36 (s, 1 H), 7.63 (d, $J = 8.9$ Hz, 2 H), 8.19 (d, $J = 8.9$ Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, Me_4Si) δ 81.56, 82.32, 123.53, 128.87, 132.93, 147.49 ppm.

Methyl 4-ethynylbenzoate:[17] ^1H NMR ($CDCl_3$, Me_4Si) δ 3.23 (s, 1 H), 3.89 (s, 3 H), 7.52 (d, $J = 8.5$ Hz, 2 H), 7.97 (d, $J = 8.5$ Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, Me_4Si) δ 52.18, 80.04, 82.70, 126.64, 129.35, 130.01, 131.97, 166.27 ppm.

2-Ethynylanisole:[18] ^1H NMR ($CDCl_3$, Me_4Si) δ 3.31 (s, 1 H), 3.85 (s, 3 H), 6.8–7.0 (m, 2 H), 7.2–7.5 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$, Me_4Si) δ 55.50, 79.95, 81.03, 110.40, 110.94, 120.22, 130.10, 133.93, 160.36 ppm.

Mesitylacetylene:[19] the reactions were carried out at 60 °C in DMF or THF with 3 equiv of DMF relative to iodomesitylene; ^1H NMR ($CDCl_3$, Me_4Si) δ 2.23 (s, 3 H), 2.39 (s, 6 H), 3.40 (s, 1 H), 6.81 (s, 2 H) ppm; ^{13}C NMR ($CDCl_3$, Me_4Si) δ 20.79, 21.20, 81.35, 84.48, 118.96, 127.51, 137.97, 140.71 ppm.

Pd-Catalyzed Cross Coupling of Alkenyl Iodides with Ethynylmetals. (a) Reaction of (*E*)-4-Iodo-4-octene with Ethynylmagnesium Bromide. Representative Procedure for the Use of Ethynylmagnesium Bromide. To a flame-dried 50-mL flask equipped with a magnetic stirring bar were sequentially added under an Ar atmosphere THF (10 mL), (*E*)-4-iodo-octene (1.19 g, 5 mmol), $Pd(PPh_3)_4$ (285 mg, 0.25 mmol), and $HC\equiv CMgBr$ (7.5 mmol, 15 mL of a 0.5 M solution in THF). Gas chromatographic analysis indicated that the reaction was complete in 1 h at 22 °C. The reaction mixture was quenched with aqueous NH_4Cl, extracted with pentane, dried over $MgSO_4$, and concentrated *in vacuo*. ^1H NMR analysis revealed that (*E*)-3-(*n*-propyl)-3-hepten-1-yne was formed in 95% yield. Bulb-to-bulb distillation afforded this product (0.60 g, 89%) as a colorless oil: ^1H NMR ($CDCl_3$, Me_4Si) δ 0.91 (t, $J = 7.6$ Hz, 6 H), 1.3–1.7 (m, 4 H), 2.0–2.2 (m, 4 H), 2.73 (s, 1 H), 5.96 (t, $J = 7.6$ Hz, 1 H) ppm; ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.56, 13.75, 21.40, 23.37, 30.23, 32.37, 73.68, 85.99, 122.05, 139.73 ppm; IR (neat) 3280, 2116, 1636 cm^{-1}; HRMS calcd for $C_{10}H_{16}$ (M^+) 136.1252, found 136.1249. **(b) Reaction of (*E*)-4-Iodo-4-octene with Ethynylzinc Bromide.** This reaction was carried out in the same manner as above except that $HC\equiv CZnBr$ was used. A solution of $HC\equiv CZnBr$ was prepared by the reaction of $HC\equiv CMgBr$ and

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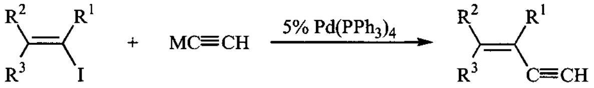
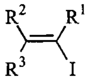
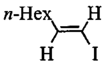
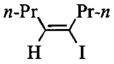
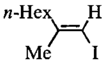
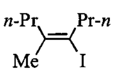
Table 3. Direct Synthesis of 3-En-1-yne *via* Pd-Catalyzed Coupling of Alkenyl Iodides with Ethynylmetals Containing Mg and Zn[a]



	M of MC≡CH	Solvent	Temp. °C	Time h	Product yield[b)] %
	MgBr	THF	22	1	95
	$\mathrm{ZnBr}^{c)}$	THF	22	1	96
	$\mathrm{SnBu_3}^{d)}$	THF	22	6	95
	MgBr	THF	22	1	98
	$\mathrm{ZnBr}^{c)}$	THF	22	1	98
	MgBr	THF	22	1	94
	$\mathrm{ZnBr}^{c)}$	THF	22	1	94
	$\mathrm{MgBr}^{e)}$	DMF	50	24	82
	$\mathrm{ZnBr}^{c)e)}$	DMF	50	3	95
	$\mathrm{ZnBr}^{c)}$	DMF	22	20	93

[a] 1.5 equiv of MC≡CH was used. [b] NMR yield. The stereoisomeric purity in each case was ≥98%. [c] Generated *in situ* from HC≡CMgBr and dry $\mathrm{ZnBr_2}$. [d] Generated *in situ* from HC≡CMgBr and $\mathrm{ClSnBu_3}$. [e] 5 mol % of $\mathrm{Cl_2Pd(PPh_3)_2}$ was used.

dry $\mathrm{ZnBr_2}$ in THF. ^{1}H NMR analysis indicated the formation of (*E*)-3-(*n*-propyl)-3-hepten-1-yne in 96% yield. **(c) Reaction of (*E*)-1-iodo-1-octene with Ethynyltributyltin.** This reaction was carried out in the same manner as above except that HC≡CSn(Bu-*n*)$_3$ was used and reaction time was 6 h. ^{1}H NMR analysis indicated the formation of (*E*)-3-decen-1-yne in 95% yield: ^{1}H NMR ($\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$) δ 0.88 (t, J = 6.8 Hz, 3 H), 1.2−1.5 (m, 8 H), 2.0−2.2 (m, 2 H), 2.76 (d, J = 2.2 Hz, 1 H), 5.4−5.6 (m, 1 H), 6.2−6.4 (m, 1 H) ppm; ^{13}C NMR ($\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$) δ 14.10, 22.63, 28.57, 28.82, 31.69, 33.08, 75.55, 82.61, 108.49, 146.96 ppm; IR (neat) 3312, 2186, 1654 cm^{-1}; HRMS calcd for $\mathrm{C_{10}H_{16}}$ (M$^+$) 136.1252, found 136.1253.

The reaction conditions for the other cases are shown in Table 3.

(*E*)-4-Methyl-3-decen-1-yne: ^{1}H NMR ($\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$) δ 0.88 (t, J = 6.2 Hz, 3 H), 1.2−1.5 (m, 8 H), 1.89 (s, 3 H), 2.07 (t, J = 7.0 Hz, 2 H), 2.99 (d, J = 2.2 Hz, 1 H), 5.2−5.3 (m, 1 H) ppm; ^{13}C NMR ($\mathrm{CDCl_3}$, $\mathrm{MeSi_4}$) δ 14.02, 19.14, 22.55, 27.45, 28.85, 31.65, 38.59, 79.26, 81.82, 103.55, 154.53 ppm; IR (neat) 3314, 2100, 1654 cm^{-1}; HRMS calcd for $\mathrm{C_{11}H_{18}}$ (M$^+$) 150.1408, found 150.1405.

(*E*)-4-Methyl-3-(*n*-propyl)-3-hepten-1-yne: ^{1}H NMR ($\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$) δ 0.90 (t, J = 6.2 Hz, 6 H), 1.3−1.6 (m, 3 H), 1.94 (s, 3 H), 2.0−2.2 (m, 4 H), 3.02 (s, 1 H) ppm: ^{13}C NMR ($\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$) δ 13.73, 14.02, 21.25, 21.35, 21.94, 33.56, 35.53, 79.12, 84.76, 116.77, 145.44 ppm; IR (neat) 3314, 2088, 1684 cm^{-1}; HRMS calcd for $\mathrm{C_{11}H_{18}}$ (M$^+$) 150.1408, found 150.1405.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of three iodoalkenes, *i.e.*, (*E*)-4-iodo-4-octene, (*E*)-1-iodo-2-methyl-1-octene, and (*E*)-4-iodo-5-methyl-4-octene, their ethynylated derivatives, and six phenylethyne derivatives containing 2,5-dimethyl, *p*-F, *p*-NO$_2$, *p*-COOMe, *o*-MeO, and 2,4,6-trimethyl groups (24 pages). This material is contained in libraries on microfiche, immediately follows this article, and can be ordered from the ACS; see any current masthead page for ordering information.

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Additions and Corrections

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W. E. Acree, Jr.,* Joyce R. Powell, Sheryl A. Tucker, Maria D. M. C. Ribeiro da Silva, M. Agostinha R. Matos, J. M. Gonçalves, L. M. N. B. F. Santos, V. M. F. Morais, and G. Pilcher. Thermochemical and Theoretical Study of Some Quinoxaline 1,4-Dioxides and of Pyrazine 1,4-Dioxide.

Page 3724, Table 3. The last four column headings should read as follows: $-\Delta_c H^0_m$(cr), $\Delta_f H^0_m$(cr), $\Delta^g_{cr} H^0_m$, and $\Delta_f H^0_m$(g).

JO974016S

Leo A. Paquette,* Thomas M. Mitzel, Methvin B. Isaac, Curtis F. Crasto, and William W. Schomer. Diastereoselection during 1,2-Addition of the Allylindium Reagent to α-Thia and α-Amino Aldehydes in Aqueous and Organic Solvents.

Page 4293. The elegant studies by Duhamel and by Dondoni on a tunable stereoselectivity of organometallic additions to variously protected α-amino aldehydes were inadvertently not acknowledged. The relevant references are as follows:

(1) Duhamel, P.; Duhamel, L.; Gralak, J. *Tetrahedron Lett.* **1972**, 2329.

(2) Dondoni, A.; Fantin, G.; Fogagnolo, M.; Pedrini, O. *J. Org. Chem.* **1990**, *55*, 1439.

(3) Dondoni, A.; Perrone, D. *Synthesis* **1993**, 1162.

(4) Dondoni, A.; Perrone, D.; Semola, T. *Synthesis* **1995**, 181.

(5) Dondoni, A.; Perrone, D.; Semola, M. T. *J. Org. Chem.* **1995**, *60*, 7927.

(6) Dondoni, A.; Perrone, D.; Merino, P. *J. Org. Chem.* **1995**, *60*, 8074.

JO974021W

Sergey P. Verevkin, Margot Nölke, Hans-Dieter Beckhaus, and Christoph Rüchardt*. Enthalpies of Formation of Hexaethylethane, Octamethylhexane, and Tri-*tert*-butylmethane. Extremely Strained Hydrocarbons.

Page 4684. In the Discussion the following numbers should be corrected: line 9, H_s = 177.2 kJ·mol^{-1}; line 10, H_s = 156.1 kJ·mol^{-1}; line 11 H_s = 118.1 kJ·mol^{-1}. The strain enthalpies H_s are correctly recorded in Table 1.

JO9740204