

methylbutadiene (1,3), 78-79-5; 3-methylpentadiene (2,4), 4549-74-0; (*E,E*)-hexadiene (2,4), 5194-51-4; butadiene (1,3), 106-99-0; 2,3-dimethylbutadiene (1,3), 513-81-5; ethylene-*d*₄, 683-73-8.

Supplementary Material Available: Tables of ¹H and ¹³C NMR data for 9a-n, 10a, 10d, and 10e, electron-impact mass spectra for 9a-n and 10a-e, melting points and elemental analysis for 9b, 9d, 9g, 9i, and 10d, crystal data for 9g and 10d, crystal

data in German for 9g and 10d, bond distances and angles for 9g and 10d, general temperature factors for 9g and 10d, refined temperature factors for 9g and 10d, least-squares planes for 9g and 10d, root-mean-square amplitudes for 9g and 10d, positional parameters for 9g and 10d, and torsional angles for 10d and ORTEP and unit cell drawings for 9g and 10d (64 pages); listings of structure factors for 9g and 10d (52 pages). Ordering information is given on any current masthead page.

Preparation and Reactivity of Mixed Benzylic 1,1-Dimetalloalkanes

Paul Knochel,* Ming Chang P. Yeh, and Chaodong Xiao

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109

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The carbometalation of (α -styryl)magnesium or -lithium organometallics with various allylic zinc bromides allows a general preparation of mixed benzylic 1,1-dimetalloalkanes in good to excellent yields. Their low reactivity can be increased by a transmetalation with copper cyanide leading to copper, zinc dimetallic reagents which are readily bis-allylated with allyl bromide or bis-stannylated with trimethyltin chloride. Transmetalation with 1 equiv of trimethyltin chloride in the absence of copper salts affords tin, zinc 1,1-dimetallo derivatives that can be cleanly oxidized by air to aromatic ketones under very mild conditions (-10 to 0 °C, 0.5-4 h). The monolithiation of the bis(trimethylstannyl) derivative 7 provides the α -lithiated benzylic tin compound 8 whose reactivity is also described.

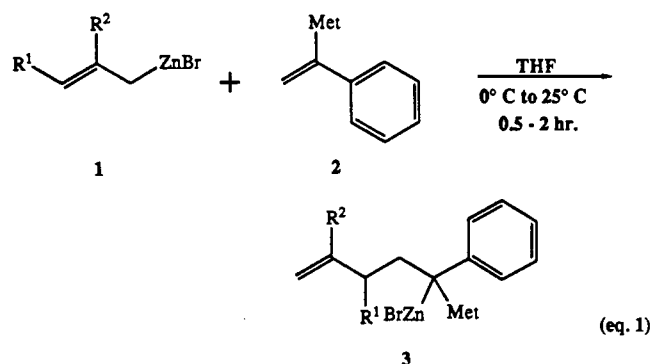
Introduction

The carbozincation of alkenylmagnesium^{1,2} and -lithium² organometallics is a unique approach to the preparation of mixed 1,1-dimetalloalkanes of magnesium (or lithium) and zinc. Since carbon-magnesium (or -lithium) and carbon-zinc bonds exhibit very different reactivities, these dimetallic reagents are able to react stepwise with two different electrophiles allowing the preparation of various classes of organic compounds.² Mixed benzylic 1,1-dimetalloalkanes are an unknown class of compounds,³ and we wish to report therein the first preparative access to these organometallics by performing a regioselective allylzincation of (α -styryl)lithium or (α -styryl)magnesium bromide. The characteristic aspects of their reactivity and some synthetic applications will be indicated.

Results and Discussion

The addition of a THF solution of an allylic zinc bromide 1 prepared in high yields from the corresponding allylic bromide and zinc⁴ (1.1 equiv, 1-1.5 M solution) at 0 °C to a THF solution of (α -styryl)magnesium bromide⁵ (1.0 equiv, 0.8-1.0 M solution) leads to the fast formation (1-2 h at 25 °C) of the benzylic 1-magnesium-1-zincaalkane 3 (eq 1 and Table I). Similarly, the addition of (α -styryl)lithium⁵ to allylzinc bromide affords the benzylic 1-lithia-1-

Table I. Benzylic Mixed 1,1-Dimetalloalkanes 3a-g Obtained by the Allylzincation of (α -Styryl)Lithium and -magnesium Bromide



Met: Li, MgBr

entry	Met	R ¹	R ²	product	yield, ^a %
1	Mg	H	H	3a	91 ^a
2	Li	H	H	3b	72 ^a
3	Mg	H	Me	3c	87 ^a
4	Mg	Me	H	3d	65 ^b
5	Mg	H	4-methyl-3-cyclohexen-1-yl	3e	57 ^b
6	Mg	H	CH ₃ OCH ₂ O	3f	89 ^c
7	Mg	H	Bu	3g	91 ^b

^a Yields of the isolated hydrolysis products of the 1,1-dimetalloalkanes 3. Satisfactory spectral data (IR, ¹H and ¹³C NMR, mass spectra) were obtained for all compounds. ^b Yield of the corresponding ketone obtained after oxidation of the 1,1-dimetalloalkane 3 (see text and Scheme III). ^c The product 3f was directly converted into 5-phenyl-2-pentanone (wet ether, 12 h) and isolated after flash chromatography as a pure compound in 89% yield.

zincaalkane 3b (see entry 2 of Table I) under even milder conditions (0 °C, 3 h). Although this addition is very fast, it is less efficient than the addition to (α -styryl)magnesium bromide (compare entries 1 and 2). Several allylic zinc

(1) (a) Gaudemar, M. C. R. *Seances Acad. Sci. Ser. C* 1971, 273, 1669. (b) Frangin, Y.; Gaudemar, M. C. R. *Seances Acad. Sci., Ser. C* 1974, 278, 885. (c) Bellasoued, M.; Frangin, Y.; Gaudemar, M. *Synthesis* 1977, 205.

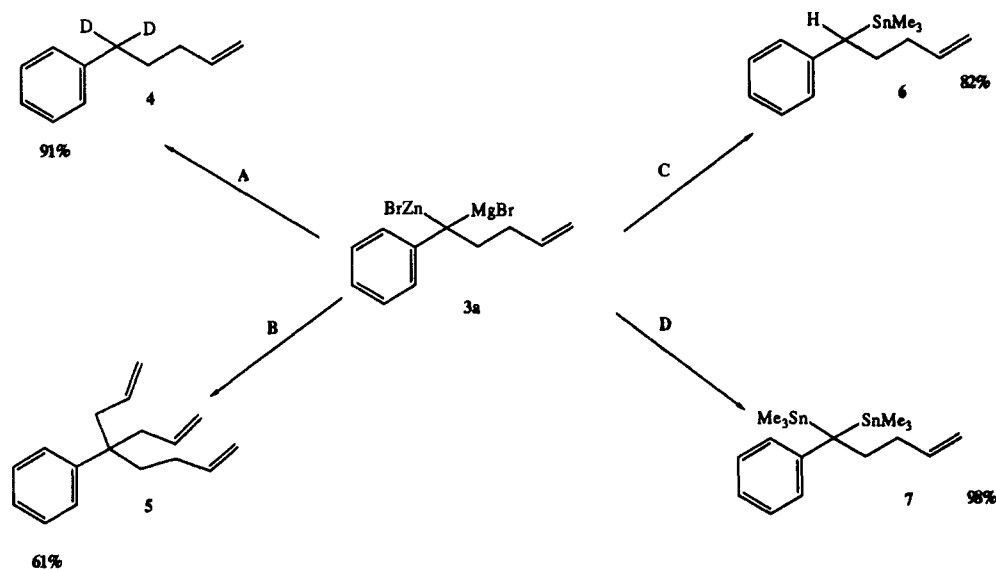
(2) Knochel, P.; Normant, J. F. *Tetrahedron Lett.* 1986, 27, 1039, 1043, 4427, 4431, 5727.

(3) (a) A benzylic disodium derivative was detected as an intermediate in the metalation of ethylbenzene see: Crimmins, T. F.; Rather, E. M. *J. Org. Chem.* 1978, 43, 2170. (b) For the synthesis of stabilized benzylic diorganometallics see: Hoberg, H.; Aznar, F. *J. Organomet. Chem.* 1980, 193, 155. (c) Klein, J.; Becker, J. Y. *J. Chem. Soc. Chem. Commun.* 1973, 576.

(4) Gaudemar, M. *Bull. Soc. Chim. Fr.* 1962, 974.

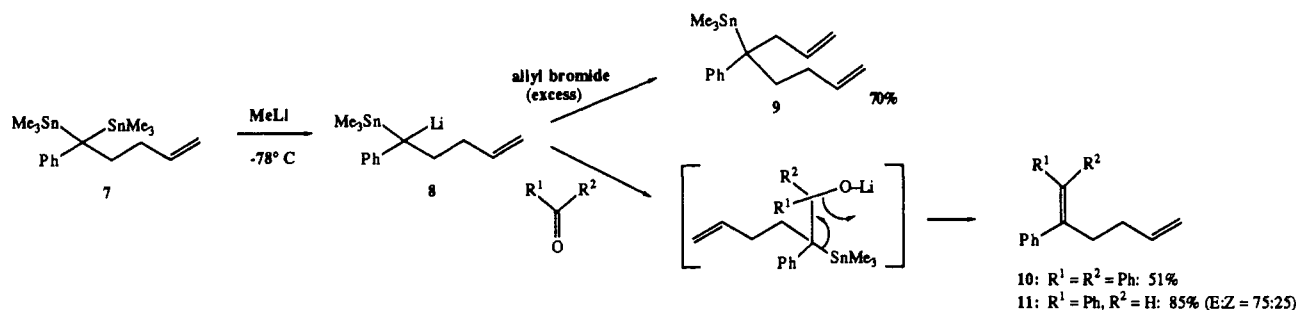
(5) Brandsma, L.; Verkruisje, H. *Preparative Polar Organometallic Chemistry*; Springer-Verlag: New York, 1987; Vol. 1, pp 72-73.

Scheme I



A: $D_2O/AcCl$, $-20^\circ C$ to $+25^\circ C$; B: $CuCN$ (1 eq.; $-20^\circ C$, 0.5 hr.) then excess of allylbromide;
 C: Me_3SnCl (1 eq.; $-40^\circ C$ to $0^\circ C$), then $AcOH$ (1 eq.; $-10^\circ C$ to $20^\circ C$); D: $CuCN$ (1 eq.,
 $-20^\circ C$, 0.5 hr.), then Me_3SnCl (2 eq. $-40^\circ C$ to $0^\circ C$);

Scheme II



bromides bearing substituents at the position 2 (entries 3, 5, 6, and 7, Table I) or at the position 3 (entry 4) undergo the carbometalation reaction and furnish the corresponding dimetalloalkanes in good yields. The reaction occurs with complete allylic rearrangement, so that the new carbon-carbon bond is formed from the most substituted end of the allylic system (entry 4). Of special interest is the new functionalized allylic zinc reagent 2-(methoxymethoxy)-2-propenylzinc bromide,⁶ since it allows a formal regioselective addition of an acetyl moiety across styrene. The initial adduct **3f** (entry 6) was hydrolyzed during the workup conditions to 5-phenyl-2-pentanone. The addition to substituted (α -styryl)magnesium bromides like (1-phenyl-1-pentenyl)magnesium bromide does not proceed even under forcing conditions (THF reflux, 5 h) probably because of steric effects resulting from the use of a bulky vinylic magnesium reagent.

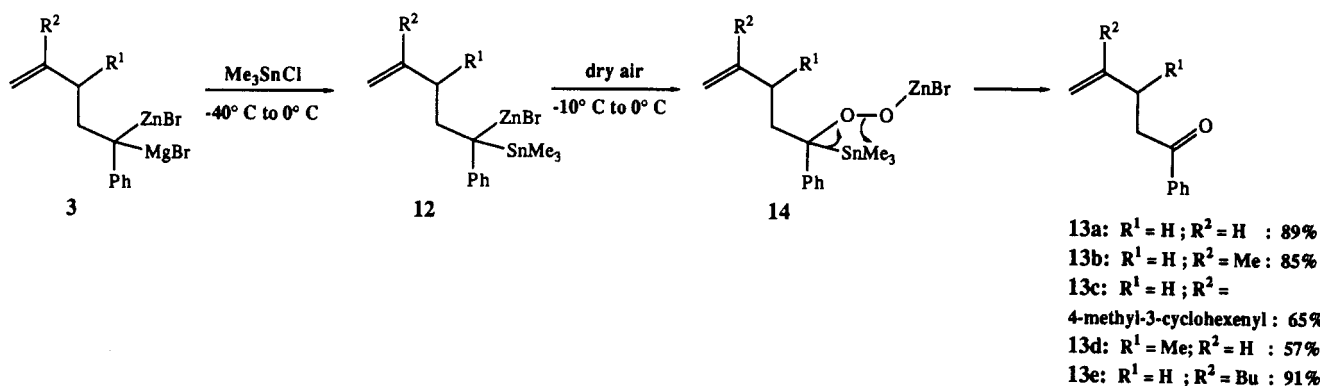
The deuterolysis of **3a** affords in 91% yield the di-deuterated product **4** with an almost complete incorpo-

ration (>99%) of deuterium at the benzylic positions (see Scheme I). The reactivity of benzylic dimetalloalkanes is strongly reduced compared to the aliphatic dimetalloalkanes.² For example, aldehydes (even in the presence of $BF_3 \cdot OEt_2$), alkylidene malonates, and acid chlorides do not react with benzylic dimetalloalkanes under our standard conditions² and lead to a mixture of products under more harsh conditions. Although **3a** does not react with allyl bromide, a transmetalation with $CuCN$ (1 equiv, $-20^\circ C$, 0.5 h) affords a green solution of the corresponding copper, zinc derivative which reacts rapidly with an excess of allyl bromide (-30 to $25^\circ C$) to afford the bis-allylated product **5** in 61% yield. The copper, zinc dimetallic reagent is first allylated leading to an intermediate zinc organometallic which after a transmetalation to the corresponding copper derivative is allylated again to afford the diene **5**. The benzylic dimetallic species **3a** reacts also readily with trimethyltin chloride and gives, after a careful protonation with stoichiometric amounts of acetic acid, the benzylic tin derivative **6** in 82% yield. Interestingly, the reaction of **3a** in the presence of $CuCN$ (1 equiv) with 2 equiv of trimethyltin chloride produces the benzylic distannane **7** in almost quantitative yield; see Scheme I. This 1,1-bis(trimethylstannyl) compound can be converted

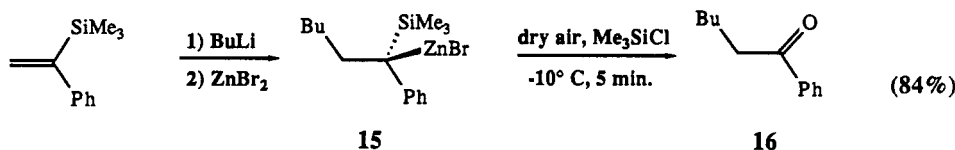
(6) For the preparation of 2-(methoxymethoxy)allyl chloride see: Gu, X.-P.; Okuhara, T.; Ikeda, I.; Okahara, M. *Synthesis* 1988, 535. The bromide was prepared by refluxing an acetone solution of 2-(methoxymethoxy)allyl chloride with $LiBr$ (2.5 equiv, 40% yield). The formation of the corresponding allylic zinc bromide has to be performed between -3 and $-6^\circ C$ by adding dropwise (1 drop each 15 s) a 1.5 M THF solution of 2-(methoxymethoxy)allyl bromide to Zn (3 equiv, 99.99% pure) previously activated with dibromoethane, see: Knochel, P.; Yeh, M. C. P.; Berk, S. C.; Talbert, J. *J. Org. Chem.* 1988, 53, 2390.

(7) Kauffmann, T. *Angew. Chem.* 1982, 94, 401; *Angew. Chem., Int. Ed. Engl.* 1982, 21, 410.

Scheme III



Scheme IV



into the α -lithiated benzylic stannane⁷ **8** which reacts with allyl bromide to afford the monoallylated benzylic tin derivative **9** (excess of allyl bromide, -78 to 25°C , 70% yield). The reaction of **8** with nonenolizable ketones or aldehydes such as benzophenone and benzaldehyde leads to the corresponding olefins **10** (51%) and **11** (85%), respectively (see Scheme II). An enolizable aldehyde like hexanal gives complex reaction mixtures.

Of special interest is the direct oxidation of the dimetallic reagents **3** with dry air.⁸ Thus a THF solution of **3** is first treated with 1 equiv of Me_3SnCl (-40 to 0°C , 15 min) furnishing a 1,1-dimetallic reagent of tin and zinc of type **12** (see Scheme III). The reaction flask is then connected to a balloon filled with dry air. The fast oxidation of **12** (30 min–4 h; -10 to 0°C) produces the aromatic ketones **13a–e** in fair to excellent yields. The reaction presumably proceeds through a zinc peroxide of type **14** that undergoes a rearrangement leading to the ketones **13**; see Scheme III. The rate of the reaction can be enhanced by the addition of Me_3SiCl (1.1–1.5 equiv) and retarded by the presence of cosolvents like DMF or Me_2S .

This oxidation can be extended to 1-(trimethylsilyl)-1-zincaalkanes. Thus the addition at -30°C of butyllithium (1.1 equiv) to a THF solution of 1-(trimethylsilyl)styrene,⁹ followed by the addition of zinc bromide (1 equiv) gives the dimetallic compound **15** which is oxidized readily by dry air (5 min; -10°C) affording 1-phenylhexanone **16** in 84% isolated yield; see Scheme IV.

Conclusion

The allylzincation of (α -styryl)magnesium bromide and (α -styryl)lithium allows an easy preparation of benzylic 1,1-dimetalloalkanes of type **3**. These organometallics, although less reactive than other 1,1-dimetalloalkanes of magnesium and zinc, display a reasonable reactivity after their transmetalation to the corresponding copper derivative. An especially mild air oxidation allows an efficient conversion of these dimetallic reagents directly to aromatic ketones.

Experimental Section

General Considerations. All reactions were carried out in an inert atmosphere (argon). Solvents (THF and ethyl ether) were dried and freshly distilled from sodium/benzophenone. Fourier transfer infrared spectra (FT-IR) were recorded under a nitrogen atmosphere on sodium chloride plates on a Nicolet 5 ZDX FT-IR spectrophotometer. Infrared frequencies are reported in wavenumber units (cm^{-1}). Broad absorption is described as b. Proton nuclear magnetic resonance spectra (^1H NMR) were recorded on a Bruker WM-300 (300 MHz) or Bruker WM-360 (360 MHz) nuclear magnetic resonance spectrometer. Chemical shifts are reported as δ in units of parts per million (ppm) relative to an internal standard of tetramethylsilane (0.00). Multiplicities are reported as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), bs (broad singlet), dd (doublet of doublet), etc. Coupling constant are reported in hertz (Hz). Carbon-13 nuclear magnetic resonance spectrometer (^{13}C NMR) were recorded on a Bruker WM-300 (75.5 MHz) or a Bruker WM-360 (90.5 MHz) nuclear magnetic resonance spectrometer. Chemical shifts are reported as δ in units of parts per million (ppm) relative to chloroform-*d* (δ 77.0) as an internal reference. Mass spectra (MS) and high-resolution mass spectra (HR-MS) were recorded on a VG-70-250 S mass spectrometer. The ionization methods used were desorption chemical ionization (DCI MS) and electron impact (EI MS). Spectra are reported in units of mass to charge.

General Procedure I. Formation of 1,1-Dimetalloalkanes. A THF solution of the allylic zinc bromide (1.2 equiv) was added dropwise at 0°C under argon to a THF solution of (α -styryl)magnesium bromide⁵ (1.0 equiv). The reaction mixture was warmed to 25°C and stirred for 1–2 h depending on the substrate. If (α -styryl)lithium is used instead of (α -styryl)magnesium bromide, the allylic zinc bromide solution was added at -40°C and the reaction was in this case complete after 2 h at 0°C . The completion of the addition was monitored by GLPC analysis of aliquots (quenching with saturated $\text{NH}_4\text{Cl}(\text{aq})$).

Hydrolysis of 1,1-Dimetalloalkanes. The reaction mixture was then cooled to 0°C and hydrolyzed by the addition of a solution of acetic acid (1.5 equiv) in THF followed by the addition of saturated $\text{NH}_4\text{Cl}(\text{aq})$. After dilution with ether, the ethereal solution was washed sequentially with saturated $\text{NH}_4\text{Cl}(\text{aq})$ and brine and dried over MgSO_4 . After evaporation of the solvent, the residue was purified by distillation or flash chromatography.

5-Phenyl-1-pentene¹⁰ (Hydrolysis of 3a). A THF solution of allylzinc bromide (18 mmol in 11 mL of THF) was mixed with a THF solution of (α -styryl)magnesium bromide (15 mmol), according to General Procedure I. The reaction was complete after

(8) Knochel, P.; Xiao, C.; Yeh, M. C. P. *Tetrahedron Lett.* 1988, 29, 6697.

(9) Reetz, M. T.; Schinzer, D. *Angew. Chem.* 1977, 89, 46; *Angew. Chem., Int. Ed. Engl.* 1977, 16, 44.

(10) Ferree, W., Jr.; Grutzner, J. B.; Morrison, H. J. *Am. Chem. Soc.* 1971, 93, 5502.

1 h at 25 °C and after workup afforded 1.98 g (13.56 mmol) of 5-phenyl-1-pentene (90%; bp 73–74 °C (10 mmHg)). ¹H NMR (CDCl₃, 300 MHz): δ 7.37 (m, 2 H), 7.24 (m, 3 H), 5.90 (m, 1 H), 5.07 (m, 1 H), 2.69 (t, 2 H), 2.16 (q, 2 H), 1.82 (m, 2 H).

2-Methyl-5-phenyl-1-pentene¹¹ (Hydrolysis of 3c). A THF solution of (2-methyl-2-propenyl)zinc bromide (15 mmol in 10 mL of THF) was mixed with (α-styryl)magnesium bromide⁵ (14 mmol in 14 mL of THF). The reaction was worked up after 1 h at 25 °C (see General Procedure I). The residue obtained after evaporation of the solvents was distilled under vacuum (107–109 °C, 9 mmHg) to afford 1.9 g (10.3 mmol) of 2-methyl-5-phenyl-1-pentene (88% yield). ¹H NMR (CDCl₃, 360 MHz): δ 7.26 (m), 7.18 (d, 3 H), 4.72 (s, 1 H), 4.69 (s, 1 H), 2.60 (t, 2 H), 2.08 (t, 2 H), 2.08 (t, 2 H), 1.78 (m, 2 H), 1.70 (s, 3 H).

5-Phenyl-2-pentanone¹² (Hydrolysis of 3f). A THF solution of (2-methoxymethoxy)-2-propenylzinc bromide (5.1 mmol) in 10 mL of THF was reacted with a THF solution of (α-styryl)magnesium bromide (4.6 mmol) in 5.4 mL of THF, according to General Procedure I and worked up after 0.5 h at 25 °C. Flash chromatography (hexane/ether, 20/1) of the residue gave 0.66 g (4.09 mmol, 89%) of 1-phenyl-4-pentanone. ¹H NMR (CDCl₃, 300 MHz): δ 7.25 (t, 2 H), 7.18 (t, 3 H), 2.62 (t, 2 H), 2.48 (t, 2 H), 2.1 (s, 3 H), 1.9 (m, 2 H). ¹³C NMR (CDCl₃, 75.5 MHz): δ 208.2, 141.4, 128.3, 128.2, 125.8, 42.6, 34.9, 29.8, 25.1.

5,5-Dideuterio-5-phenylpentene (4). A THF solution of allylzinc bromide (10.1 mL, 16.0 mmol) was reacted with a THF solution of (α-styryl)magnesium bromide (20 mL, 25 °C, 15 mmol), according to General Procedure I. After being stirred at 5 °C for 1 h, the reaction mixture was quenched with a mixture of 4 mL of D₂O and 1.42 mL (20 mmol) of acetyl chloride at 0 °C. The reaction mixture was allowed to stir at 23 °C for 0.5 h. After the usual workup, the residue was distilled (83–85 °C, 10 mmHg) to give 2.02 g (13.6 mmol, 91%) of 4. ¹H NMR (CDCl₃, 300 MHz): δ 7.3–7.1 (m, 5 H), 5.9–5.7 (m, 1 H), 5.0–4.9 (dd, 2 H), 2.1 (m, 2 H), 1.6 (t, 2 H). ¹³C NMR (CDCl₃, 75.5 MHz): δ 142.38, 138.55, 128.54, 128.29, 125.70, 114.65, 30.49, 26.72.

4-Allyl-4-phenyl-1,7-octadiene (5). Allylzinc bromide (16.5 mmol) in 9.7 mL of THF was reacted with (α-styryl)magnesium bromide (15 mmol), according to General Procedure I. The mixture was further diluted with 15 mL of THF and cooled to –78 °C. Copper cyanide (1.35 g, 15 mmol) was added to the reaction mixture. The reaction was allowed to stir at –20 °C for 30 min. Excess of allyl bromide (6 mL) was added to the reaction mixture at –40 °C. After being stirred at 0 °C for 0.5 h, the reaction mixture was diluted with 100 mL of hexane and worked up as usual. The residue obtained after evaporation of the solvents was purified by flash chromatography to give 2.19 g (9.7 mmol, 65%) of 5. IR (neat): 3088.2 (s), 2984.5 (m), 2928.3 (s), 2864.8 (w), 1648.3 (s), 1512.9 (m), 748.7 (s) cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): 7.38–7.20 (m, 5 H), 5.75 (m, 1 H), 5.55 (m, 2 H), 5.10–4.90 (m, 6 H), 2.47 (d, 4 H), 1.78 (m, 4 H). ¹³C NMR (CDCl₃, 75.5 MHz): δ 146.84, 139.81, 135.47, 128.92, 127.40, 126.50, 118.30, 114.24, 44.23, 42.51, 39.20, 28.31. MS (EI, 70 eV): 185 (M⁺ – C₃H₅, 42), 143 (52), 131 (22), 129 (41), 117 (53), 91 (100), 81 (28), 67 (10). Exact mass calculated for C₁₇H₂₂: 226.1723. Found: 226.1732.

5-(Trimethylstannyl)-5-phenyl-1-pentene (6). A THF solution of allylzinc bromide (15 mmol in 10 mL of THF) was reacted with (α-styryl)magnesium bromide (10 mmol, 1 N solution), according to General Procedure I. After 0.5 h at 25 °C, the reaction mixture was cooled to –45 °C and a solution of 2.09 g (10 mmol) of Me₃SnCl in 10 mL of THF was added. The reaction was allowed to stir 0.5 h at 0 °C and 0.5 h at 23 °C. After the reaction mixture was cooled back to –78 °C, 2 mL of acetic acid in 2 mL of THF was added. After the usual workup, the residue obtained after evaporation of the solvents was distilled (68–75 °C, 0.25 mmHg) to give 2.54 g (8.2 mmol, 82%) of 6. ¹H NMR (300 MHz, CDCl₃): δ 7.20 (m, 2 H), 7.00 (m, 3 H), 5.80 (m, 2 H), 4.47 (m, 2 H), 2.58 (m, 1 H), 2.12 (m, 2 H), 1.95 (m, 2 H), 0.00 (t, 9 H). ¹³C NMR (CDCl₃, 75.5 MHz): δ 146.15, 138.48, 128.29, 126.11, 125.96, 123.54, 114.96, 34.01, 33.91, 31.26, –10.48. MS (EI): 77 (5), 85 (10), 91 (15), 97 (2), 105 (20), 119 (20), 131 (8), 145 (65), 161 (100), 165 (90), 169 (20), 182 (15), 187 (25), 201 (75), 207 (5),

233 (15), 241 (1), 269 (15), 295 (100), 299 (20), 311 (MH⁺, 35). Exact mass calculated for C₁₄H₂₂¹²⁰SnH⁺: 311.0822. Found: 311.0817.

5,5-Bis(trimethylstannyl)-5-phenyl-1-pentene (7). A THF solution of allylzinc bromide (15 mmol in 20 mL) was reacted with (α-styryl)magnesium bromide (10 mmol, 1 N solution), according to General Procedure I. After 1 h at 25 °C, the reaction mixture was cooled to –40 °C and 0.89 g (10 mmol) of copper cyanide was added. The reaction was slowly warmed to –25 °C which led to the formation of a green solution. The reaction was cooled back to –40 °C, and 5.0 g (25 mmol) of Me₃SnCl was added. The reaction was stirred 0.5 h at 0 °C and then 0.5 h at 23 °C. After dilution with 200 mL of pentane, the reaction was worked up as usual. The distillation of the residue obtained after evaporation of the solvents gave 4.64 g (9.8 mmol) of 7 (bp 105–115 °C (0.25 mmHg)). IR (neat): 3086 (s), 2912 (s), 2848 (s), 2368 (w), 1640 (m), 1600 (s), 1496 (m), 1200 (s) cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): δ 7.12 (m, 2 H), 6.85 (m, 2 H), 5.78 (m, 1 H), 4.91 (m, 2 H), 2.20 (m, 2 H), 0.00 (m, 18 H). ¹³C NMR (CDCl₃, 75.5 MHz): δ 148.5, 138.33, 128.30, 128.25, 125.72, 122.15, 114.55, 33.49, 33.28, 31.43, –8.18. MS (EI): 39 (10), 77 (10), 91 (10), 103 (100), 117 (10), 135 (50), 143 (75), 165 (90), 191 (10), 253 (70), 279 (10), 294 (25), 308 (5), 457 (10), 472 (20). Exact mass calculated for C₁₇H₃₀¹¹⁸Sn¹²⁰Sn: 472.0386. Found: 472.0361.

5-(Trimethylstannyl)-5-phenyl-1,7-octadiene (9). To a solution of 2.37 g (5 mmol) of 7 in 10 mL of THF was added at –78 °C 6.9 mL (5.04 mmol) of MeLi in ether (0.73 N solution). After 0.5 h at –78 °C, 0.96 g (8 mmol) of allyl bromide was added. The reaction mixture was allowed to warm to 23 °C, stirred for 10 min, and worked up as usual. The distillation of the residue obtained after evaporation of the solvents affords 1.23 g (3.51 mmol) of 9 (bp 85–90 °C (0.15 mmHg)). IR (neat): 3088 (s), 2992 (s), 2920 (s), 2360 (w), 1640 (m), 1600 (m), 1504 (m), 1454 (m), 1200 (w) cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): δ 7.30–7.00 (m, 5 H), 6.82 (m, 1 H), 5.05 (m, 2 H), 2.83 (dd, 2 H), 2.00 (m, 2 H), 0.00 (s, 9 H). ¹³C NMR (CDCl₃, 75.5 MHz): δ 147.25, 138.91, 136.07, 128.21, 125.57, 123.76, 117.07, 114.25, 42.51, 40.13, 34.90, 29.01, –8.98. MS (EI): 41 (35), 55 (15), 67 (15), 77 (20), 81 (35), 91 (100), 103 (30), 117 (50), 129 (40), 143 (40), 150 (10), 165 (60), 185 (10), 335 (20), 350 (M⁺, 10), 457 (10). Exact mass calculated for C₁₇H₂₆¹²⁰Sn: 350.1057. Found: 350.1068.

1,1,2-Triphenyl-1,5-hexadiene (10). To a solution of 474 mg of 7 in 10 mL of THF was added at –78 °C 0.9 mL (1 mmol) of MeLi (1.4 N solution in ether). After 1 h at –78 °C, 182 mg (1 mmol) of benzophenone was added. The reaction was stirred for 48 h at 23 °C and afforded after the usual workup a crude oil that was purified by flash chromatography (solvent hexane/ethyl acetate) to give 0.16 g (0.51 mmol, 51% yield) of 10. IR (neat): 3072 (s), 3048 (s), 3008 (m), 2913 (m), 2352 (m), 2336 (m), 2256 (s), 1600 (m), 1512 (s), 1472 (s). ¹H NMR (CDCl₃, 300 MHz): δ 7.30–6.9 (m, 15 H), 5.75 (m, 1 H), 4.91 (q, 1 H), 4.87 (s, 1 H), 2.55 (t, 2 H), 2.08 (q, 2 H). ¹³C NMR (CDCl₃, 75.5 MHz): δ 143.25, 142.06, 140.02, 139.80, 138.19, 130.63, 129.60, 129.43, 128.1, 127.81, 126.62, 126.2, 114.50, 35.19, 32.89. MS (EI): 41 (80), 51 (15), 65 (10), 77 (17), 91 (85), 103 (5), 115 (15), 128 (5), 152 (15), 165 (40), 178 (20), 191 (100), 202 (7), 215 (5), 239 (7), 252 (10), 269 (4), 310 (M⁺, 20). Exact mass calculated for C₂₄H₂₂: 310.1722. Found: 310.1723.

(Z)- and (E)-1,2-Diphenyl-1,5-hexadiene (11). A solution of 5,5-bis(trimethylstannyl)-5-phenyl-1-pentene (7) (0.47 g, 1 mmol) in 5 mL of THF was added dropwise at –78 °C to a solution of MeLi (0.9 mL, 1.4 M) in ethyl ether. The solution was allowed to stir at –78 °C for 10 min, and then 0.11 g (1 mmol) of benzaldehyde in 1 mL of THF was added. After being stirred at 23 °C for 16 h, the solution was diluted with 100 mL of hexane. Flash chromatography (hexane/ethyl acetate, 30/1) of the residue, obtained after the usual workup, afforded 0.2 g (0.85 mmol, 85%) of compound 11 (E:Z = 75:25). IR (neat): 3072 (s), 3034 (s), 3008 (s), 2952 (m), 2895 (s), 2824 (w), 2232 (s), 1632 (s), 1571 (s), 1450 (s), 1440 (s) cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): δ 7.46–7.00 (m, 10 H), 6.70 (s, 0.77 H), 6.43 (s, 0.33 H), 5.70 (m, 1 H), 4.97 (q, 2 H), 2.82 (t, 1.54 H), 2.57 (t, 0.57 H), 2.20 (q, 2 H). ¹³C NMR (CDCl₃, 75.5 MHz): δ 142.4, 137.9, 128.95, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 127.1, 126.6, 126.5, 126.0, 114.6, 76.9, 76.5, 32.6, 29.5. MS (EI): 41 (90), 51 (20), 65 (15), 77 (25), 91 (50), 115 (100), 128 (10), 135 (5), 152 (10), 165 (25), 178 (30), 193 (50), 234 (M⁺, 20).

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Exact mass calculated for $C_{18}H_{18}$: 234.1049. Found: 234.1049.

General Procedure II. The Oxidation of Benzylic 1,1-Dimetalloalkanes. The reaction mixture obtained from the General Procedure I was diluted with 15 mL of THF and cooled to -20°C . Trimethyltin chloride (1.79 g, 9.0 mmol) in 5 mL of THF was added dropwise via syringe. After 15 min at 0°C , the reaction mixture was diluted with 10 mL of THF and 1.5 mL (16 mmol) of Me_2SiCl was added. The reaction was cooled to -10°C , and the argon inlet was replaced by a balloon filled with dry air. The oxidation (usually 1–4 h at -5°C) was monitored by quenching reaction aliquots with saturated $\text{NH}_4\text{Cl}(\text{aq})$ and analyzing them by GLPC. After completion of the reaction, it was worked up as in General Procedure I. (*Caution!* Although no incident occurred during the performance of these oxidations; the presence of peroxide should be checked, especially in large-scale experiments and a washing with aqueous sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) should be done during the workup.) The flash-chromatographical purification (solvent hexane/ether) of the residue obtained after evaporation of the solvents affords the analytically pure aromatic ketones **13a–e**.

1-Phenyl-4-penten-1-one (13a).¹³ The 1,1-dimetalloalkane **3a** prepared from 12 mmol of allylzinc bromide and 10 mmol of (α -styryl)magnesium bromide⁵ (see General Procedure I) was oxidized (see General Procedure II) with dry air (-5 – 0°C , 1 h) to afford after flash-chromatographical purification (solvent hexane/ether, 20:1) 1.42 g (8.9 mmol) of the ketone **13a** (89% yield). IR (neat): 3072 (w), 2987.0 (w), 2976.3 (w), 1686.7 (s), 1449.0 (s), 1207.0 (s) cm^{-1} . ^1H NMR (CDCl_3 , 360 MHz): δ 7.97 (m, 2 H), 7.55 (m, 1 H), 7.42 (m, 2 H), 5.90 (m, 1 H), 5.10 (d, 1 H), 5.00 (d, 1 H), 3.06 (t, 2 H), 2.50 (t, 2 H). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 199.13, 137.18, 136.85, 132.82, 128.44, 127.87, 115.12.

4-Methyl-1-phenyl-4-penten-1-one (13b). The 1,1-dimetalloalkane **3c** prepared from (2-methyl-2-propenyl)zinc bromide (19 mmol, 1.53 N solution) and (α -styryl)magnesium bromide (17 mmol, 1.0 N solution), according to the General Procedure I was oxidized (see General Procedure II) with dry air (-5°C , 0.5 h) to afford after flash-chromatographical purification (solvent hexane/ether, 20:1) 2.7 g (15.5 mmol) of the ketone **13b** (85% yield). IR (neat): 2960.0 (w), 2890.7 (w), 1687.0 (s), 1448.7 (s) cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz): δ 7.96 (m, 2 H), 7.58 (m, 1 H), 7.45 (m, 2 H), 4.76 (d, 2 H), 3.13 (t, 2 H), 2.47 (t, 2 H), 1.78 (s, 3 H). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 199.44, 144.3, 136.73, 132.64, 128.28, 127.73, 109.97, 36.56, 31.65, 22.46. MS (EI, 70 eV): 174 (M^+ , 2), 105 (100), 91 (6), 77 (78), 55 (11). Exact mass calculated for $\text{C}_{12}\text{H}_{14}\text{O}$: 174.105. Found: 174.106.

4-(4-Methylcyclohexen-3-yl)-1-phenyl-4-pentenone (13c). Limonene (4.36 g, 32 mmol) was added dropwise to a solution of 30 mL of *n*-BuLi (1.6 N in hexanes) and 5.5 g (48 mmol) of TMEDA¹⁴ at 23°C . After 5 h at this temperature, the reaction mixture was cooled to -78°C and a solution of 11.2 g (50 mmol) of ZnBr_2 in 30 mL of THF was added dropwise via cannulation. After addition, the reaction was warmed up to 0°C for 15 min and cooled back to -78°C . Then 8.05 g (50 mmol) of *N*-bromosuccinimide was added in small portions to the reaction mixture at -78°C . After being stirred at 23°C for 14 h, the reaction was worked up as usual (see General Procedure I). The residue was distilled under vacuum (76 – 78°C , 0.1 mmHg) to give 5.01 g (23 mmol) of the 3-bromo-2-(4-methylcyclohexen-3-yl)-1-propene (48% yield). The corresponding allylic zinc bromide was made under standard conditions.⁴ A solution of 6.37 g (29 mmol) of the allylic bromide in 20 mL of THF was slowly added at 15°C to a suspension of 3.0 g (47 mmol) of zinc cut foil. After addition, the reaction mixture was allowed to warm to 25°C . A complete conversion was observed after 2 h. The above prepared allylic zinc bromide (15 mmol) was mixed with 10 mmol of (α -styryl)magnesium bromide in 10 mL of THF. After 3 h at 35°C the maximum conversion was reached (see General Procedure I)

and the dimetallic reagent **3e** was oxidized according to General Procedure II (0 – 5°C , 4 h). The crude residue obtained after workup was purified by flash chromatography (solvent hexane/ethyl acetate, 20/1) to give 1.64 g (6.5 mmol) of the ketone **13c** (65% yield). IR (neat): 2961.5 (w), 2917.8 (s), 2855.7 (m), 1687.8 (s), 1642.2 (m), 1448.9 (s), 1205.2 (s) cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz): δ 7.97–7.95 (m, 2 H), 7.59–7.51 (m, 1 H), 7.48–7.40 (m, 2 H), 5.39 (s, 1 H), 4.82 (s, 1 H), 4.73 (s, 1 H), 3.13 (t, 2 H), 2.49 (t, 2 H), 2.15–1.49 (m, 10 H). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 198.5, 152.62, 136.6, 132.84, 132.32, 128, 127.6, 127.5, 120.27, 107.02, 39.72, 39.75, 38.47, 36.72, 30.96, 30.26, 28.5, 27.8, 23.0. MS (EI, 70 eV): 254 (M^+ , 2), 134 (79), 119 (25), 105 (100), 91 (13), 77 (52). Exact mass calculated for $\text{C}_{18}\text{H}_{20}\text{O}$: 254.167. Found: 254.165.

3-Methyl-1-phenyl-4-penten-1-one (13d).¹⁵ A THF solution of 2-butenylzinc bromide⁴ (13.5 mmol in 10 mL of THF) was heated with 11.3 mL of a THF solution of (α -styryl)magnesium bromide (10°C , 1.5 h) to provide the 1,1-dimetallic reagent **3d** (see General Procedure I) which was oxidized under our standard conditions (0°C , 2 h) (see General Procedure II) to provide after the usual workup a crude oil which was purified by flash chromatography (solvent hexane/ether, 20/1) to give 1.19 g (6.84 mmol) of the ketone **13d** (57% yield). ^1H NMR (CDCl_3 , 360 MHz): δ 7.93 (d, 2 H, $J = 7.3$ Hz), 7.55 (t, 1 H, $J = 7.0$ Hz), 7.45 (t, 2 H, $J = 7.4$ Hz), 5.85 (m, 1 H), 5.04 (d, 1 H, $J = 17.2$ Hz), 4.96 (d, 1 H, $J = 10.8$ Hz), 3.1 (m, 1 H), 2.92 (m, 2 H), 1.09 (d, 3 H, $J = 6.3$ Hz).

4-Butyl-1-phenyl-4-pentenone (13e). A THF solution of 2-butyl-2-propenylzinc bromide¹⁶ was mixed with 10 mL (10 mmol) of a THF solution of (α -styryl)magnesium bromide according to the General Procedure I to afford the 1,1-dimetallic reagent **3g** which was oxidized according to the General Procedure II (0°C , 2 h) to provide after a flash-chromatographical purification (solvent hexane/ethyl acetate, 30/1) 1.82 g (8.4 mmol) of the ketone **13e** (91% yield). IR (neat): 2957 (s), 2930 (s), 2872 (s), 2859 (s), 1688 (s), 1645 (m), 1598 (m), 1449 (w), 1024 (s) cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz): δ 7.96 (m, 2 H), 7.58 (m, 1 H), 7.45 (m, 2 H), 4.80 (s, 1 H), 4.75 (s, 1 H), 3.11 (t, 2 H), 2.42 (t, 2 H), 2.06 (t, 2 H), 1.45 (t, 2 H), 1.32 (tt, 2 H), 0.91 (t, 3 H). ^{13}C NMR (CDCl_3 , 300 MHz): δ 199.23, 148.53, 136.83, 132.65, 128.33, 127.78, 108.79, 36.77, 36.00, 29.97, 29.81, 22.26, 13.78. MS (EI, 70 eV): 216 (M^+ , 8), 120 (17), 105 (100), 96 (12), 77 (74), 55 (25). Exact mass calculated for $\text{C}_{16}\text{H}_{20}\text{O}$: 216.151. Found: 216.153.

1-Phenylpentanone (16).¹⁷ *n*-BuLi (7.05 mL, 1.56 N solution in hexanes) was added via syringe to a solution of 2.36 g (10 mmol) of α -styryltrimethylsilane⁹ in 20 mL of THF at -60°C . The reaction was allowed to stir at -30°C for 30 min. ZnBr_2 (2.5 g, 11 mmol) in 8 mL of THF was added to the reaction mixture. The reaction was warmed to -20°C , and 1.5 mL of $(\text{CH}_3)_2\text{SiCl}$ was added. The argon inlet was then replaced by a balloon filled with dry air. The oxidation was complete after 0.5 h at -20°C , and the reaction was worked up as usual to afford after a flash-chromatographical purification (hexane/ether, 19/1) 1.48 g (8.4 mmol) of the ketone **16** (84% yield). IR (neat): 3070 (w), 2988 (w), 2987.0 (w), 1687.0 (s), 1449.0 (s), 1205.0 (s) cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz): δ 7.97 (m, 2 H), 7.55 (m, 2 H), 2.95 (t, 2 H), 1.74 (m, 2 H), 1.38 (m, 4 H), 0.93 (t, 3 H).

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