Stereospecific Palladium-Catalyzed Coupling Reactions of Vinyl Iodides with Acetylenic Tin Reagents

J. K. Stille* and James H. Simpson

Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523. *Received September 10, 1986*

Abstract: The palladium-catalyzed coupling of alkenyl iodides with alkynylstannanes takes place under mild conditions, stereospecifically and chemoselectively, to give high yields of conjugated enynes. The reaction of (*E*)- or (*Z*)-vinyl iodides with alkynyltrimethylstannanes in the presence of catalytic amounts of bis(acetonitrile)(dichloro)palladium(II) is complete within a few minutes at 22 °C, providing geometrically pure products. The coupling reaction has been applied to the synthesis of a number of natural products, including insect pheremones possessing the enyne and diene structures.

Most aliphatic natural products contain one or more di- or trisubstituted double bonds,[1] often present in the 1,3-diene or 1,3-enyne array, with a specific double bond geometry being a requirement for biological activity. Conjugated enynes are widely distributed, being present, for example, in the sex pheremones of the family of Lepidoptera insects (e.g., (*Z*)-13-hexadec-11-yn-1-yl acetate[2]), in tropical poison frogs of the genus *Dendrobates* (e.g., histrionicotoxin,[3] which contains two terminal acetylenic units conjugated to a *Z* double bond), and in sea hares of the order Anaspidea (e.g., laurencin,[4] possessing a terminal acetylene attached to an *E* olefin). Among those natural products containing the 1,3-diene structure are the insect pheremones, which often contain an aldehyde, alcohol, or acetate function at the terminus of an unbranched carbon chain[5] and the array of products in the arachadonic cascade.

Thus it is not surprising that considerable effort has been expended in the stereospecific synthesis of such conjugated structures. Standard organic techniques lack the ability to form carbon–carbon bonds between unsaturated units; the difficulty of nucleophilic substitution at an sp^2 carbon atom can, however, be overcome by using transition metals.

Stereospecific dienes and enynes have been prepared through coupling reactions which use either vinyl halides or vinyl organometallic compounds. Although these methods have their own advantages, the scope of many of these reactions has still been limited by the nature of the organometallic involved or the procedure employed.[1,6] The cross-coupling reaction using vinyl borates requires strongly basic conditions, thus precluding the use of complex organic compounds containing reactive functionality or centers which could undergo isomerization. Vinyl cuprates formed from carbometalations are extremely sensitive to trace amounts of oxygen, are unstable above ~0 °C, and have to be converted to the zinc reagent before coupling will occur. The highly reducing property of aluminum reagents limits the use to unfunctionalized compounds; Grignard reagents also have this limitation. Monosubstituted acetylenes have been coupled with vinyl halides at 100 °C in the presence of a basic amine and palladium(II) catalyst; the stereochemistry and the scope of this reaction were not addressed, however. The mildest and most common procedure is the direct coupling of acetylenes with vinyl halides catalyzed by Pd/Cu(I). Conflicting reports on the stereochemical control of this procedure raises questions concerning its predictability.

A number of syntheses of pheremones containing the conjugated diene structure have been explored,[5b] the most straightforward of which are the direct coupling of two alkenyl units[7] and the stereospecific reduction of the triple bond of an enyne.[8] Because the enyne can be converted stereospecifically to the corresponding diene,[9] the direct, stereospecific coupling of an acetylenic group with a vinyl group emerges as a particularly attractive synthetic method.

The cross-coupling reaction of vinyl halides with acetylenic tin reagents offers a unique solution to the conjugated enyne construction. A wide variety of organic electrophiles undergo a palladium-catalyzed coupling with various organostannanes.[10] This reaction type tolerates sensitive functional groups on either coupling partner and gives high yields of coupled products under mild reaction conditions. The organotin reagent can be purified and, most importantly, organic groups on tin undergo the transmetalation reaction with palladium selectively, the acetylenic group having the fastest transfer rate of all the organic groups observed,[11] thereby entering into the coupling reaction.

$$RX + R'—\equiv—SnR_3'' \xrightarrow{Pd} R—\equiv—R' + XSnR_3'' \quad (1)$$

Alkynylstannanes readily undergo the palladium-catalyzed coupling with cyclic vinyl triflates in the presence of stoichiometric amounts of a halide salt.[12] However, to date there is no good method for the preparation of pure (*E*)- or (*Z*)-vinyl triflates from a convenient source such as aldehydes. Thus an effort was directed toward the coupling reactions of pure (*E*)- or (*Z*)-vinyl iodides with alkynylstannanes.

Results and Discussion

The synthesis of alkynylstannanes is straightforward. In this work, they were prepared both by the reaction of the lithium acetylide with trimethyl or tributyltin chloride (eq 2) and by the reaction of the terminal acetylene with (diethylamino)trimethylstannane (eq 3).[13] The synthesis of pure (*E*)- or (*Z*)-vinyl

$$R—\cdot\equiv\cdot + ClSnR_3' \rightarrow R—\cdot\equiv\cdot SnR_3' + Cl^- \quad (2)$$

$$R—\cdot\equiv\cdot—H + Et_2NSnMe_3 \rightarrow R—\cdot\equiv\cdot—SnMe_3 + Et_2NH \quad (3)$$

(1) Normant, J. F.; Alexakis, A. *Synthesis* **1981**, 841.
(2) Guerrero, A.; Camps, F.; Coll, J.; Riba, M.; Einhorn, J.; Descoins, Ch.; Lallemand, J. Y. *Tetrahedron Lett.* **1981**, *22*, 2013.
(3) (a) Witkop, B. *Experientia* **1971**, *27*, 1121. (b) Daly, J. W.; Karle, I.; Myers, W.; Tokuyama, T.; Waters, J. A.; Witkop, B. *Proc. Natl. Acad. Sci. U.S.A.* **1971**, *68*, 1870. (c) Tokuyama, T.; Uenoyama, K.; Brown, G.; Daly, J. W.; Witkop, B. *Helv. Chim. Acta* **1974**, *57*, 2597. (d) Karle, I. *J. Am. Chem. Soc.* **1973**, *95*, 4036.
(4) Irie, T.; Suzuki, M.; Masamune, T. *Tetrahedron* **1968**, *24*, 4193.
(5) (a) Gardette, M.; Jabri, N.; Alexakis, A.; Normant, J. F. *Tetrahedron* **1984**, *40*, 2741. (b) Mori, K. *The Total Synthesis of Natural Products*; ApSimon, J., Ed.; Wiley: New York, 1981.
(6) (a) Miyaura, N.; Yamada, K.; Suginome, H.; Suzuki, A. *J. Am. Chem. Soc.* **1985**, *107*, 972. (b) Miyaura, N.; Yamada, K.; Suzuki, A. *Tetrahedron Lett.* **1979**, 3437. (c) Dang, H. P.; Linstrumelle, G. *Tetrahedron Lett.* **1979**, 191. (d) Dieck, H. A.; Heck, F. R. *J. Organomet. Chem.* **1975**, *93*, 259. (e) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467.
(7) Cassani, G.; Massardo, P.; Piccardi, P. *Tetrahedron Lett.* **1979**, 633.
(8) Rossi, R.; Carpita, A.; Quirici, M. G.; Gaudenzi, M. L. *Tetrahedron* **1982**, *38*, 631.
(9) (a) Butenandt, A.; Hecker, E.; Hopp, M.; Koch, W. *Justus Liebigs Ann. Chem.* **1962**, *658*, 39. (b) Zweifel, G.; Polston, N. L. *J. Am. Chem. Soc.* **1970**, *92*, 4068. (c) Naf, F.; Decorzant, R.; Thommen, W.; Willhalm, B.; Ohloff, G. *Helv. Chim. Acta* **1975**, *58*, 1016.
(10) (a) Stille, J. K. *Angew Chem., Int. Ed. Engl.* **1986**, *25*, 508. (b) Stille, J. K. *Pure Appl. Chem.* **1985**, *57*, 1771.
(11) Labadie, J. W.; Stille, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 6129.
(12) (a) Scott, W. J.; Crip, G. T.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4630. (b) Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 3033.

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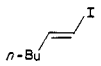
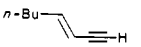
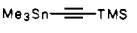
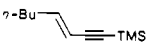
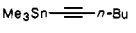
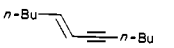
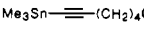
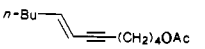
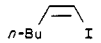
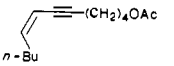
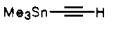
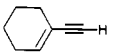
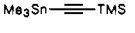
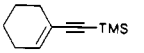
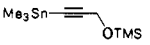
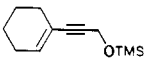
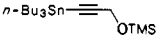
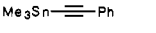
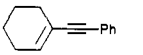
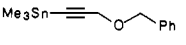
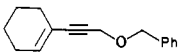
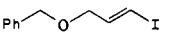
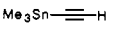
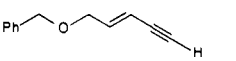
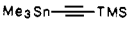
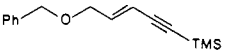
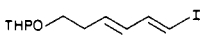
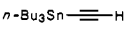
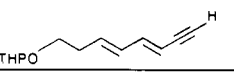
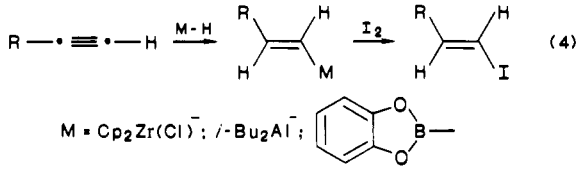
Table I. Vinyl Iodide/Alkynylstannane Coupling[a]

entry	vinyl iodide	alkynylstannane	catalyst[b]	solvent	T (°C)	t(h)	enyne	yield[c] (%)
1			La_4Pd	Et_2O	22–25	22		50[d]
2			L_4Pd	THF	50	24		78
3			L_2PdCl_2	THF	22–25	3		89
4			$(MeCN)_2PdCl_2$	DMF	−50	0.05		88
5			$(MeCN)_2PdCl_2$	DMF	22–25	<0.02		97
6			$(MeCN)_2PdCl_2$	DMF	22–25	1		91
7			L_4Pd	THF	22–25	15		39[e]
8			L_4Pd	THF	22–25	24		90[d]
9			L_4Pd	THF	22–25	3		96
10			L_2PdCl_2	THF	22–25	2		92
11			L_4Pd	THF	22–25	3		76
12			L_2PdCl_2	THF	50	10		67
13			L_4Pd	THF	22–25	10		90
14			L_2PdCl_2	THF	22–25	50		92
15			L_2PdCl_2	THF	22–25	18		91
16			L_4Pd	THF	22–25	24		59
17			L_4Pd	THF	22–25	24		85
18			$(MeCN)_2PdCl_2$	DMF	22–25	<0.02		68

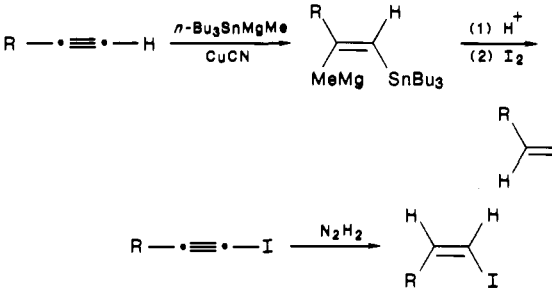
[a] Coupling reactions were carried out in solutions 0.1 M in vinyl iodide, usually with a slight excess (0.12 M) of the alkenylstannane and 1.0–5.0% catalyst (0.01–0.05 M) based on the vinyl iodide. [b] L = PPh_3. [c] Isolated yield. [d] NMR yield. [e] GC yield.

iodides is not as trivial; however, there are a number of methods by which this can be accomplished. In this effort, hydrometalation of a terminal acetylene followed by the stereospecific electrophilic substitution of the metal atom with iodine[14] was utilized extensively. The applicability of this general method is often limited by the inability of the metal reagent or the product vinyl metal to tolerate certain functional groups on the acetylene. Thus the hydrozirconation,[15] hydroalumination,[16] or hydroboration[17] reactions of terminal acetylenes followed by cleavage of the metal–carbon bond by iodine were the methods of choice for the generation of pure (*E*)-vinyl iodides (eq 4). Alternatively, the



(4)

addition of tributylstannylmagnesium methyl followed by protonation of the magnesium–carbon bond and then iodination of the tin–carbon bond (both with retention, eq 5) was used.[18] Pure (*Z*)-vinyl iodides were obtained by the diimide reduction of acetylenic iodides (eq 6).[19] The stereospecific syntheses of various



(5)

(6)

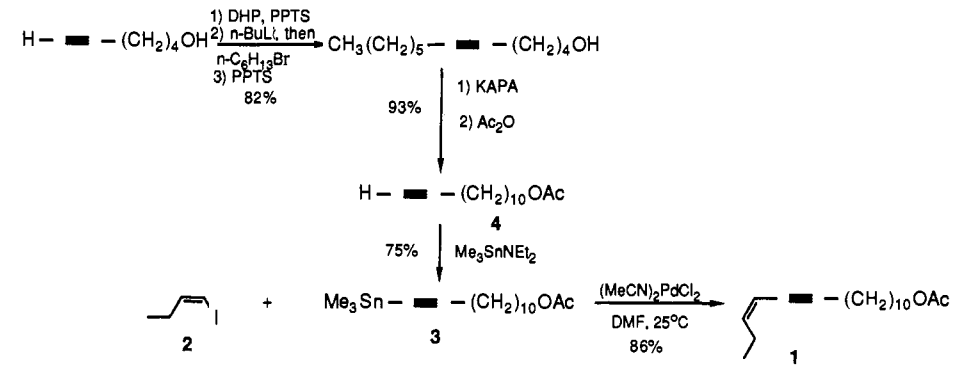
(*E*)- and (*Z*)-vinyl iodides (detailed in the Experimental Section) will be discussed only when a specific methodology is key to the synthesis of a desired product.

Coupling Reactions. The palladium-catalyzed coupling reaction of vinyl iodides with acetylenic tin reagents takes place under mild reaction conditions to give high yields of enynes (Table I); no reaction occurs in the absence of the palladium catalyst. The reactions were monitored for the disappearance of vinyl iodide by GLC or TLC, and in most examples the reactions appeared to be complete. However, in certain reactions isolation of the pure product, free of solvent, was difficult.

Terminal enynes could be prepared by this procedure (Table I, entries 1, 8, 16, and 18). The coupling of vinyl iodides with trimethyl[(trimethylstannyl)ethynyl]silane (entries 2, 3, 9, and

(13) Jones, K.; Lappert, M. F. *J. Organomet. Chem.* **1965**, *3*, 295.
(14) Jung, M. E.; Light, L. A. *Tetrahedron Lett.* **1982**, *23*, 3851.
(15) Schwartz, J. *J. Organomet. Chem. Lib. 1* **1977**, 468.
(16) Zweifel, G.; Whitney, C. C. *J. Am. Chem. Soc.* **1967**, *89*, 2753.
(17) Brown, H. C.; Hamaoka, T.; Ravindran, N. *J. Am. Chem. Soc.* **1973**, *95*, 5786.
(18) Hibino, J.; Matsubara, S.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1984**, *25*, 2151.
(19) Dieck, H. A.; Heck, F. R. *J. Org. Chem.* **1975**, *40*, 1083.

Scheme I



17) gave the trimethylsilyl protected enyne in high isolated yields, demonstrating the selectivity of the transmetalation reaction of tin as opposed to silicon. Both cyclic and linear vinyl iodides undergo the coupling reaction, the best yields of product from cyclic iodides being obtained under the milder (22–25 °C) reaction conditions made possible by the use of alkynyltrimethylstannanes (vide infra). Certain palladium-catalyzed cross coupling reactions do not proceed readily with linear vinyl iodides to give high yields of products.[20]

Two types of acetylenic tin reagents, tributyl or trimethyl, were used. The trimethyl tin reagents have the advantage that they are more reactive, and the byproduct of the coupling, trimethyltin iodide, is water soluble and, therefore, can be removed easily from the coupled product. They are, however, unstable relative to the tributyl analogue and cannot be stored for long periods or readily purified by silica chromatography. Usually, the trimethyltin reagents were prepared just prior to their use. In many examples, they are not stable enough such that satisfactory elemental analyses can be obtained. Their greater reactivity is demonstrated by a comparison of entries 10 (22–25 °C, 2 h, 92% yield) and 12 (50 °C, 10 h, 67% yield) in which the same catalyst and solvent were used. The tributyltin reagents are more stable and, therefore, can be purified and stored. In addition they are less toxic. Removal of the byproduct tributyltin iodide requires an aqueous potassium fluoride wash, producing insoluble tributyltin fluoride. Only about 90% of the tributyltin byproduct was removed by this procedure, and further purification by chromatography was necessary.

The rate of the coupling reaction and/or the reaction temperature was very sensitive to the catalyst. Higher ratios of phosphine ligand to palladium slowed the reaction, as expected, and generally higher temperatures were required to achieve the same yields of products. Thus higher temperatures and/or longer reaction times were required for tetrakis(triphenylphosphine)-palladium than bis(triphenylphosphine)dichloropalladium, which is reduced under the reaction conditions to the 14-electron complex, bis(triphenylphosphine)palladium (compare entries 2 with 3 and 10 with 11). The use of bis(acetonitrile)dichloropalladium[21] in the weakly coordinating solvent, DMF, produced the most active palladium catalyst which gave high yields of coupled product instantaneously at ambient temperatures and allowed the coupling reaction to proceed within 3 min, even at −50 °C (entries 4–6 and 18). The difference in the catalytic activity shown by bis(acetonitrile)dichloropalladium and tetrakis(triphenylphosphine)-palladium is emphasized in the coupling reactions with (*Z*)-1-iodo-1-hexene (entries 6 and 7) in which the steric bulk presented by the ligands on palladium plays an important role in the oxidative addition, the transmetalation or both.

Most importantly, the coupling reaction proceeds stereospecifically with retention of the double bond geometry of the vinyl iodide in the coupled product. This was achieved only when relatively mild reaction conditions and/or short reaction times were possible. For example, when the reactants in entry 3 were coupled utilizing tetrakis(triphenylphosphine)palladium, a mixture of isomers was obtained, even at 22–25 °C, because of the long reaction times required for completion. Although both the oxidative addition[22] and reductive elimination[23] steps proceed with retention of geometry, the product slowly isomerizes under the reaction conditions. By combining ^1H and ^{13}C NMR as well as GLC, the stereoisomeric purity of the products (e.g., entries 5 and 6) could be determined to be ≥97%. Thus this coupling provides a stereospecific high yield synthesis of 1,3-enynes, and the chemoselectivity of the reaction allows the presence of a wide variety of other functional groups on either coupling partner.

Application to the Synthesis of Natural Products. Among the aliphatic natural products that contain one or more di- or trisubstituted double bonds are the insect sex pheremones. The simplicity of many of these pheremones is striking. Although they contain conventional elaborations of the normal straight chain fatty acids, the double bond geometry is critical, and in many cases a content of 1% or less of the wrong isomer acts as an inhibitor of the biological activity.[24]

The sex pheremone of the processionary moth (*Thaumetopoea pityocampa*), a defoliator of pine trees in Mediterranean countries,[2] is (*Z*)-13-hexadec-11-yn-1-yl acetate (**1**) (Scheme I). Its synthesis required the availability of pure (*Z*)-1-iodo-1-butene (**2**) and 12-trimethylstannyl-11-dodecyn-1-yl acetate (**3**) as coupling partners. The (*Z*)-vinyl iodide was readily obtained isomerically pure by the reduction of 1-iodo-1-butyne with diimide, generated in situ from dipotassium azodicarboxylate with methanolic acetic acid. The overreduction product, 1-iodobutane, was removed by treatment with butylamine.

Pure 11-dodecyn-1-yl acetate (**4**) was prepared from 5-hexyn-1-ol by its homologation to a 12 carbon unit with 1-bromohexane followed by isomerization ("zipper reaction") of the acetylenic unit to a terminal position with the potassium salt of 1,3-diaminopropane (KAPA).[25] Acylation followed by the reaction of the acetylene with exactly 1 equiv of (diethylamino)-trimethylstannane gave **3**.

The coupling reaction of iodide **2** with the acetylenic tin reagent **3** in the presence of bis(acetonitrile)dichloropalladium in DMF at ambient temperature gave the isomerically pure coupled product **1** in 86% yield, identical with the natural compound.[26] The synthesis of **1** has been reported[27] via the coupling of 11-dodecyn-1-ol with a molar excess of (*Z*)-1-iodo-1-butene under phase-transfer conditions in the presence of a large excess of sodium hydroxide and a catalyst, tetrakis(triphenylphosphine)-palladium/cuprous iodide.

Crysanthemum macrotum (Dur.) Ball. contains (3*E*,5*E*)-8-(2-thienyl)-3,5-octadien-7-yn-1-ol (**5**), one of four acetylenic compounds isolated, and a potential natural insecticide.[28] The

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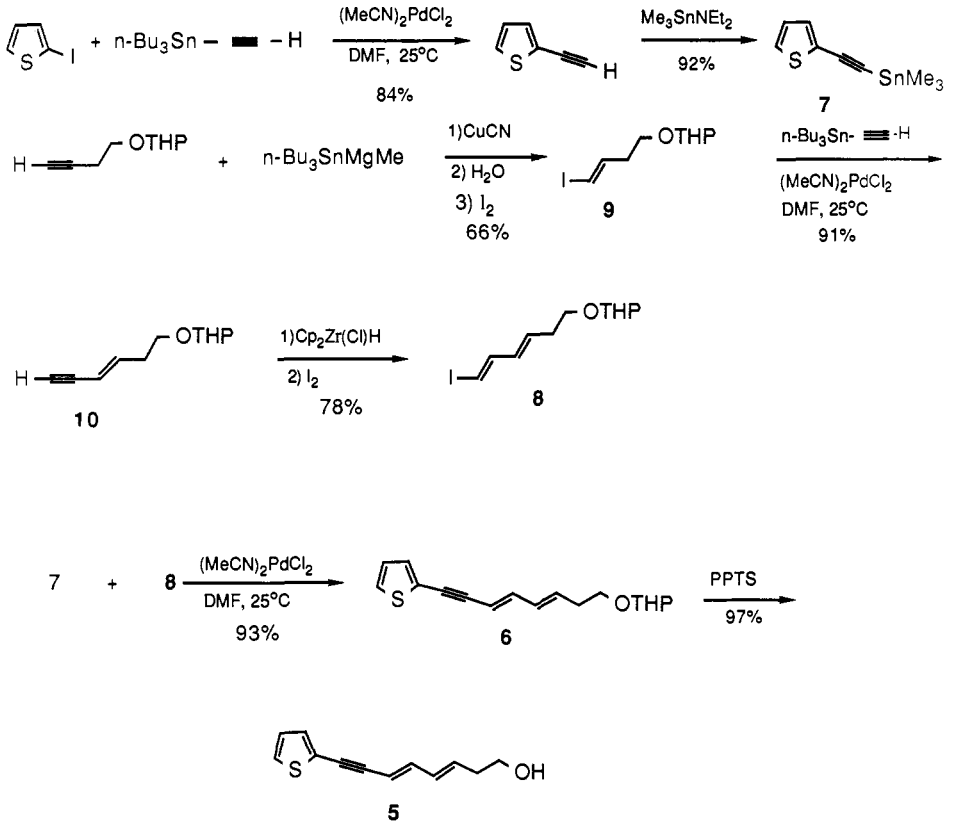
(28) Bohlmann, F.; Zdero, C. *Chem. Ber.* **1975**, *108*, 739.

Scheme II



stereospecific synthesis of **5** (Scheme II) depended on the coupling of the organostannane, 2-(2-thienyl)-1-trimethylstannylethyne (**7**) and (3*E*,5*E*)-tetrahydro-2-[(6-iodo-3,5-hexadienyl)oxy]-2*H*-pyran (**8**).

Synthesis of the tin reagent **7** was accomplished by first joining the acetylenic unit to thiophene by the palladium-catalyzed coupling of 2-iodothiophene with ethynyltributylstannane. The reaction of the resulting 2-ethynylthiophene with (diethylamino)trimethylstannane to yield **7** was carried out just prior to its use in the coupling reaction. The key (*E*,*E*)-diene unit was prepared by a stereospecific metalation and a two carbon homologation followed by another stereospecific hydrometalation. The addition of tributylstannylmagnesium methyl across the terminal alkyne of THP-protected 3-butyn-1-ol followed by protonation and cleavage of the intermediate vinylstannane[29] with iodine provided isomerically pure (*E*)-vinyl iodide **9**. This iodide was converted to enyne **10** in 91% yield by the palladium-catalyzed coupling with ethynyltributylstannane. Hydrometalation of **10** with tributylstannylmagnesium methyl followed by cleavage with iodine did not yield isomerically pure **8**. Hydrozirconation of **10** with zirconocene hydrochloride[30] followed by cleavage with iodine gave pure (*E*,*E*)-**8**, contaminated with some of the terminal diene, (3*E*)-tetrahydro-2-[(3,5-hexadienyl)oxy]-2*H*-pyran. Attempts to remove this olefin by chromatography on silica gel resulted in isomerization of the (*E*)-vinyl iodide **8**.

The key coupling reaction of **7** with **8** to yield isomercially pure dienyne **6** was effected in 93% yield with the bis(acetonitrile)-dichloropalladium catalyst. Purification by silica gel chromatography at this stage separated out the olefin contaminant without loss of stereochemistry in the diene unit. The THP ether was subsequently hydrolyzed under mild conditions to give stereochemically pure **5**.

This sequence of reactions not only constitutes an efficient synthesis of **5** but also represents a method of constructing isomerically pure conjugated dienynes. In three recent reports, for example, on the total synthesis of the products lipoxin A,[31] lipoxin B,[32] and kijanimicin,[33] in which the synthesis of a dienyne unit was required, in no case was this conjugated system obtained stereoisomerically pure.

The sex pheremone of the forest tent caterpillar, *Malacosoma disstria*,[26] a defoliator of the trembling aspen tree, is (5*Z*,7*E*)-5,7-dodecadien-1-ol (**11**);[34] that of the pine moth, *Dendrolimus spectrobilis* is (5*E*,7*Z*)-5,7-dodecadien-1-ol (**15**).[35] These two pheremones are interesting targets for the coupling of a vinyl iodide with an acetylenic tin reagent, because they are identical, with the exception that the geometries of the two double bonds have been transposed. In addition, their synthesis requires a stereospecific reduction of the acetylenic group of the enyne coupled product.

Synthesis of the sex pheremone of the forest tent caterpillar **11** required vinyl iodide **13**, (*E*)-1-iodo-1-hexene, and the acetylenic tin reagent **14**, trimethyl[6-(tetrahydro-2*H*-pyran-2-yl)oxy-1-hexynyl]stannane as coupling partners (Scheme III). Vinyl iodide **13** was prepared isomerically pure, as reported[16] by the hydroaluminations of 1-hexyne, followed by cleavage of the aluminum–carbon bond with iodine. Alkynylstannane **14** was prepared in an overall 77% yield starting from 5-hexyn-1-ol.

The coupling of **13** with **14** was carried out by using bis(acetonitrile)dichloropalladium to give a 91% yield of the (*E*)-1,3-enyne **12**. Stereospecific cis reduction of the acetylenic unit was accomplished with disiamylborane[34] and mild hydrolysis of the protecting group gave pure **11**. The catalytic hydrogenation of **12** with palladium(II)–nickel[36] gave a mixture of unreacted enyne, the diene and over-reduced product. This is somewhat surprising since this type of reduction has been reported to proceed stereo-

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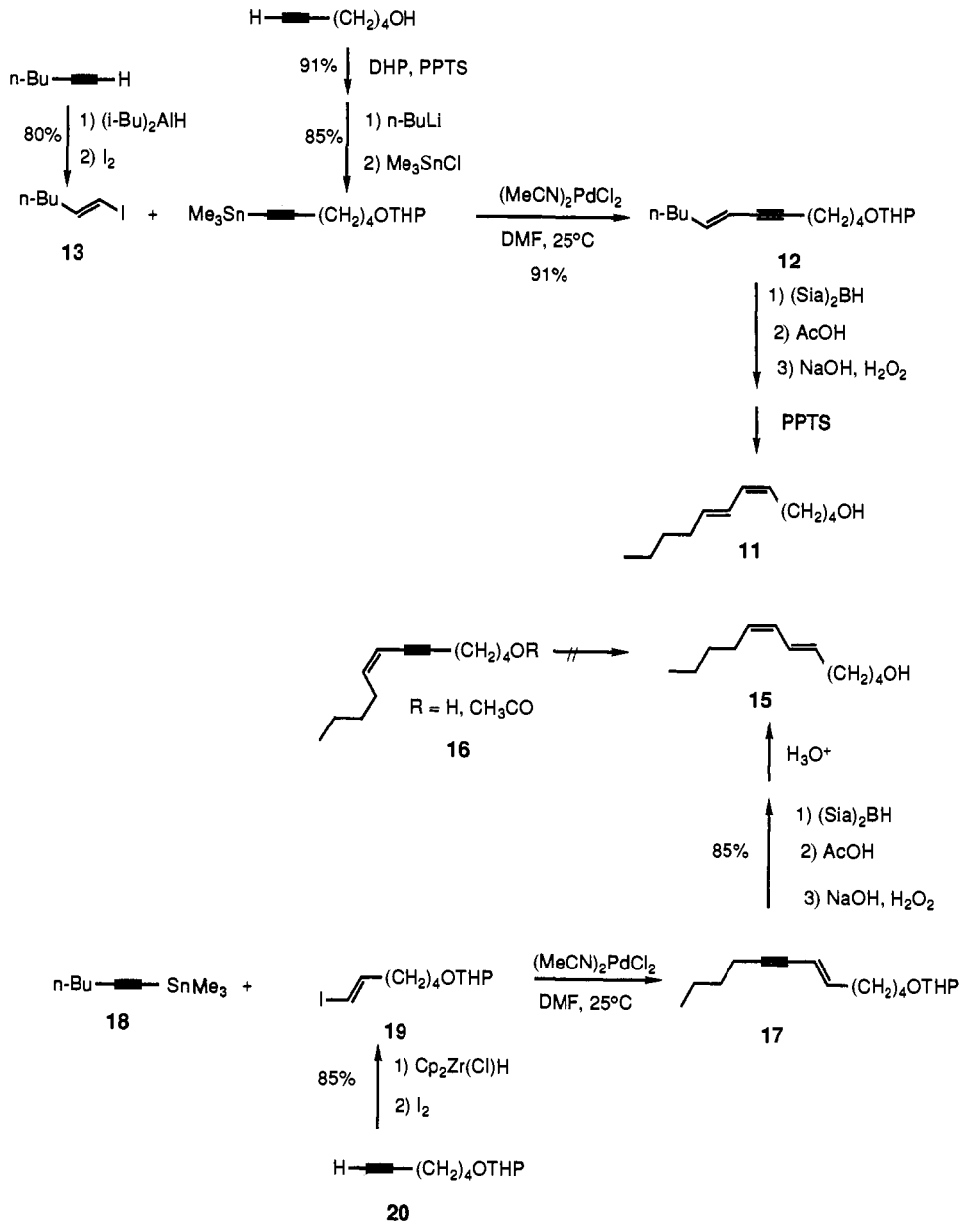
Scheme III



specifically without over-reduction.

The synthesis of (5*Z*,7*E*)-5,7-dodecadien-1-ol (**11**) has been effected[27] by a scheme similar, in part, to that reported here, the critical coupling reaction involving 5-hexyn-1-ol and **13** under phase-transfer conditions in the presence of 2.5 N sodium hydroxide, catalyzed by palladium in the presence of cuprous iodide.

Presumably, the synthesis of the pine moth pheremone (**15**, Scheme III) could be achieved by the stereospecific trans reduction of (*Z*)-7-dodec-en-5-yn-1-ol (**16**) or a derivative thereof, such as the acetate (Table I, entry 6). Although lithium aluminum hydride reduces alkynyl alcohols to *E* olefins under rather vigorous conditions, conjugated dienes are reduced to monoolefins.[37] Thus, it is not surprising that reduction of the acetate either gave monoolefin or mixtures of products (under less vigorous conditions). Dissolving metal reductions[38] also gave over-reduced product.

As a result, the coupling reaction was approached by using hexynyltrimethylstannane, obtained by the reaction of 1-hexyne with (diethylamino)trimethylstannane and (*E*)-tetrahydro-2-[(6-iodo-5-hexenyl)oxy]-2*H*-pyran (**19**) and prepared by the hydrozirconation/iodination of the THP-protected acetylenic alcohol **20**. Enyne **17** was obtained in a 95% yield by the coupling procedure, and the reduction of the acetylenic group to the *Z* olefin was accomplished by hydroboration.

The sex attractant of the virgin female silkworm moth, *Bombyx mori*, (10*E*,12*Z*)-10,12-hexadecadien-1-ol (bombykol, **21**) has only recently been synthesized in geometrically pure form.[39] Two routes to **21** were envisioned, one utilizing a coupling reaction to yield a (*Z*)-12-en-10-yne **22** and the other, a coupling to give the (*E*)-10-en-12-yne **25**.

The former pathway (Scheme IV) required the synthesis of tetrahydro-2-[(10-undecynyl)oxy]-2*H*-pyran (**25**) and its conversion to tin reagent **23** for coupling with pure (*Z*)-1-iodo-1-pentene (**24**). Alkylation of 1-nonyne with ethylene oxides gave 3-undecyn-1-ol, which was converted to the terminal alkyne by the "zipper" reaction.[40] Protection of the alcohol followed by reaction with (diethylamino)trimethylstannane gave acetylenic reagent **23**. The (*Z*)-vinyl iodide was obtained by reduction of the acetylenic iodide with diimide.[19] The coupling of **23** with **24** gave isomerically pure **22**, but the selective trans reduction of the

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(38) (a) Warthen, D.; Jacobson, J. *J. Med. Chem.* **1967**, *10*, 1190. (b) Dear, R. E. A.; Pattison, F. L. M. *J. Am. Chem. Soc.* **1962**, *85*, 622. (c) Caine, D. *Org. React.* **1976**, *23*, 1.

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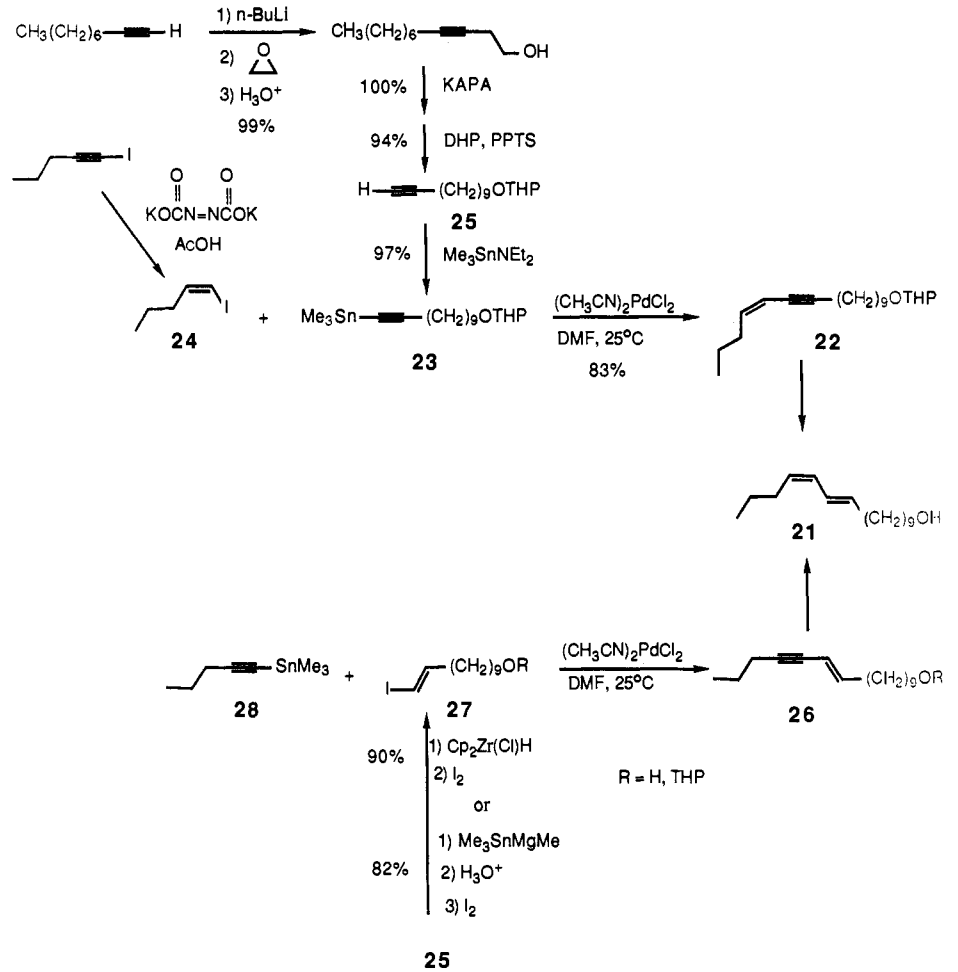
Scheme IV



acetylenic group could not be accomplished.

An alternative pathway (Scheme IV) necessitated (*E*)-11-iodo-10-undecen-1-ol (**27**) and pentynyltrimethylstannane (**28**) as coupling partners for the synthesis of **26**. Both the hydrozirconation[35] and tributylstannylmagnesium methyl[18] procedures were utilized in the preparation of pure **26** from THP-protected 10-undecynol **25**, with the hydrozirconation method giving slightly better yields. The coupling reaction of **27** with **28** provided a high yield of isomerically pure **25**, which has been converted to bombykol (**21**) by a cis reduction of the acetylene.[41] This palladium-catalyzed coupling reaction of vinyl iodides with acetylenic tin reagents illustrates that stereospecific construction of the enyne unit can be effected in high yield. The mild conditions are tolerant of ester, alcohol, and alcohol functions protected by benzyl, trimethylsilyl, and tetrahydropyranyl groups. Furthermore, the conjugated acetylenic group can be stereospecifically reduced to a *Z* olefin, thereby providing a facile route to conjugated *Z,E* or *Z,Z* dienes.

Experimental Section

Starting materials were obtained either from Aldrich Chemicals or from other commercial suppliers, as identified in the experimental procedures. Solvents were purified as follows: benzene, diethyl ether (ether), and tetrahydrofuran (THF), by distillation from benzophenone ketyl under nitrogen; hexanes and ethyl acetate by distillation; methylene chloride, *N,N*-dimethylformamide (DMF), hexamethylphosphoramide (HMPA), pentane, trimethylamine, 1,3-diaminopropane, and diglyme by distillation from calcium hydride.

All melting points and boiling points are uncorrected. Atmospheric boiling points recorded at Colorado State University are uncorrected for the altitude, approximately 640 mmHg. Boiling points recorded from bulb-to-bulb distillations are the temperatures of the air bath in the Kugelrohr apparatus. ^{1}H NMR spectra were recorded at 270 MHz by using an IBM WP-270 spectrometer. Chemical shifts are in parts per million downfield from internal tetramethylsilane (0.00 ppm). When specifically noted, chloroform (7.24 ppm) was used as the internal standard. Coupling constants are given in hertz. ^{13}C NMR spectra were recorded at 68 MHz by using an IBM WP-270 spectrometer, with deuteriochloroform (77.060 ppm) as the internal standard. Infrared spectra were recorded on a Beckman Model 4240 grating spectrophotometer. Low resolution mass spectra were obtained on a VG Micromass 16F spectrometer. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA.

All reactions described were carried out under an atmosphere of nitrogen or argon. Unless otherwise indicated, all yields reported are isolated yields of material judged homogeneous by thin-layer chromatography (TLC) or gas-liquid chromatography (GLC) and NMR spectroscopy. [Compounds prepared stereospecifically showed a high stereoisomeric purity (>98%) as checked by ^{1}H and ^{13}C NMR spectra and capillary glass chromatography.] TLC was performed on Merck 0.25-mm glass silica gel plates; visualization of developed plates was by fluorescence and staining with phosphomolybdic acid. Column chromatography was performed by using Merck silica gel 60 (60–200 mesh). Medium-pressure liquid chromatography (MPLC) was performed with an ISCO Model UA-5 absorbance/fluorescence monitor equipped with a Type 6 optical unit and a Model 1133 multiplexersampler. Universal Adsorbents silica gel 32–63, using Michel–Miller columns, were used for MPLC. Radial chromatography was carried out with a Harrison Chromatotron (Harrison Research Co.) on 1-, 2-, or 4-mm silica gel plates (Merck silica gel 60 for TLC) at a flow rate of 5 mL per min. GLC analyses were carried out on a Varian Model 3700 gas chromatography by using several different types of columns. The specific column used has been given an abbreviated identification, included in parentheses following the column's description and again where it is used in the experimental text: SE-30 packed glass capillary column (50 m length × 0.25 mm i.d.) (SE-30, FID); DB1 fused silica capillary column (30 m length × 0.25 mm i.d.) (DB1, FID), OV-17 packed column (6 ft. length × $^1/_8$ in. o.d.) (OV-17, TCD), SE-30 packed column (6 ft. length × $^1/_8$ in. o.d.) (SE-30, TCD) with helium as the carrier gas.

The palladium catalysts were prepared by literature procedures: (dichloro)bis(acetonitrile)palladium(II),[42] (dichloro)bis(triphenyl-

(41) Schlenk, H. *J. Am. Oil Chem. Soc.* **1961**, *38*, 733.

phosphine)palladium(II),[43] and tetrakis(triphenylphosphine)palladium-(0).[44]

Table I. Vinyl Iodide/Alkynylstannane Coupling. The preparation of the vinyl iodides and alkynylstannanes as well as a description of the procedures for the coupling reactions and the isolation and characterization of the coupling products are described in the following section.

(*E*)-1-Iodo-1-hexene (13). This compound was prepared by a modification of the reported procedure.[16] To a solution of 9.78 g (119 mmol) of 1-hexyne in 30 mL of dry hexane was added 119 mL (119 mmol, 1.0 M) of diisobutylaluminum hydride while maintaining the temperature below −40 °C. The reaction mixture was heated for 4 h at 50 °C, after the addition was complete, and the initial exothermic reaction had subsided. This mixture was then cooled to −40 °C, and 30.2 g (119 mmol) of iodine dissolved in 60 mL of dry THF was added dropwise at such a rate that the color disappeared between drops. A brown color persisted while adding the last 10 mL of iodine solution. This reaction mixture was slowly warmed to room temperature while stirring for 12 h. The colorless solution was then cooled to 0 °C, and 50 mL of 20% sulfuric acid was added dropwise. The vinyl iodide was extracted into pentane, and the combined extracts were washed with water, sodium thiosulfate, and sodium bicarbonate and then dried over potassium carbonate. Distillation gave 19.9 g (79.6%) of a colorless liquid, bp 85 °C (5 mmHg) [lit.[16] bp 50–52 °C (3 mmHg)]; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, 3, J = 7.1 Hz), 1.26–1.38 (m, 4), 1.98–2.06 (m, 2), 5.95 (dt, 1, J = 1.8, 14.7 Hz, CH=C*H*—I), 6.49 (dt, 1, J = 6.9, 14.5 Hz, C*H*=CH—I); ^{13}C NMR ($CDCl_3$) δ 13.59, 21.93, 30.55, 35.60, 73.96, 146.64; IR (neat) 3050, 2950, 2850, 1610, 1420, 1225, 1190, 955 cm^{-1}. The ^{1}H NMR spectrum was identical with that reported.[35]

1-Iodocyclohexene. This compound was prepared according to a known procedure:[45] ^{1}H NMR ($CDCl_3$) δ 1.58–1.76 (m, 4), 2.04–2.14 (m, 2), 2.45–2.54 (m, 2), 6.30–6.36 (m, 1); ^{13}C NMR ($CDCl_3$) δ 20.97, 25.41, 29.04, 39.55, 96.62, 137.37; IR (neat) 2920, 2860, 1640, 1440, 1335, 990 cm^{-1}. The ^{1}H NMR spectrum matched the published data.[45]

(*E*)-[[(3-Iodo-2-propenyl)oxy]methyl]benzene. This compound was prepared by the hydroboration/iodination method.[17] A mixture of 14.6 g (0.100 mol) of [[(2-propynyl)oxy]methyl]benzene[46] and 12.1 g (0.101 mol) of catecholborane[47] were stirred for 6 h under nitrogen at 70 °C to form the catechol ester. Analysis by GLC (OV-101, TCD) indicated the presence of both starting reagents and product, and the ratio between them was constant after 1 and 6 h. Further addition of 1.2 g (0.010 mol) of catecholborane and heating to 70 °C for 12 h did not change the ratio between the starting propyne and product. The mixture was cooled to room temperature and stirred with 100 mL of water for 2 h to effect the hydrolysis of the ester. The resulting mixture was cooled to 0 °C, and the white solid was collected by filtration and washed free of catechol by using ice-cold water. The boronic acid was then dissolved in 50 mL of ether in a 500-mL flask and cooled to 0 °C. Aqueous sodium hydroxide (50 mL, 3 N) was then added followed by 16 g (62 mmol) of elemental iodine in 100 mL of THF, while stirring at 0 °C. The mixture was stirred for 2 h at 0 °C. The excess iodine was then destroyed with 10% aqueous sodium thiosulfate. The ether solution was separated, and the aqueous phase was back-extracted (3 × 50 mL) with ether. The ethereal extracts were washed once with 50 mL of water and then brine (2 × 50 mL) and dried over potassium carbonate. After removing the solvent, 7.0 g (18%) of a colorless liquid was obtained by distillation, bp 80–84 °C (0.12 mmHg). Further purification was achieved by MPLC by using hexane–ethyl acetate (95:5) at a flow rate of 5 mL per min: ^{1}H NMR ($CDCl_3$) δ 3.94 (dd, 2, J = 1, 6 Hz), 4.50 (s, 2), 6.39 (dt, 1, J = 14 Hz, CH=C*H*—I), 6.65 (dt, 1, J = 6, 14 Hz, C*H*=CH—I), 7.31–7.34 (m, 5); ^{13}C NMR ($CDCl_3$) δ 71.74, 72.28, 78.58, 127.6, 127.7, 128.4, 137.9, 142.4; IR (neat) 3029, 2854, 1604, 1494, 1451, 1354, 1185, 1095, 1075, 1028, 935 cm^{-1}. The ^{1}H NMR spectrum matched the published data.[14]

(*Z*)-1-Iodo-1-hexene. This compound was prepared by the reduction of 1-iodo-1-hexyne[16] with diimide: ^{1}H NMR ($CDCl_3$) ($CHCl_3$) δ 0.90 (t, 3, J = 7.1 Hz), 1.23–1.48 (m, 4), 2.12 (q, 2, J = 5.3 Hz), 6.15 (s, 2); ^{13}C NMR ($CDCl_3$) δ 13.84, 22.20, 30.14, 34.42, 81.91, 141.44; IR (neat) 3065, 2960, 2870, 1610, 675 cm^{-1}. The ^{1}H NMR spectrum matched the published data.[19]

Ethynyltrimethylstannane. This compound was prepared by the reaction of sodium acetylide with trimethyltin chloride:[48,49] bp 95–100 °C (640 mmHg) [lit.[50] bp 92–95 °C (760 mmHg)]; ^{1}H NMR ($CDCl_3$) δ 0.28 (s, 9), 2.15 (s, 1); ^{13}C NMR ($CDCl_3$) δ 7.94, 89.10, 95.90; IR (CH_2Cl_2) 3280, 2005 cm^{-1}.[51]

Ethynyltributylstannane. This compound was prepared by the reaction of sodium acetylide with tributyltin chloride:[49] bp 130–135 °C (0.7 mmHg) [lit.[52] bp 200 °C (2 mmHg)]; 46.4 g (83.0%) of a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3, J = 7.2 Hz), 0.99 (t, 2, J = 7.8 Hz), 1.31 (sept, 2, J = 7.7 Hz), 1.46–1.62 (m, 2), 2.17 (s, 1);[52] ^{13}C NMR ($CDCl_3$) δ 11.15, 13.52, 26.91, 28.82, 88.84, 96.77; IR (neat) 3280, 2950, 2850, 2005, 1455, 1065, 865 cm^{-1}.

Trimethyl[(trimethylstannyl)ethynyl]silane. This compound was prepared by the reaction of the acetylene with the tin amide.[13] A mixture of 0.707 g (3.00 mmol) of (diethylamino)trimethylstannane[53,54] and 0.295 g (3.00 mmol) of trimethylsilylacetylene was stirred at room temperature for 15 min. Purification was achieved by bulb-to-bulb distillation, bp 110–120 °C (137 mmHg), to yield 0.677 g (86.5%) of a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 9), 0.21 (s, 9); ^{13}C NMR ($CDCl_3$) δ −7.72, 0.17, 92.98, 113.1.[55]

1-Hexynyltrimethylstannane (18). Method 1.[13] A mixture of 1.63 g (19.9 mmol) of 1-hexyne and 4.68 g (19.9 mmol) of (diethylamino)trimethylstannane[53,54] was heated to 50 °C for 12 h. Purification was achieved by bulb-to-bulb distillation, bp 82–88 °C (7 mmHg) [lit.[13] bp 82 °C (12 mmHg)], to afford 4.35 g (89.2%) of a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 0.22 (s, 9), 0.87 (t, 3, J = 6.9 Hz), 1.34–1.47 (m, 4), 2.20 (t, 2, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ −7.85, 13.53, 19.78, 21.93, 31.20, 81.78, 111.02; IR (neat) 2144 cm^{-1}.[56]

Method 2.[57] To a solution of 0.863 g (10.5 mmol) of 1-hexyne in 10 mL of dry ether was added dropwise 6.0 mL (10.5 mmol, 1.74 M) of *n*-butyllithium at −78 °C. This mixture was stirred for 30 min at −78 °C followed by warming to 0 °C and stirring for 30 min. To this mixture was added dropwise a solution of 2.0 g (10 mmol) of trimethyltin chloride in 25 mL of dry ether at −78 °C. This reaction mixture was slowly warmed to room temperature over a 12 h period. The ether was removed by fractional distillation followed by vacuum transferring all volatiles at 0.35 mmHg with an oil bath temperature of 45–48 °C. The distillate was collected at −78 °C. Further purification was achieved by distillation, bp 26 °C (0.35 mmHg) [lit.[13] bp 82 °C (12 mmHg)], to yield 2.27 g (92.5%) of a colorless liquid. The spectral data was consistent with the previous product.

Trimethyl[(3-(trimethylstannyl)-2-propynyl)oxy]silane. This compound was prepared by the reaction of the acetylene with the tin amide.[13] A mixture of 1.49 g (6.32 mmol) of (diethylamino)trimethylstannane[53,54] and 0.922 g (7.20 mmol) of 1-(trimethylsiloxy)-2-propyne[58] was stirred at 50 °C under nitrogen for 15 min. Analysis by GLC (OV-101, TCD) indicated that the reaction was complete. Purification was achieved by bulb-to-bulb distillation, bp 77–80 °C (11 mmHg), to yield 1.78 g (96.8%) of a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 9), 0.24 (s, 9), 4.25 (s, 2); ^{13}C NMR ($CDCl_3$) δ −8.01, −0.24, 51.68, 88.49, 107.71; IR (CCl_4) 3160, 2150 cm^{-1}. Anal. Calcd for $C_9H_{20}OSi$: C, 37.14; H, 6.93. Found: C, 36.92; H, 6.98.

Trimethyl(phenylethynyl)stannane.[56] This compound was prepared by the reaction of the acetylide with the tin amide.[13] A mixture of 0.707 g (3.00 mmol) of (diethylamino)trimethylstannane[53,54] and 0.709 g (3.00 mmol) of phenylacetylene was stirred at room temperature for 15 min. Purification was accomplished by bulb-to-bulb distillation, bp 100–110 °C (1 mmHg) [lit.[56b] bp 68 °C (0.3 mmHg)], and provided 0.725 g (91.0%) of a colorless liquid. Further purification of the product by sublimation 60 °C (0.3 mmHg) gave a white solid, mp 63.5–64.0 °C: ^{1}H NMR ($CDCl_3$) δ 0.35 (s, 9), 7.26–7.47 (m, 5); ^{13}C NMR ($CDCl_3$) δ −7.72, 92.76, 108.96, 123.69, 126.46, 128.12, 131.92; IR (CCl_4) 3150, 2130 cm^{-1}.[56]

6-(Trimethylstannyl)-5-hexyn-1-yl Acetate. This compound was prepared by the tin amide reaction.[13] To a flame dried, 5-mL flask was

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added 1.19 g (5.06 mmol) of (diethylamino)trimethylstannane[53,54] and 0.700 g (5.00 mmol) of 5-hexyn-1-yl acetate.[59] After having been stirred for 1 h at room temperature, the reaction was complete as shown by GLC (OV-101, TCD) analysis. Purification was achieved by bulb-to-bulb distillation, bp 100–110 °C (0.15 mmHg), to yield 1.43 g (93.2%) of a colorless liquid: ^{1}H NMR ($CDCl_3$) ($CHCl_3$) δ 0.22 (s, 9), 1.48–1.61 (m, 2), 1.64–1.76 (m, 2), 2.00 (s, 3), 2.24 (t, 2, J = 6.9 Hz), 4.04 (t, 2, J = 6.3 Hz); ^{13}C NMR ($CDCl_3$) δ −7.80, 19.72, 20.78, 25.52, 27.87, 64.00, 82.68, 110.0, 170.84; IR (neat) 2142, 1745 cm^{-1}. This compound was unstable and was used in coupling reactions immediately after preparation.

[[(3-(Trimethylstannyl)-2-propynyl)oxy]methyl]benzene. This compound was prepared by reaction with the tin amide.[13] A mixture of 1.49 g (6.31 mmol) of (diethylamino)trimethylstannane[53,54] and 0.924 g (6.32 mmol) of 1-benzoxy-2-propyne was stirred under nitrogen for 1 h before GLC (OV-101, TCD) analysis indicated that the reaction was complete. Purification by bulb-to-bulb distillation, bp 151–156 °C (7 mmHg); provided 1.52 g (77.8%) of a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 0.30 (s, 9), 4.17 (s, 2), 4.60 (s, 2), 7.33–7.36 (m, 5); ^{13}C NMR ($CDCl_3$) δ −7.88, 58.13, 71.48, 90.19, 104.95, 127.70, 127.83, 128.06, 128.34, 137.78; IR (neat) 2150 cm^{-1}. This compound was unstable and was prepared immediately before its use in the coupling reaction.

(*E*)-3-Octen-1-yne. Synthesis Using Ethynyltrimethylstannane. (Entry 1). To a solution of 0.289 g (0.250 mmol) of $(PPh_3)_4Pd$ and 1.05 g (5.00 mmol) of (*E*)-1-iodo-1-hexene in 50 mL of ether was added 0.990 g (5.24 mmol) of ethynyltrimethylstannane. The mixture was then stirred at 22–25 °C for 22 h during which time a white solid formed. Analysis by TLC (hexane–ethyl acetate 95:5) indicated complete consumption of the vinyl iodide (R_f 0.8). The reaction mixture was transferred to a separatory funnel with 25 mL of ether and washed with water (3 × 25 mL) and brine (1 × 25 mL). The ethereal extract was dried over magnesium sulfate. All volatiles were then vacuum transferred at 0.05 mmHg and collected at liquid nitrogen temperature. The ether was removed by fractional distillation. The colorless residue was then bulb-to-bulb distilled, bp 80–85 °C (640 mmHg) [lit.[60a] bp 60–62 °C (50 mmHg)], under nitrogen and collected at −78 °C. A mixture of ether and (*E*)-3-octen-1-yne was collected. A yield of 50% was calculated by ^{1}H NMR integration: ^{1}H NMR ($CDCl_3$) δ 0.85 (t, 3, J = 7.1 Hz), 1.22–1.38 (m, 4), 2.07 (q, 1, J = 7.1 Hz), 2.72 (d, 1, J = 2.6 Hz), 5.40 (dm, 1, J = 15.7 Hz, CH=C*H*—C≡C), 6.20 (dt, 1, J = 7.0, 15.8 Hz, C*H*=CH—C≡C); ^{13}C NMR ($CDCl_3$) δ 13.6, 22.1, 30.7, 32.6, 77.5, 82.6, 108.7, 146.6; IR (CCl_4) 3320, 3160, 2100, 1635 cm^{-1}.[60b]

(*E*)-[Trimethyl-3-octen-1-ynyl]silane Synthesis Using $(PPh_3)_4Pd$. (Entry 2). Trimethyl[(trimethylstannyl)ethynyl]silane (0.391 g, 1.50 mmol) was added to a solution of 0.0187 g (0.0162 mmol) of $(PPh_3)_4Pd$ and 0.210 g (1.00 mmol) of (*E*)-1-iodo-1-hexene (**13**) in 1 mL of THF. The mixture was then stirred at 50 °C for 24 h. The reaction mixture was vacuum transferred at 0.01 mmHg and collected at liquid nitrogen temperature. The distillate was diluted with 50 mL of pentane and washed with 20 mL of water. The aqueous phase was back-extracted with pentane and the pentane extracts were washed with water (3 × 10 mL) and brine (3 × 10 mL). The organic layer was dried over potassium carbonate, and the pentane was removed by fractional distillation. Further purification was achieved by radial chromatography by using pentane to yield 0.141 g (78.3%) of product: ^{1}H NMR ($CDCl_3$) δ 0.15 (s, 9), 0.86 (t, 3, J = 7.3 Hz), 1.24–1.37 (m, 4), 2.06 (q, 2, J = 5.9 Hz), 5.47 (dt, 1, J = 1.3, 16.1 Hz, CH=C*H*—C≡C), 6.19 (dt, 1, J = 7.1, 15.9 Hz, C*H*=CH—C≡C); ^{13}C NMR ($CDCl_3$) δ −0.01, 13.75, 22.12, 30.78, 32.71, 92.47, 104.28, 109.70, 146.16; IR (neat) 3020, 2175, 2135, 2065, 1252, 1085, 955 cm^{-1}. Anal. Calcd for $C_{11}H_{20}Si$: C, 73.25; H, 11.18. Found: C, 73.28; H, 11.11.

Synthesis Using $(PPh_3)_2PdCl_2$. (Entry 3). To a solution of 0.578 g (2.75 mmol) of (*E*)-1-iodo-1-hexane (**13**) and 0.762 g (2.92 mmol) of trimethyl[(trimethylstannyl)ethynyl]silane in 27 mL of dry THF was added 0.0292 g (0.0416 mmol) of $(PPh_3)_2PdCl_2$. The mixture was then stirred at 22–25 °C for 3 h during which time the yellow solution turned orange. Analysis by TLC using hexane–ethyl acetate (95:5) indicated complete consumption of the vinyl iodide (R_f 0.8). The reaction mixture was added to 7.5 g of alumina with the aid of 10 mL of methylene chloride, and the solvent was removed under reduced pressure to a dry powder. A chromatography column was prepared with the coated alumina, and the products were eluted with pentane. The pentane was evaporated, and the residue was dissolved in 50 mL of ether. The organics were washed with water (3 × 20 mL) and brine (1 × 20 mL) and dried over potassium carbonate. Further purification was achieved by radial chromatography by using hexane. Removal of the solvent provided 0.444 g (89.4%) of a pale yellow liquid, which was further purified by bulb-to-bulb distillation, bp 65–70 °C (0.1 mmHg).

(*E*)-5-Dodecen-7-yne. Synthesis Using $(MeCN)_2PdCl_2$. (Entry 4). To a dry and degassed solution of 0.0130 g (0.0500 mmol) of $(MeCN)_2PdCl_2$ in 10 mL of DMF was added 0.211 g (1.00 mmol) of (*E*)-1-iodo-1-hexene (**13**) and 0.316 g (1.29 mmol) of 1-hexynyltrimethylstannane (**18**) at −50 °C. The homogeneous yellow reaction mixture turned black within 3 min. Analysis by GLC (DB1, FID) indicated complete consumption of the vinyl iodide. The black reaction mixture was added to 50 mL of water in a separatory funnel, and this aqueous mixture was extracted with ether (3 × 50 mL). The combined ethereal extracts were washed with water (3 × 25 mL) and brine (1 × 25 mL) and dried over potassium carbonate. The dried extracts were filtered through a plug of alumina and concentrated under reduced pressure. Purification was accomplished by radial chromatography by using pentane, followed by bulb-to-bulb distillation, bp 63–64 °C (0.3 mmHg) [lit.[61] bp 63 °C (1 mmHg)] to yield 0.155 g (88.3%) of a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 0.86–0.94 (m, 6), 1.02–1.14 (m, 8), 2.03–2.10 (m, 2), 2.88 (dt, 2, J = 1.9, 15.9 Hz), 5.44 (dt, 1, J = 1.6, 16.0 Hz, CH=C*H*—C≡C), 6.03 (dt, 1, J = 7.0, 16.0 Hz, C*H*=CH—C≡C); ^{13}C NMR ($CDCl_3$) δ 13.46, 13.72, 19.08, 22.00, 22.13, 31.10, 32.55, 79.34, 88.59, 110.14, 142.98; IR (neat) 3018, 2200, 1670, 1466, 945 cm^{-1}. The ^{1}H NMR and IR spectra matched the published data.[62]

(*E*)-7-Dodecen-5-yn-1-yl Acetate. (Entry 5). A dry 10-mL Schlenk tube was charged with 0.0103 g (0.0397 mmol) of $(MeCN)_2PdCl_2$ flushed with argon. The palladium complex was dissolved in 5 mL of dry DMF. This yellow solution was degassed 3 times by evacuating to 10 mmHg and flushing with argon. Dry, iodine free (*E*)-1-iodo-1-hexene (**13**) (0.0964 g, 0.459 mmol) was added to the palladium solution causing a slight darkening to occur. To this mixture was added 0.180 g (0.596 mmol) of 6-(trimethylstannyl)-5-hexyn-1-yl acetate at 22–25 °C causing the reaction mixture to immediately become black. Analysis by GLC (DB1, FID) indicated that the reaction had gone to completion. The black reaction mixture was added to 25 mL of water in a separatory funnel, and this aqueous mixture was extracted with ether (3 × 25 mL). The combined ethereal extracts were washed with water (3 × 25 mL) and brine (1 × 25 mL) and dried over potassium carbonate. The dried extracts were filtered through a plug of alumina and concentrated under reduced pressure. Analysis by ^{1}H NMR indicated only the E coupled product had formed. Purification was accomplished by radial chromatography by using hexane–ethyl acetate (9:1). Removal of the solvents provided 0.099 g (97%) of a pale yellow liquid, which was further purified by bulb-to-bulb distillation, bp 72–78 °C (0.02 mmHg) [lit.[27] bp 101 °C (0.1 mmHg)]: ^{1}H NMR ($CDCl_3$) δ 0.89 (t, 3, J = 7.0 Hz), 1.27–1.42 (m, 4), 1.54–1.64 (m, 4), 2.05 (s, 3), 2.05–2.12 (m, 2), 2.34 (dt, 2, J = 1.8, 6.8 Hz), 4.09 (t, 2, J = 6.3 Hz), 5.44 (dt, 1, J = 1.7, 15.8 Hz, CH=C*H*—C≡C), 6.06 (dt, 1, J = 7.1, 15.8 Hz, C*H*=CH—C≡C); ^{13}C NMR ($CDCl_3$) δ 13.72, 19.04, 20.78, 22.09, 25.36, 27.90, 30.98, 32.54, 63.97, 79.82, 87.62, 109.80, 143.43, 170.87; IR (neat) 3018, 2950, 2200, 1740, 1455, 950 cm^{-1}. The ^{1}H NMR and IR spectra matched the published data.[27]

(*Z*)-7-Dodecen-5-yn-1-yl Acetate (16). Synthesis Using $(MeCN)_2PdCl_2$. (Entry 6). A dry 10-mL Schlenk tube was charged with 0.0106 g (0.0409 mmol) of $(MeCN)_2PdCl_2$ and flushed with argon. DMF (5 mL) was added, and this solution was degassed 3 times by evacuating to 10 mmHg and flushing with argon. Dry, iodine free (*Z*)-1-iodo-1-hexene (0.109 g, 0.519 mmol) was added to the yellow solution causing a slight darkening to occur. To this mixture was added 0.269 g (0.890 mmol) of 6-(trimethylstannyl)-5-hexyn-1-yl acetate at 22–25 °C causing the reaction mixture to immediately become black. Analysis by GLC (DB1, FID) indicated that the reaction had gone to completion. The black reaction mixture was added to 25 mL of water in a separatory funnel, and this aqueous mixture was extracted with ether (3 × 25 mL). The combined ethereal extracts were washed with water (3 × 25 mL) and brine (1 × 25 mL) and then dried over potassium carbonate. The dried extracts were filtered through a plug of alumina and concentrated under reduced pressure. Analysis by ^{1}H NMR indicated only the *Z* coupled product had formed. Further purification was accomplished by radial chromatography by using hexane–ethyl acetate (9:1). Removal of the solvents provided 0.105 g (90.8%) of a pale yellow liquid, which was further purified by bulb-to-bulb distillation, bp 75–80 °C (0.01 mmHg): ^{1}H NMR ($CDCl_3$) δ 0.91 (t, 3, J = 6.8 Hz), 1.30–1.41 (m, 4), 1.56–1.66 (m, 2), 1.71–1.80 (m, 2), 2.05 (s, 3), 2.23–2.32 (m, 2), 2.39 (dt, 2, J = 2.0, 6.8 Hz), 4.10 (t, 2, J = 6.3 Hz), 5.42 (dt, 1, J = 1.7, 10.7 Hz, CH=C*H*—C≡C), 5.82 (dt, 1, J = 7.4,

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10.7 Hz, C*H*=CH—C≡C); ^{13}C NMR ($CDCl_3$) δ 13.78, 19.17, 20.78, 22.22, 25.36, 27.84, 29.30, 31.01, 63.94, 77.96, 93.40, 109.25, 142.67, 170.88; IR (neat) 3020, 2200, 1740, 730 cm^{-1}. Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.45; H, 10.01.

Synthesis Using $(PPh_3)_4Pd$. (Entry 7). To a dry 10-mL Schlenk tube was added 0.0297 g (0.0257 mmol) of $(PPh_3)_4Pd$, 6 mL of dry THF, 0.128 g (0.610 mmol) of (*Z*)-1-iodo-1-hexene, 0.228 g (0.753 mmol) of 6-(trimethylstannyl)-4-hexyn-1-yl acetate, and 0.0310 g (0.234 mmol) of 1,2,3,4-tetrahydronaphthalene. Analysis by GLC (DB1, FID) indicated that 39% of 1-iodo-1-hexene was consumed within the first 15 min. However, stirring at 22–25 °C for 19 h or heating to 60 °C for 21 h failed to improve the percent conversion.

Ethynylcyclohexene. Synthesis Using Ethynyltrimethylstannane. (Entry 8). To a solution of 0.115 g (0.0997 mmol) of $(PPh_3)_4Pd$ and 0.416 g (2.00 mmol) of 1-iodocyclohexene in 20 mL of dry THF was added 0.397 g (2.10 mmol) of ethynyltrimethylstannane. The mixture was then stirred at 22–25 °C for 24 h. The THF was removed by fractional distillation, and 50 mL of pentane was added to the residue. The organics were extracted with water (3 × 10 mL) and brine (5 × 10 mL) and dried over magnesium sulfate. All volatiles were then vacuum transferred at 0.01 mmHg and collected at liquid nitrogen temperature. The pentane was removed by fractional distillation, and the remaining liquid was concentrated at reduced pressure to provide 0.191 g (90.1%) of a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 1.44–1.63 (m, 4), 1.97–2.18 (m, 4), 2.75 (s, 1), 6.14 (m, 1). The ^{1}H NMR spectrum matched the published data.[63]

(1-Cyclohexen-1-ylethynyl)trimethylsilane. (Entry 9). To a solution of 0.058 g (0.050 mmol) of $(PPh_3)_4Pd$ and 0.0208 g (1.00 mmol) of 1-iodocyclohexene in 10 mL of dry THF was added 0.274 g (1.05 mmol) of trimethyl[(trimethylstannyl)ethynyl]silane. The reaction mixture was stirred at 22–25 °C for 3 h. The solvent was removed under reduced pressure, and the resulting oil was dissolved in 50 mL of ether and washed with water (1 × 10 mL). The aqueous phase was back-extracted with ether (1 × 10 mL), and the combined ethereal extracts were washed with water (2 × 10 mL) and brine (2 × 10 mL). The organic layer was dried over potassium carbonate, filtered, and concentrated under reduced pressure. The crude product was purified by radial chromatography by using hexane to yield 0.177 g (96.4%) of a colorless liquid. Further purification was achieved by bulb-to-bulb distillation: bp 25–30 °C (0.15 mmHg) [lit.[64] 107–108 °C (20 mmHg)]; ^{1}H NMR ($CDCl_3$) δ 0.15 (s, 9), 1.52–1.61 (m, 4), 2.04–2.10 (m, 4), 6.13–6.16 (m, 1); ^{13}C NMR ($CDCl_3$) δ 0.1, 21.5, 22.3, 25.7, 29.2, 90.8, 107.4, 121.0, 135.9; IR (neat) 3020, 2920, 2117, 1430, 1243, 1157 cm^{-1}.

Trimethyl[[3-(cyclohexen-1-yl)-2-propynyl]oxy]silane. Synthesis Using $(PPh_3)_2PdCl_2$. (Entry 10). To a solution of 0.424 g (2.04 mmol) of 1-iodocyclohexene and 0.592 g (2.04 mmol) of trimethyl[(3-(trimethylstannyl)-2-propynyl)oxy]silane in 25 mL of dry THF was added 0.0215 g (0.0306 mmol) of $(PPh_3)_2PdCl_2$. The mixture was then stirred at 22–25 °C for 2 h. Analysis by TLC using hexane–ethyl acetate (95:5) indicated complete consumption of the vinyl iodide (R_f 0.43). The reaction mixture was then diluted with 20 mL of methylene chloride and coated on 10 g of alumina. The alumina was eluted with pentane. The pentane eluted was washed with water (3 × 25 mL) and brine (1 × 25 mL) and dried over potassium carbonate. Removal of the pentane under reduced pressure provided 0.388 g (91.6%) of a pale yellow liquid: ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 9), 1.48–1.68 (m, 4), 2.00–2.15 (m, 4), 4.36 (s, 2), 6.04–6.12 (m, 1); ^{13}C NMR ($CDCl_3$) δ −0.31, 21.51, 22.29, 25.56, 29.06, 51.53, 84.86, 86.82, 120.48, 134.54; IR (neat) 3040, 2218, 1442, 1322, 1258 cm^{-1}. Anal. Calcd for $C_{12}H_{20}OSi$: C, 69.17; H, 9.67. Found: C, 68.93; H, 9.70.

Synthesis Using $(PPh_3)_4Pd$. (Entry 11). A mixture of 0.062 g (0.054 mmol) of $(PPh_3)_4Pd$, 0.311 g (1.50 mmol) of 1-iodocyclohexene, and 0.390 g (1.34 mmol) of trimethyl[(3-(trimethylstannyl)-2-propynyl)-oxy]silane in 13 mL of dry THF was stirred at 22–25 °C for 3 h. During the reaction a white precipitate formed. The solvent was removed under reduced pressure. The residue was redissolved in 50 mL of ether, and the ether layer was extracted with water (1 × 10 mL). The aqueous phase was back-extracted with ether (1 × 10 mL), and the combined ethereal extracts were washed with water (2 × 10 mL) and brine (2 × 10 mL). The organic layer was dried over potassium carbonate, and the ether was removed under reduced pressure. Addition of pentane precipitated the palladium which was removed by filtration through a Celite pad. The crude product was purified by radial chromatography by using hexane–ethyl acetate (95:5). Further purification was achieved by bulb-to-bulb distillation, bp 85–95 °C (12 mmHg), to yield 0.212 g (76.1%) of a colorless liquid. Spectral data was consistent with the previous product.

Synthesis Using Trimethyl-3-(tributylstannyl)-2-propynylsilane. (Entry 12). To a solution of 0.0105 g (0.0150 mmol) of $(PPh_3)_2PdCl_2$ and 0.209 g (1.00 mmol) of 1-iodocyclohexene in 1 mL of dry THF was added 0.419 g (1.01 mmol) of trimethyl-[(3-(tributylstannyl)-2-propynyl)-oxy]silane. The reaction mixture was stirred at 50 °C for 10 h. Concentration of the mixture under reduced pressure provided an oil. Addition of pentane precipitated the palladium which was removed by filtration through a plug of alumina. The pentane was removed to yield 0.14 g (67%) of product contaminated with tributyltin iodide. Radial chromatography with hexane failed to further purify the product.

(1-Cyclohexen-1-ylethynyl)benzene. Synthesis Using Trimethyl(phenylethynyl)stannane. (Entry 13). A mixture of 0.0611 g (0.0529 mmol) of $(PPh_3)_4Pd$, 0.232 g (1.12 mmol) of 1-iodocyclohexene, and 0.298 g (1.12 mmol) of trimethyl(phenylethynyl)stannane in 10 mL of dry THF was stirred at 22–25 °C for 10 h. During the reaction, a white precipitate formed. The solvent was removed under reduced pressure, the residue was redissolved in 50 mL of ether, and the ether layer was extracted with water (1 × 10 mL). The aqueous phase was back-extracted with ether (1 × 10 mL), and the combined ethereal extracts were washed with water (2 × 10 mL) and brine (2 × 10 mL). The organic layer was dried over potassium carbonate, and the ether was removed under reduced pressure. Addition of pentane precipitated the palladium which was removed by filtration through a Celite pad. The crude product was further purified by radial chromatography with hexane to yield 0.184 g (90.5%) of a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 1.58–1.68 (m, 4), 2.12–2.22 (m, 4), 6.20–6.21 (m, 1), 7.26–7.43 (m, 5); ^{13}C NMR ($CDCl_3$) δ 21.65, 22.45, 25.83, 29.38, 86.88, 91.37, 120.97, 127.64, 128.17, 131.50, 132.55, 134.92; IR (neat) 2195, 1594, 1490, 1435, 750, 688 cm^{-1}. The ^{1}H NMR and IR spectra matched the published data.[65]

Synthesis Using Tributyl(phenylethynyl)stannane. (Entry 14). To a solution of 0.0111 g (0.0158 mmol) of $(PPh_3)_2PdCl_2$ and 0.200 g (0.960 mmol) of 1-iodocyclohexene in 1 mL of dry THF was added 0.461 g (2.00 mmol) of tributyl(phenylethynyl)stannane.[56] The reaction mixture was stirred at 48 °C for 50 h. Concentration of the mixture under reduced pressure provided an oil. Addition of pentane precipitated the palladium which was removed by filtration through a plug of alumina. Further purification was achieved by radial chromatography by using hexane to yield 0.161 g (92.2%) of a pale yellow liquid. Spectral data was consistent with the previous product.

[[[3-(Cyclohexen-1-yl)-2-propynyl]oxy]methyl]benzene. (Entry 15). To a solution of 0.353 g (1.70 mmol) of 1-iodocyclohexene and 0.418 g (1.36 mmol) of [[(3-(trimethylstannyl)-2-propynyl)oxy]methyl]benzene in 13 mL of dry THF was added 0.0141 g (0.0201 mmol) of $(PPh_3)_2PdCl_2$. The mixture was then stirred at 22–25 °C for 18 h. The reaction mixture was coated on 1.3 g of alumina with the aid of 10 mL of methylene chloride and concentrated under reduced pressure to a dry powder. A chromatography column was prepared with the coated alumina and eluted with pentane. The organics were washed with water (3 × 25 mL) and brine (1 × 25 mL) and dried over potassium carbonate. Purification was achieved by radial chromatography by using hexane–ethyl acetate (95:5). Removal of the solvents provided 0.279 g (90.8%) of a pale yellow liquid, which was further purified by bulb-to-bulb distillation, bp 65–70 °C (0.01 mmHg): ^{1}H NMR ($CDCl_3$) δ 1.47–1.70 (m, 4), 1.98–2.19 (m, 4), 4.27 (s, 2), 4.59 (s, 2), 6.08–6.18 (m, 1), 7.21–7.48 (m, 5); ^{13}C NMR ($CDCl_3$) δ 21.48, 22.28, 25.59, 29.18, 57.94, 71.36, 82.33, 88.39, 120.35, 127.64, 127.99, 128.28, 135.08, 137.84; IR (neat) 2119 cm^{-1}. Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.94; H, 8.05.

(*E*)-[[(2-Penten-4-ynyl)oxy]methyl]benzene. (Entry 16). A mixture of 0.058 g (0.050 mmol) of $(PPh_3)_4Pd$, 0.274 g (1.00 mmol) of (*E*)-[[(3-iodo-2-propenyl)oxy]methyl]benzene, and 0.198 g (1.05 mmol) of ethynyltrimethylstannane in 10 mL of dry THF was stirred at 22–25 °C for 24 h. The solvent was removed under reduced pressure, and the residue was dissolved in 50 mL of ether. The organics were washed with water (3 × 10 mL) and brine (3 × 10 mL) and dried over magnesium sulfate. The crude product was purified by radial chromatography by using hexane–ethyl acetate (9:1). Further purification was achieved by bulb-to-bulb distillation, bp 45–50 °C (0.1 mmHg), to provide 0.102 g (59.3%) of a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 2.88 (d, 1, *J* = 2.4 Hz), 4.05 (dd, 1, *J* = 2.0, 5.4 Hz), 4.50 (s, 2), 5.75 (dq, 1, *J* = 2.0, 16.0 Hz, CH=C*H*—C≡C), 6.29 (dt, 1, *J* = 5.4, 16.1 Hz, C*H*=CH—C≡C), 7.32 (s, 5); ^{13}C NMR ($CDCl_3$) δ 69.47, 72.41, 77.77, 81.62, 110.41, 127.61, 127.67, 128.38, 137.94, 141.38; IR (neat) 3290, 3030, 2850, 2055, 1495, 1455, 1360 cm^{-1}; MS, *m/z* (rel intensity) 172 (M^+, 0.3). Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.77; H, 7.01.

(*E*)-[[(5-(Trimethylsilyl)-2-penten-4-ynyl)oxy]methyl]benzene. (Entry 17). To a solution of 0.115 g (0.0996 mmol) of $(Ph_3P)_4Pd$ and 0.549 g (2.00 mmol) of (*E*)-[[(3-iodo-2-propenyl)oxy]methyl]benzene in 20 mL of dry THF was added 0.562 g (2.15 mmol) of trimethyl[(trimethylstannyl)ethynyl]silane. The homogeneous yellow solution was stirred at 22–25 °C for 24 h. The solvent was removed under reduced pressure.

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Pentane was added to precipitate the palladium which was removed by filtration through a Celite pad. The pentane was removed under reduced pressure, and the residue was redissolved in 50 mL of ether. The ethereal solution was extracted with water (5 × 10 mL) and brine (2 × 10 mL) and was dried over potassium carbonate. Concentration under reduced pressure provided 0.416 g (85.2%) of a yellow liquid. Further purification was achieved by bulb-to-bulb distillation, bp 100–105 °C (0.025 mmHg): ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 9), 3.93 (dd, 2, J = 2, 5 Hz), 4.38 (s, 2), 5.67 (dt, 1, J = 2, 16 Hz, CH=C*H*—C≡C), 6.14 (dt, 1, J = 6, 16 Hz, C*H*=CH—C≡C), 7.20 (s, 5); ^{13}C NMR ($CDCl_3$) δ −0.1, 69.7, 72.4, 95.1, 103.2, 111.8, 127.6, 128.4, 138.2, 140.6; IR (neat) 3035, 2960, 2170, 2130, 1495, 1455, 1360 cm^{-1}; MS, m/z (rel intensity) 244 (M^+, 0.3). Anal. Calcd for $C_{15}H_{20}OSi$: C, 73.72; H, 8.24. Found: C, 73.94; H, 8.13.

(3*E*,5*E*)-Tetrahydro-2-[(3,5-octadien-7-ynyl)oxy]-2*H*-pyran. (Entry 18). To a dry and degassed solution of 0.0085 g (0.033 mmol) of $(MeCN)_2PdCl_2$ in 1.0 mL of DMF was added 0.201 g (0.652 mmol) of (3*E*,5*E*)-tetrahydro-2-[(6-iodo-3,5-hexadienyl)oxy]-2*H*-pyran (vide infra) and 0.220 g (0.700 mmol) of ethynyltributylstannane. The yellow solution immediately turned black upon addition of the stannane at 22–25 °C. Analysis by GLC (DB1, FID) indicated complete consumption of the starting iodide. The reaction mixture was diluted with 25 mL of ether, washed with water (1 × 5 mL), and back-extracted with ether (1 × 5 mL). The combined ethereal extracts were washed with water (3 × 5 mL) and stirred for 1 h with 25 mL of half-saturated potassium fluoride. The resulting white precipitate was removed by filtering through glass wool and then the phases were separated. The ether phase was washed with water (2 × 10 mL) and brine (1 × 10 mL) and dried over potassium carbonate. The ether was removed, and the product was purified by MPLC by using hexane–ethyl acetate (95:5) to yield 0.0911 g (68.0%) of a pale yellow liquid. Further purification was achieved by bulb-to-bulb distillation, bp 65–70 °C (0.12 mmHg): ^{1}H NMR ($CDCl_3$) δ 1.45–1.92 (m, 6), 2.42 (q, 2, J = 6.8 Hz), 3.00 (d, 1, J = 2.4 Hz), 3.39–3.55 (m, 2), 3.73–3.91 (m, 2), 4.59 (t, 1, J = 3.9 Hz), 5.48 (dd, 1, J = 2.4, 15.6 Hz, HC≡C—C*H*=CH—CH=CH), 5.85 (dt, 1, J = 6.8, 15.6 Hz, HC≡C—CH=CH—CH=C*H*), 6.16 (dd, 1, J = 10.7, 15.1 Hz, HC≡C—CH=CH—C*H*=CH), 6.64 (dd, 1, J = 10.7, 15.6 Hz, HC≡C—CH=C*H*—CH=CH); ^{13}C NMR ($CDCl_3$) δ 19.52, 25.52, 30.69, 33.20, 62.20, 66.51, 78.77, 83.06, 98.82, 108.35, 130.98, 134.70, 143.47; IR (neat) 3290, 3020, 2930, 2870, 2090, 1645, 1445, 1355, 1205, 1138, 1125, 1075, 1035, 980, 900, 865, 810 cm^{-1}. HRMS Calcd for $C_{13}H_{18}O_2$ 206.1307, found 206.1303.

Processionary Moth Pheremone 1: Scheme I. 1-Iodo-1-butene (2). This compound was prepared[19] by the reduction of 1-iodo-1-butyne[66] with diimide: ^{1}H NMR ($CDCl_3$) ($CHCl_3$) δ 1.00 (t, 3, J = 7.4 Hz) 2.07–2.16 (m, 2), 6.10–6.16 (m, 2); ^{13}C NMR ($CDCl_3$) δ 13.94, 28.25, 81.27, 142.79; IR (neat) 3058, 1600, 1266, 894, 718 cm^{-1}. The ^{1}H NMR spectrum matched the published data.[67]

5-Dodecyn-1-ol. This compound was prepared by the alkylation[68] of the lithium salt of tetrahydro-2-[5-hexynyloxy]-2*H*-pyran (prepared from 9.11 g (50.09 mmol) of the acetylene in 50 mL of THF and 60.0 mmol of *n*-butyllithium at 0 °C) with 9.90 g (60.0 mmol) of 1-bromohexane in 50 mL of dry HMPA. The reaction temperature during addition was held between 4–6 °C, followed by gradual warming to room temperature and stirring for 12 h. The resulting yellow solution was poured into 200 mL of ice water then transferred to a separatory funnel. The aqueous phase was washed with hexane (3 × 100 mL), and the aggregate hexane extracts were washed with water (3 × 50 mL) and dried over potassium carbonate. The hexane was removed under reduced pressure. The resulting yellow oil was chromatographed on silica gel with hexane–ethyl acetate (95:5) to yield 13.0 g (97.6%) of a pale yellow liquid. Purification was achieved by distillation, bp 118–120 °C (0.35 mmHg) [^{1}H NMR ($CDCl_3$) ($CHCl_3$) δ 0.85 (t, 3, J = 6.4 Hz), 1.18–1.84 (m, 18), 2.06–2.20 (m, 4), 3.37 (dt, 1, J = 6.4, 9.8 Hz), 3.42–3.51 (m, 1), 3.72 (dt, 1, J = 6.4, 9.8 Hz), 3.77–3.88 (m, 1), 4.55 (t, 1, J = 2.9 Hz); ^{13}C NMR ($CDCl_3$) δ 13.88, 18.66, 18.78, 19.65, 22.51, 25.62, 26.08, 28.54, 29.05, 29.18, 30.85, 31.37, 62.61, 67.09, 79.88, 80.50, 98.83; IR (neat) 2910, 1452, 1350, 1200 cm^{-1}]. This compound was carried on to the free alcohol by deprotection[69] of a solution of 11.0 g (41.4 mmol) of the THP protected alcohol with 1.0 g (4.14 mmol) of pyridinium *p*-toluenesulfonate in 330 mL of ethanol at 55 °C for 16 h. The solvent was evaporated under reduced pressure, and the resulting white solid was dissolved in 100 mL of pentane and extracted with 50 mL of water. The aqueous phase was back-extracted with pentane (3 × 50 mL). The combined pentane extracts were washed with water (3 × 50 mL) and saturated sodium bicarbonate (1 × 50 mL) and dried over potassium carbonate. Filtration and removal of the solvents provided 7.3 g (97%) of a pale yellow liquid. Purification was accomplished by distillation, bp 99–102 °C (0.4 mmHg): ^{1}H NMR ($CDCl_3$) ($CHCl_3$) δ 0.83 (t, 3, J = 7.8 Hz), 1.15–1.67 (m, 12), 1.84–1.89 (br s, 1), 2.03–2.19 (m, 4), 3.60 (t, 2, J = 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ 13.84, 18.53, 18.72, 22.48, 25.46, 28.49, 29.12, 31.33, 31.94, 62.43, 79.73, 80.69; IR (neat) 3340 cm^{-1}. Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 78.90; H, 12.18.

11-Dodecyn-1-ol. This compound was prepared by isomerization[70,71] of the previous product. At room temperature 3.31 g (18.2 mmol) of 5-dodecyn-1-ol was added under argon to 90 mL (61 mmol) of potassium 3-aminopropylamine (KAPA).[72,73] After vigorous stirring for 1.5 h, the reaction was quenched by addition of 10 mL of water with ice cooling. The reaction mixture was transferred to a separatory funnel and further diluted with 100 mL of water and 100 mL of ether. The aqueous phase was extracted with ether (3 × 50 mL), and then 100 mL of cold 20% HCl was added to the aqueous phase. After mixing the aqueous phase was extracted again with ether (3 × 50 mL). The combined ethereal extracts were washed with water (1 × 50 mL), saturated ammonium chloride (3 × 50 mL), water (1 × 50 mL), and saturated sodium bicarbonate (1 × 50 mL) and dried over potassium carbonate. Filtration and removal of the solvent under reduced pressure provided 3.30 g (100%) of a pale yellow liquid. Sublimation, 50–60 °C (0.2 mmHg) [lit.[74] bp 83–86 °C (0.005 mmHg)], provided pure product as a waxy white solid, mp 28–30 °C: ^{1}H NMR ($CDCl_3$) δ 1.15–1.67 (m, 16), 1.97 (t, 1, J = 2.6 Hz), 2.12 (dt, 2, J = 2.6, 6.9 Hz), 3.63 (t, 2, J = 6.6 Hz); ^{13}C NMR ($CDCl_3$) δ 18.34, 25.72, 28.48, 28.68, 29.00, 29.35, 29.47, 32.81, 62.94, 67.98, 84.66; IR (neat) 3340, 3308, 2920, 2850, 2105, 1050 cm^{-1}. The ^{1}H NMR and IR spectra matched the published data.[75]

11-Dodecyn-1-yl Acetate (4). This compound was prepared in a 93.6% by the acylation[76] of 11-dodecyn-1-ol: ^{1}H NMR ($CDCl_3$) ($CHCl_3$) δ 1.15–1.61 (m, 16), 1.88 (t, 1, J = 2.8 Hz), 1.98 (s, 3), 2.12 (dt, 2, J = 2.8, 7.0 Hz), 3.99 (t, 2, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 18.34, 20.81, 25.86, 28.47, 28.62, 28.67, 29.00, 29.33, 64.51, 67.98, 84.57, 170.90; IR (neat) 3300, 2100, 1740, 1235 cm^{-1}. The ^{1}H NMR and IR spectra matched the published data.[75]

12-(Trimethylstannyl)-11-dodecyn-1-yl Acetate (3). This compound was prepared by the reaction of the acetylene with the tin amide.[13] A mixture of 1.03 g (4.38 mmol) of (diethylamino)trimethylstannane and 0.973 g (4.34 mmol) of 11-dodecyn-1-yl acetate (**4**) was stirred at room temperature under nitrogen for 30 min before a white precipitate formed. Analysis by GLC (OV-17, TCD) indicated that the reaction had not gone to completion. After heating at 50 °C for 1 h all of the starting stannane was consumed. Purification by bulb-to-bulb distillation, 155–165 °C (0.01 mmHg), provided 1.26 g (75.0%) of a colorless homogeneous product: ^{1}H NMR ($CDCl_3$) ($CHCl_3$) δ 0.23 (s, 9), 1.15–1.38 (m, 12), 1.38–1.58 (m, 4), 2.02 (s, 3), 2.20 (t, 2, J = 7.2 Hz), 4.02 (t, 2, J = 6.7 Hz); ^{13}C NMR ($CDCl_3$) δ −7.88, 18.37, 20.07, 20.81, 25.91, 28.51, 28.68, 28.77, 29.03, 29.18, 29.37, 64.52, 81.84, 111.03, 170.88; IR (neat) 2140, 1743 cm^{-1}. This compound was somewhat unstable, so it was used in the coupling reaction immediately.

(*Z*)-13-Hexadecen-11-yn-1-yl Acetate (1). To a dry Schlenk tube was added 0.0204 g (0.0786 mmol) of $(MeCN)_2PdCl_2$. The system was flushed with nitrogen, and then 10 mL of DMF was added. The solution was degassed 3 times by evacuating to 10 mmHg and flushing with nitrogen. To the yellow solution was added 0.156 g (0.857 mmol) of (*Z*)-1-iodo-1-butene (**2**) (dry and iodine free) which caused the yellow solution to darken. The mixture was then stirred at 22–25 °C for 5 min before 0.603 g (1.56 mmol) of freshly prepared and distilled (12-(trimethylstannyl)-11-dodecyn-1-yl acetate (**3**) was added. The reaction mixture immediately became black. Analysis by GLC (DB1, FID) indicated that the reaction had gone to completion. This mixture was added to 50 mL of water and extracted with 25 mL of ether. The aqueous phase was back-extracted with 10 mL of ether, and the combined ethereal extracts were washed with water (3 × 10 mL) and brine

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(1 × 10 mL). The organics were dried over potassium carbonate and filtered through a plug of alumina. Removal of the solvents under reduced pressure resulted in a yellow liquid. Analysis by ^{1}H NMR indicated that the *Z* isomer was the only coupled product. Further purification was accomplished by radial chromatography by using hexane–ethyl acetate (9:1). The resulting product was contaminated by 11-dodecynyl acetate produced from the hydrolysis of excess tin reagent. This terminal acetylene was removed by radial chromatography on a 2-mm silica gel plate impregnated with 10% silver nitrate by using hexane–ethyl acetate (95:5). Removal of the solvents provided 0.206 g (86.2%) of a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 1.00 (t, 3, J = 7.5 Hz), 1.24–1.47 (m, 12), 1.47–1.69 (m, 4), 2.04 (s, 3), 2.24–2.36 (m, 4), 4.05 (t, 2, J = 6.7 Hz), 5.41 (dt, 1, J = 1.5, 10.6 Hz, CH=C*H*—C≡C), 5.81 (dt, J = 7.2, 10.6 Hz, C*H*=CH—C≡C); ^{13}C NMR ($CDCl_3$) δ 13.34, 19.52, 20.84, 23.35, 25.93, 28.67, 28.84, 28.92, 29.09, 29.22, 29.41, 64.58, 77.32, 94.46, 108.93, 143.82, 170.97; IR (neat) 3010, 2185, 1736, 1228, 720 cm^{-1}. The ^{1}H NMR, ^{13}C NMR, and IR spectra matched the published data.[27,77]

Dienyne 5 from *Crysanthemum macrotum*: Scheme II. 2-Ethynylthiophene. To a dry and degassed solution of 0.130 g (0.500 mmol) of $(MeCN)_2PdCl_2$ in 100 mL of DMF was added 2.10 g (10.0 mmol) of 2-iodothiophene and 4.72 g (15.0 mmol) of ethynyltributylstannane. Addition of the stannane caused the orange solution to immediately turn black. The mixture was then stirred at 22–25 °C for 48 h. Analysis by GLC (DB1, FID) indicated complete consumption of the iodide. This mixture was diluted with 200 mL of ether and washed with 50 mL of water. The aqueous phase was diluted with 100 mL of water and back-extracted with 50 mL of ether. The combined ethereal extracts were washed with water (3 × 50 mL) and brine (1 × 50 mL) and dried over magnesium sulfate. The ether was removed by distillation by using a concentrator condenser at 40 °C under argon. The residue was bulb-to-bulb distilled, bp 65–67 °C (117 mmHg) [lit.[78] bp 46 °C (15 mmHg)], to provide 0.911 g (84.4%) of a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 3.33 (s, 1), 6.96 (dd, 1, J = 3.6, 5.2 Hz), 7.24–7.28 (m, 2); ^{13}C NMR ($CDCl_3$) δ 81.07, 122.40, 126.84, 127.38, 133.02; IR (neat) 3300, 3110, 2290, 1418, 1225, 846 cm^{-1}. The ^{1}H NMR[78] and IR[79] spectra matched the published data.

2-(2-Thienyl)-1-(trimethylstannyl)ethyne. Method 1.[13] Synthesis Using (Diethylamino)trimethylstannane.[53,54] Under anhydrous conditions 0.283 g (1.20 mmol) of (diethylamino)trimethylstannane was added to 0.120 g (1.12 mmol) of 2-ethynylthiophene. Analysis by GLC (DB1, FID) indicated complete consumption of the starting alkyne after 17 h of stirring at 22–25 °C. Distillation by bulb-to-bulb distillation, bp 94–96 °C (6 mmHg), provided 0.279 g (92.3%) of a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 0.36 (s, 9), 6.93 (dd, 1, J = 3.8, 5.1 Hz), 7.17–7.26 (m, 2); ^{13}C NMR ($CDCl_3$) δ −7.78, 101.29, 126.39, 126.64, 131.91; IR (neat) 2980, 2910, 2118 cm^{-1}. This compound was used immediately after its preparation.

(*E*)-Tributyl[4-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1-butenyl]stannane. This compound was prepared by using known methodology. An ethereal solution of methylmagnesium iodide (1.3 M, 25 mL, 32.9 mmol) was added to a THF solution of tributylstannyllithium, prepared from 5.66 g (30.0 mmol) of anhydrous stannous chloride and 38 mL (90 mmol, 2.4 M) of *n*-butyllithium at 0 °C under argon atmosphere. After stirring for 15 min, 0.134 g (1.50 mmol) of cuperous cyanide and 1.54 g (10.0 mmol) of tetrahydro-1-[(3-butynyl)oxy]-2*H*-pyran in 50 mL of dry THF was added, and the reaction mixture was stirred for 1 h at 0 °C. Cautiously, water was added until no further reaction was observed. The reaction mixture was extracted with ether, washed with water and brine, and then dried over sodium sulfate. Flash chromatography through alumina using pentane provided 3.12 g (70.0%) of a pale yellow liquid. Further purification was achieved by bulb-to-bulb distillation, bp 104–106 °C (0.07 mmHg): ^{1}H NMR ($CDCl_3$) δ 0.72–1.01 (m, 15), 1.17–1.39 (m, 6), 1.39–1.91 (m, 12), 2.39–2.50 (m, 2), 3.35–3.55 (m, 2), 3.74–3.92 (m, 2), 4.61 (t, 1, J = 2.9 Hz), 5.98 (t, 2, J = 2.9 Hz); ^{13}C NMR ($CDCl_3$) δ 9.61, 13.58, 19.56, 25.68, 27.23, 29.15, 30.82, 38.23, 62.14, 66.99, 98.76, 129.98, 145.77; IR (neat) 2925, 1600, 980 cm^{-1}. Anal. Calcd for $C_{21}H_{45}O_2Sn$: C, 56.65; H, 9.51. Found: C, 56.54; H, 9.46.

(*E*)-Tetrahydro-2-[(4-iodo-3-butenyl)oxy]-2*H*-pyran (9). Method 1. This compound was prepared by cleavage of the vinyl tin with iodine.[14] To a solution of 4.44 g (10.0 mmol) of (*E*)-tributyl[4-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1-butenyl]stannane in 100 mL of methylene chloride was added a solution of 2.54 g (10.0 mmol) of iodine in 125 mL of methylene chloride until a pink color persisted. The methylene chloride was then removed at reduced pressure, and 100 mL of half-saturated potassium fluoride and 200 mL of ether were added. After stirring overnight, the precipitates were removed by filtration through glass wool, and the phases were then separated. The aqueous phase was back-extracted with ether (1 × 50 mL), and the combined ethereal extracts were washed with water (3 × 50 mL) and brine (1 × 50 mL) and dried over potassium carbonate. Further purification was achieved by MPLC on silica gel by using hexane–ethyl acetate (9:1). From the chromatography, 1.86 g (66.1%) of product **9** was isolated. The product was bulb-to-bulb distilled, bp 84–85 °C (0.15 mmHg): ^{1}H NMR ($CDCl_3$) δ 1.45–1.93 (m, 6), 2.35 (q, 2, J = 6.8 Hz), 3.39–3.57 (m, 2), 3.73–3.94 (m, 2), 4.58 (br s, 1), 6.11 (d, 1, J = 14.3 Hz), 6.57 (dt, 1, J = 7.1, 14.3 Hz); ^{13}C NMR ($CDCl_3$) δ 19.52, 25.52, 30.69, 36.32, 62.27, 65.68, 76.07, 98.82, 143.17; IR (neat) 2940, 1605, 975, 935 cm^{-1}. Anal. Calcd for $C_9H_{15}IO_2$: C, 38.32; H, 5.36. Found: C, 38.41; H, 5.38.

Method 2. This compound was prepared by hydrozirconation of the acetylene followed by cleavage with iodine.[15,35] To a solution of 5.38 g (20.9 mmol) of $Cp_2Zr(Cl)H$[30,80] in 20 mL of dry benzene was added 2.69 g (17.5 mmol) of tetrahydro-2-[(3-butynyl)oxy]-2*H*-pyran at 22–25 °C. The white suspension had turned to an orange solution after stirring for 5.5 h in the dark. Sufficient iodine (ca. 4.4 g) was added to maintain the pink color of iodine. This mixture was transferred to a separatory funnel with 100 mL of ether and washed with 100 mL of water. The aqueous phase was back-extracted with 25 mL of ether. The combined ethereal extracts were washed with water (1 × 25 mL), 10% sodium thiosulfate (2 × 25 mL), and brine (1 × 25 mL) and dried over potassium carbonate. The dried ethereal solution was filtered through a plug of alumina and concentrated under reduced pressure. The resulting residue was purified by MPLC by using hexane–ethyl acetate (9:1) on silica gel. Removal of the solvents provided 7.92 g (59.1%) of isomerically pure product. The spectral data were consistent with the previous product.

(*E*)-Tetrahydro-2-[(3-hexen-5-ynyl)oxy]-2*H*-pyran. Method 1. Synthesis Using $(MeCN)_2PdCl_2$. To a 10-mL Schlenk tube was added 0.0065 g (0.025 mmol) of $(MeCN)_2PdCl_2$ and 5.0 mL of DMF. This solution was degassed 3 times by evacuating to 7 mmHg and flushing with argon. Under a stream of argon, 0.123 g (0.436 mmol) of (*E*)-tetrahydro-2-[(4-iodo-3-butenyl)oxy]-2*H*-pyran (**9**) and 0.158 g (0.500 mmol) of ethynyltributylstannane were added. Upon addition of the stannane at 22–25 °C, the reaction mixture instantaneously turned black. Analysis by GLC (DB1, FID) indicated complete consumption of the iodide. Water (5 mL) was added to the reaction mixture followed by transferring to a separatory funnel with the aid of 50 mL of ether. The phases were separated, and the aqueous phase was diluted with 25 mL of water and back-extracted with 10 mL of ether. The combined ethereal extracts were washed with water (3 × 10 mL) and stirred for 1 h with 25 mL of half-saturated potassium fluoride. The resulting precipitate was removed by filtering through glass wool, and the phases were separated. The ethereal phase was washed with water (2 × 10 mL) and brine (1 × 10 mL) and dried over potassium carbonate. Further purification was achieved by radial chromatography by using hexane–ethyl acetate (95:5) followed by bulb-to-bulb distillation, bp 74–75 °C (0.07 mmHg), to yield 0.0819 g (90.9%) of a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 1.45–1.93 (m, 6), 2.40 (q, 1, J = 6.4 Hz), 2.80 (d, 1, J = 1.5 Hz), 3.40–3.56 (m, 2), 3.74–3.92 (m, 2), 4.59 (t, 1, J = 3.9 Hz), 5.54 (dt, 1, J = 1.5, 16.1 Hz), 6.28 (dt, 1, J = 6.8, 16.1 Hz); ^{13}C NMR ($CDCl_3$) δ 19.56, 25.62, 30.78, 33.52, 62.27, 66.15, 75.90, 82.42, 98.92, 110.53, 142.95; IR (neat) 3300, 2940, 2098, 1632, 950 cm^{-1}. Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.39; H, 8.96.

Method 2. Synthesis Using $(PPh_3)_2PdCl_2$. Under similar anaerobic conditions as previously employed, the system was charged with 0.0175 g (0.0249 mmol) of $(PPh_3)_2PdCl_2$, 5.0 mL of DMF, 0.141 g (5.00 mmol) of (*E*)-tetrahydro-2-[(4-iodo-3-butenyl)oxy]-2*H*-pyran (**9**), and 0.158 g (0.500 mmol) of ethynyltributylstannane. By GLC (DB1, FID) analysis, complete consumption of the iodide required 9 h at 22–25 °C. An aqueous and potassium fluoride workup, followed by purification by using radial chromatography with hexane–ethyl acetate (95:5) afforded 0.0802 g (89.0%) of product **10**. Spectral data was consistent with the previous product.

(3*E*,5*E*)-Tetrahydro-2-[(6-iodo-3,5-hexadienyl)oxy]-2*H*-pyran (8). This compound was prepared by a hydrozirconation[15]–iodination[14] sequence. To a solution of 0.261 g (1.01 mmol) of $Cp_2Zr(Cl)H$[30,80] in 1.5 mL of dry benzene was added 0.174 g (0.967 mmol) of (*E*)-tetrahydro-2-[(3-hexen-5-ynyl)oxy]-2*H*-pyran (**10**) at 22–25 °C. The white suspension had turned to a yellow solution after stirring for 1.5 h in the dark.

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Sufficient iodine (ca. 0.25 g) was added to maintain the pink color of iodine. This mixture was transferred to a separatory funnel with 50 mL of ether and washed with 50 mL of water. The aqueous phase was back-extracted with 25 mL of ether. The combined ethereal extracts were washed with water (3 × 25 mL), 10% sodium thiosulfate (1 × 25 mL), and brine (1 × 25 mL) and dried over potassium carbonate. The dried extracts were filtered through a plug of alumina and concentrated under reduced pressure. Analysis by ^{1}H NMR indicated that stereochemically pure **8** and (*E*)-tetrahydro-2-[(3,5-hexadienyl)oxy]-2*H*-pyran had been isolated as a 60:40 mixture. From the isolated mass of 0.256 g and the ^{1}H NMR integration, it was determined that 47.1% of **8** had been produced: ^{1}H NMR ($CDCl_3$) δ 1.42–1.88 (m, 6), 2.34 (q, 2, J = 6.8 Hz), 3.39–3.55 (m, 2), 3.72–3.90 (m, 2), 4.58 (t, 1, J = 3.4 Hz), 4.98 (d, 1, J = 10.2 Hz, $H_t(H_c)$C=CH—CH=CH), 5.10 (d, 1, J = 17.1 Hz, $H_t(H_c)$C=CH—CH=CH), 5.51–5.58 (m, 1, $H_t(H_c)$C=CH—CH=CH), 5.75 (dt, 1, J = 6.8, 15.1 Hz, I—CH=CH—CH=C*H*), 6.04 (dd, 1, J = 10.3, 15.1 Hz, I—CH=CH—C*H*=CH), 6.19 (d, 1, J = 14.2 Hz, I—C*H*=CH—CH=CH), 6.20–6.35 (m, 1, $H_t(H_c)$C=CH—CH=CH), 6.50–6.62 (m, 1, $H_t(H_c)$C=CH—CH=CH), 6.99 (dd, 1, J = 10.3, 14.2 Hz, I=CH=C*H*—CH=CH).

A small sample of this mixture was chromatographed by MPLC by using hexane–ethyl acetate (95:5). Removal of the solvents provided a mixture of stereoisomers plus (*E*)-tetrahydro-2-[(3,5-hexadienyl)oxy]-2*H*-pyran. The 3*E*,5*Z* isomer has a ^{1}H NMR absorption at 6.70 (dd, 1, J = 6.8, 10.3 Hz, I—CH=CH—CH=CH).

The reaction of (*E*)-**10** with tributylstannylmagnesium methyl[18] followed by protonation and iodination gave an 80:20 mixture of (3*E*,5*E*):(3*E*,5*Z*)-**8**—uncontaminated with (*E*)-tetrahydro-2-[(3,5-hexadienyl)oxy]-2*H*-pyran—which on purification by radial chromatography gave a 63:37 *E*,*E*:*E*,*Z* ratio of analytically pure product. Anal. Calcd for $C_{11}H_{17}IO_2$: C, 42.87; H, 5.56. Found: C, 42.62; H, 5.55.

(3*E*,5*E*)-Tetrahydro-2-[(8-(2-thienyl)-3,5-octadien-7-ynyl)oxy]-2*H*-pyran (6). To a solution of 0.0057 g (0.022 mmol) of $(MeCN)_2PdCl_2$ in 4 mL of dry DMF was added 0.189 g of a mixture containing 0.439 mmol of (3*E*,5*E*)-tetrahydro-2-[(6-iodo-3,5-hexadienyl)oxy]-2*H*-pyran (**8**) and 0.293 mmol of (*E*)-tetrahydro-2-[(3,5-hexadienyl)oxy]-2*H*-pyran. To this mixture was added 0.119 g (0.439 mmol) of 2-(2-thienyl)-1-(trimethylstannyl)ethyne (**7**). Addition of the stannane caused the mixture to immediately turn black. Analysis by GLC (DB1, FID) indicated complete consumption of the starting iodide within 5 min of adding the stannane. This black mixture was transferred to a separatory funnel with the aid of 25 mL of ether and washed with 25 mL of water. The aqueous phase was diluted with 20 mL of water and extracted with ether (3 × 10 mL). The combined ethereal extracts were washed with water (3 × 10 mL) and brine (1 × 10 mL) and dried over potassium carbonate. The dried extracts were filtered through a plug of alumina. Removal of the solvents under reduced pressure gave 0.169 g of a red oil containing a 60:40 mixture of **6** and (*E*)-tetrahydro-2-[(3,5-hexadienyl)oxy]-2*H*-pyran. Purification by radial chromatography by using hexane–ethyl acetate (95:5) provided 0.118 g (93.2%) of isomerically pure product **6**: ^{1}H NMR ($CDCl_3$) δ 1.38–1.86 (m, 6), 2.37 (q, 2, J = 6.8 Hz), 3.36–3.50 (m, 2), 3.69–3.86 (m, 2), 4.54 (t, 1, J = 4.4 Hz), 5.66 (d, 1, J = 15.1 Hz, C≡C—C*H*=CH—CH=CH), 5.80 (dt, 1, J = 6.8, 15.1 Hz, C≡C—CH=CH—CH=C*H*), 6.14 (dd, 1, J = 10.7, 15.1 Hz, C≡C—CH=CH—C*H*=CH), 6.58 (dd, 1, J = 11.2, 15.6 Hz, C≡C—CH=C*H*—CH=CH), 6.88–6.93 (m, 1), 7.10–7.20 (m, 2); ^{13}C NMR ($CDCl_3$) δ 19.56, 25.52, 70.72, 33.29, 62.25, 66.57, 84.57, 92.92, 98.82, 109.09, 123.88, 126.90, 126.97, 131.40, 134.44, 141.89; IR (neat) 3100, 3020, 2940, 2870, 2250, 1643, 1445, 1387, 1203, 1138, 1123, 1073, 1030, 975, 900, 840 cm^{-1}. This compound was carried on to the known alcohol **5**.

(3*E*,5*E*)-8-(2-Thienyl)-3,5-octadien-7-yn-1-ol (5). This compound was prepared by deprotection of **6** under mild conditions.[45] To a solution of 0.0243 g (0.0843 mmol) of (3*E*,5*E*)-tetrahydro-2-[(8-(2-thienyl)-3,5-octadien-7-ynyl)oxy]-2*H*-pyran (**6**) in 1 mL of absolute ethanol was added 0.0020 g (0.0080 mmol) of pyridinium *p*-toluene sulfinate (PPTS). This mixture was stirred at 55 °C for 3 h. Analysis by TLC using hexane–ethyl acetate (8:2) indicated consumption of the starting THP ether (R_f 0.45). The ethanol was removed under reduced pressure. To the residue was added 1 mL of ether. This ethereal solution was washed with half-saturated brine (3 × 0.5 mL) and dried over potassium carbonate. Removal of the ether provided 0.0167 g (97.1%) of a pale yellow liquid: ^{1}H NMR ($CDCl_3$) δ 1.54 (br s, 1, OH), 2.40 (q, 2, J = 6.8 Hz), 3.71 (t, 2, J = 6.4 Hz), 5.75 (d, 1, J = 15.6 Hz, C≡C—C*H*=CH—CH=CH), 5.82 (dt, 1, J = 7.8, 15.1 Hz, C≡C—CH=CH—CH=C*H*), 6.24 (dd, 1, J = 10.8, 14.6 Hz, C≡C—CH=CH—C*H*=CH), 6.64 (dd, 1, J = 10.8, 15.6 Hz, C≡C—CH=C*H*—CH=CH), 6.94–7.00 (m, 1), 7.15–7.28 (m, 2); ^{13}C NMR ($CDCl_3$) δ 36.18, 61.82, 84.83, 92.75, 109.67, 127.03, 131.52, 132.33, 133.51, 141.41; IR ($CHCl_3$) 3620, 3090, 3030, 2950, 2205, 1635, 1600, 1260, 1195, 1035 cm^{-1}; UV–vis ($CHCl_3$)$_{\lambda max}$ 341, 320 nm. The ^{1}H NMR, IR, and UV–vis spectra matched the published data.[28]

Pheremone of the Forest Tent Caterpillar: Scheme III. Trimethyl[(6-(tetrahydro-2*H*-pyran-2-yl)oxy)-1-hexynyl]trimethylstannane (14). Tetrahydro[(5-hexynyl)oxy]-2*H*-pyran (**20**) was prepared by the reaction of 5-hexyn-1-ol with dihydropyran to yield a product whose properties were identical with those reported.[35,81,82]

Method 1. Using (Diethylamino)trimethylstannane.[13] A mixture of 1.97 g (8.37 mmol) of (diethylamino)trimethylstannane and 1.37 g (7.53 mmol) of tetrahydro[(5-hexynyl)oxy]-2*H*-pyran (**20**) was stirred for 17 h at 22–25 °C. Analysis by GLC (OV-17, TCD) indicated complete consumption of the starting alkyne. Purification was achieved by distillation, bp 97–98 °C (0.15 mmHg), to yield 2.24 g (77.6%) of a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 0.25 (s, 9), 1.42–1.90 (m, 10), 2.28 (t, 2, J = 6.4 Hz), 3.41 (dt, 1, J = 6.3, 9.8 Hz), 3.46–3.55 (m, 1), 3.75 (dt, 1, J = 6.4, 9.8 Hz), 3.81–3.93 (m, 1), 4.58 (t, 1, J = 3.9 Hz); ^{13}C NMR ($CDCl_3$) δ −7.91, 19.65, 19.94, 25.62, 25.97, 29.02, 30.85, 62.22, 67.05, 82.14, 98.86, 110.68; IR (neat) 2930, 2855, 2130 cm^{-1}. Anal. Calcd for $C_{14}H_{26}O_2Sn$: C, 48.73; H, 7.59. Found: C, 48.94; H, 7.69.

Method 2. Using *n*-Butyllithium. To a solution of 1.82 g (10.0 mmol) of tetrahydro-2-[(5-hexynyl)oxy]-2*H*-pyran (**20**) in 40 mL of dry ether was added dropwise 6.0 mL (10.5 mmol, 1.74 M) of *n*-butyllithium at −78 °C. This mixture was stirred for 30 min at −78 °C followed by warming to 0 °C and stirring for 30 min. To this mixture was added dropwise a solution of 2.1 g (10.5 mmol) of trimethyltin chloride in 25 mL of dry ether at −78 °C. This reaction mixture was slowly warmed to room temperature over a 12-h period. The ether was removed by fractional distillation and then all volatiles were vacuum transferred at 0.25 mmHg with an oil bath temperature of 137–140 °C. Further purification was achieved by distillation, bp 104–105 °C (0.25 mmHg), to yield 2.93 g (85.1%) of a colorless liquid. Spectral data was consistent with the previous product.

(*E*)-Tetrahydro-2-[(7-dodecen-5-ynyl)oxy]-2*H*-pyran (17). To a solution of 0.0659 g (0.254 mmol) of $(MeCN)_2PdCl_2$ in 40 mL of dry DMF was added 0.549 g (4.99 mmol) of (*E*)-1-iodohexene (**13**) and 1.96 g (5.68 mmol) of tetrahydro-2-[(6-(trimethylstannyl)-5-hexynyl)oxy]-2*H*-pyran (**14**). The yellow solution immediately turned black upon addition of the stannane. This reaction mixture was stirred for 40 min at 22–25 °C. Analysis by GLC (DB1, FID) indicated complete consumption of the vinyl iodide. The reaction mixture was transferred to a separatory funnel with 150 mL of ether and washed with 50 mL of water. The aqueous phase was diluted with 100 mL of water and back-extracted with 50 mL of ether. The combined ethereal extracts were washed with water (3 × 50 mL) and brine (1 × 50 mL) and dried over potassium carbonate. The solvents were removed under reduced pressure, and the remaining liquid was purified by MPLC by using hexane–ethyl acetate (95:5). Removal of the solvents provided 1.20 g (90.8%) of the pure *E* product **46**: ^{1}H NMR ($CDCl_3$) δ 0.89 (t, 3, J = 7.3 Hz), 1.22–1.92 (m, 14), 2.07 (q, 2, J = 6.8 Hz), 2.32 (t, 2, J = 4.9 Hz), 3.40 (dt, 1, J = 6.4, 9.8 Hz), 3.45–3.56 (m, 1), 3.76 (dt, 1, J = 6.8, 9.8 Hz), 3.81–3.92 (m, 1), 4.58 (t, 1, J = 3.9 Hz), 5.44 (dt, 1, J = 1.5, 16.1 Hz, CH=C*H*—C≡C), 6.04 (dt, 1, J = 6.8, 16.1 Hz, C*H*=CH—C≡C); ^{13}C NMR ($CDCl_3$) δ 13.68, 19.28, 19.69, 22.12, 25.65, 25.85, 29.12, 30.88, 32.52, 62.24, 67.06, 79.63, 88.30, 98.91, 110.11, 143.08; IR (neat) 3015, 2940, 2875, 2210, 1138, 1118, 1075, 1030, 953 cm^{-1}. The ^{1}H NMR and IR spectra matched the published data.[35]

(5*Z*,7*E*)-5,7-Dodecadien-1-ol (11). Reduction of 17 by Disiamylborane[27] Followed by Deprotection. A THF solution of disiamylborane (2.26 mmol), which was prepared from a 10 M solution of borane–methylsulfide and 2-methyl-2-butene, was slowly added to a solution of 0.370 g (1.40 mmol) of (*E*)-tetrahydro-2-[(7-dodecen-5-ynyl)oxy]-2*H*-pyran (**17**) in dry THF (2 mL) cooled to −5 °C. The mixture was stirred for 5 h at 0 °C, then 0.53 mL of acetic acid was added, and the mixture was heated for 12 h at 60 °C. After evaporation of the volatile substances under reduced pressure, 3 mL of 6 N sodium hydroxide was added, followed by addition of 0.8 mL of 30% hydrogen peroxide, while maintaining the temperature below 40 °C. The mixture was stirred for 40 min at 40 °C and cooled. Brine (10 mL) was added, and the mixture was transferred to a separatory funnel with the aid of 40 mL of ether. The phases were separated, and the organics were washed with half-saturated brine (3 × 20 mL) and brine (1 × 10 mL) and dried over potassium carbonate. The concentrated extracts were purified by radial chromatography by using hexane–ethyl acetate (95:5). Removal of the solvent provided 0.322 g (86.4%) of a pale yellow liquid: ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 3, J = 7.3 Hz), 1.23–1.90 (m, 14), 2.09 (q, 2, J = 6.8 Hz), 2.19 (dq, 2, J = 1.0, 7.3 Hz), 3.38 (dt, 1, J = 6.3, 9.8 Hz),

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3.44–3.55 (m, 1), 3.74 (dt, 1, J = 6.8, 9.3 Hz), 3.81–3.92 (m, 1), 4.58 (t, 1, J = 4.4 Hz), 5.29 (t, 1, J = 7.3, 10.7 Hz, CH=CH—CH=C*H*), 5.65 (dt, 1, J = 6.8, 15.1 Hz, C*H*=CH—CH=CH), 5.95 (t, 1, J = 10.7 Hz, CH=CH—C*H*=CH), 6.29 (ddd, 1, J = 1.5, 11.2, 15.1 Hz, CH=C*H*—CH=CH); ^{13}C NMR ($CDCl_3$) δ 13.73, 19.66, 22.19, 25.64, 26.51, 27.52, 29.44, 30.85, 31.62, 32.43, 62.14, 67.40, 98.82, 125.78, 129.03, 129.49, 134.61; IR (neat) 3017, 2925, 2850, 1645, 1465, 1450, 1387, 1133, 1115, 1073, 1030, 975, 920 cm^{-1}. This compound was carried on to the known alcohol **11**.

Deprotection of the alcohol was accomplished by acid catalysis.[69] A solution of 0.108 g (0.406 mmol) of (5*Z*,7*E*)-tetrahydro-2-[(5,7-dodecadienyl)oxy]-2*H*-pyran and 0.0102 g (0.0406 mmol) of PPTS in 3.2 mL of absolute ethanol was heated to 55 °C for 3 h. Analysis by TLC using hexane–ethyl acetate (8:2) indicated complete consumption of the tetrahydropyranyl ether (R_f 0.56). The ethanol was removed under reduced pressure, and the resulting oil was transferred to a separatory funnel with 40 mL of ether. The organics were washed with half-saturated brine (3 × 20 mL) and brine (1 × 20 mL) and dried over potassium carbonate. Removal of the solvent provided 0.0726 g (98.2%) of a pale yellow liquid: ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 3, J = 7.3 Hz), 1.71–1.81 (m, 8), 2.09 (q, 2, J = 6.8 Hz), 2.19 (q, 2, J = 7.8 Hz), 2.25–2.35 (m, 1, OH), 3.62 (t, 2, J = 6.3 Hz), 5.28 (dt, 1, J = 7.3, 10.7 Hz, CH=CH—CH=C*H*), 5.66 (dt, 1, J = 7.3, 14.6 Hz, C*H*=CH—CH=CH), 5.95 (t, 1, J = 11.2 Hz, CH=CH—C*H*=CH), 6.28 (ddd, 1, J = 1.0, 10.7, 14.6 Hz, CH=C*H*—CH=CH); ^{13}C NMR ($CDCl_3$) δ 13.72, 22.17, 25.94, 27.39, 31.56, 32.39, 62.72, 125.62, 129.15, 129.25, 134.80; IR (neat) 3330, 3015, 2950, 2920, 2850, 1645, 1463, 1453, 1430, 1405, 1373, 1050, 1025, 975, 942, 825, 720 cm^{-1}. The ^{1}H NMR,[83] ^{13}C NMR,[82] and IR[83] spectra matched the published data.

Pheremone of the Pine Moth: Scheme III. (*E*)-Tetrahydro-2-[(5-dodecen-7-ynyl)oxy]-2*H*-pyran (17). The *E*-vinyl iodide[10] required for the coupling reaction was obtained by the hydrozirconation of tetrahydro-2-[(5-hexynyl)oxy]-2*H*-pyran (**20**) followed by iodination to yield (*E*)-tetrahydro-2-[(6-iodo-5-hexenyl)oxy]-2*H*-pyran (**19**).[35] To a solution of 0.0184 g (0.0708 mmol) of $(MeCN)_2PdCl_2$ in 10 mL of dry DMF was added 0.439 g (1.42 mmol) of (*E*)-tetrahydro-2-[(6-iodo-5-hexenyl)-2*H*-pyran and 0.347 g (1.42 mmol) of 1-hexynyltrimethylstannane (**18**). The yellow solution immediately turned black upon addition of the stannane. This reaction mixture was stirred for 30 min at 22–25 °C. Analysis by GLC (DB1, FID) indicated complete consumption of the vinyl iodide. The reaction mixture was transferred to a separatory funnel with the aid of 50 mL of ether and washed with 25 mL of water. The aqueous phase was diluted with 25 mL of water and back-extracted with 25 mL of ether. The combined ethereal extracts were washed with water (3 × 10 mL) and brine (1 × 10 mL) and dried over potassium carbonate. The dried extracts were filtered through a plug of alumina and concentrated under reduced pressure. The resulting liquid was purified by radial chromatography by using hexane–ethyl acetate (95:5). Removal of the solvents provided 0.356 g (95.0%) of a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 0.91 (t, 3, J = 7.3 Hz), 1.31–1.92 (m, 14), 2.11 (q, 2, J = 7.3 Hz), 2.28 (dq, 2, J = 2.0, 6.8 Hz), 3.37 (dt, 1, J = 6.4, 9.8 Hz), 3.44–3.54 (m, 1), 3.72 (dt, 1, J = 6.8, 9.8 Hz), 3.80–3.90 (m, 1), 4.57 (t, 1, J = 2.4 Hz), 5.46 (dt, 1, J = 2.0, 15.6 Hz, CH=C*H*—C≡C), 6.03 (dt, 1, J = 7.3, 15.6 Hz, C*H*=CH—C≡C); ^{13}C NMR ($CDCl_3$) δ 13.37, 18.98, 19.59, 21.90, 25.59, 25.65, 29.24, 30.79, 30.98, 32.59, 62.12, 67.21, 79.22, 88.65, 98.79, 110.38, 142.50; IR (neat) 3020, 2930, 2870, 2210, 1467, 1453, 1440, 1353, 1135, 1118, 1075, 1030, 953, 980, 725 cm^{-1}. The ^{1}H NMR and IR spectra matched the published data.[35]

(5*E*,7*Z*)-5,7-Dodecadien-1-ol (15). This compound was prepared by the reduction of **17** by disiamylborane.[27] A solution of disiamylborane (1.95 mmol), which was prepared from a 10 M solution of borane–methylsulfide and 2-methyl-2-butene, was slowly added to a solution of 0.318 g (1.20 mmol) of (*E*)-tetrahydro-2-[(5-dodecen-7-ynyl)oxy]-2*H*-pyran (**17**) in dry THF (2 mL) cooled to −3 °C. The mixture was stirred for 5 h at 0 °C, then 0.46 mL of acetic acid was added, and the mixture was heated for 12 h at 60 °C. After evaporation of the volatile substances under reduced pressure, 2.7 mL of 6 N sodium hydroxide was added, followed by addition of 0.7 mL of 30% hydrogen peroxide, while maintaining the temperature below 40 °C. The mixture was stirred for 40 min at 40 °C and cooled. Brine (10 mL) was added, and the mixture was transferred to a separatory funnel with the aid of 40 mL of ether. The phases were separated, and the organics were washed with half-saturated brine (3 × 20 mL) and brine (1 × 10 mL) and dried over potassium carbonate. The concentrated extracts were purified by radial chromatography by using hexane–ethyl acetate (95:5). Removal of the solvents provided 0.272 g (84.9%) of a pale yellow liquid: ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 3, J = 7.3 Hz), 1.16–1.93 (m, 14) 2.00–2.20 (m, 4), 3.38 (dt, 1, J = 6.8, 9.3 Hz), 3.45–3.55 (m, 1), 3.74 (dt, 1, J = 6.8, 9.8 Hz), 3.81–3.92 (m, 1), 4.58 (t, 1, J = 3.9 Hz), 5.30 (dt, 1, J = 7.3, 10.7 Hz, CH=CH—CH=C*H*), 5.65 (dt, 1, J = 6.8, 15.1 Hz, C*H*=CH—HC=CH), 5.94 (t, 1, J = 10.8 Hz, CH=CH—C*H*=CH), 6.31 (ddd, 1, J = 1.0, 10.7, 15.1 Hz, CH=C*H*—CH=CH); ^{13}C NMR ($CDCl_3$) δ 13.79, 19.69, 22.28, 25.66, 26.21, 27.42, 29.44, 30.91, 31.98, 32.62, 62.24, 67.44, 98.92, 126.10, 128.73, 130.11, 134.12; IR (neat) 3015, 2925, 2860, 1645, 1465, 1450, 1437, 1350, 1130, 1115, 1070, 1027, 975, 720 cm^{-1}. This compound was carried on to the known alcohol **15**.

Deprotection of the alcohol was accomplished by acid catalysis.[69] A solution of 0.100 g (0.376 mmol) of (5*E*,7*Z*)-tetrahydro-2-[(5,7-dodecadienyl)oxy]-2*H*-pyran and 0.0094 g (0.038 mmol) of PPTS in 3 mL of absolute ethanol was heated to 55 °C for 3 h. Analysis by TLC using hexane–ethyl acetate (8:2) indicated complete consumption of the tetrahydropyranyl ether (R_f 0.58). The ethanol was removed under reduced pressure, and the resulting oil was transferred to a separatory funnel with 40 mL of ether. The organics were washed with half-saturated brine (3 × 20 mL) and brine (1 × 20 mL) and dried over potassium carbonate. Removal of the solvent provided 0.0680 g (99.3%) of a pale yellow liquid: ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 3, J = 7.8 Hz), 1.14–1.68 (m, 8), 1.70–1.85 (br s, 1, OH), 1.95–2.27 (m, 4), 3.63 (t, 2, J = 6.4 Hz), 5.30 (dt, 1, J = 7.8, 10.7 Hz, CH=CH—CH=C*H*), 5.63 (dt, 1, J = 6.8, 15.2 Hz, C*H*=CH—CH=CH), 5.93 (t, 1, J = 10.7 Hz, CH=CH—C*H*=CH), 6.30 (ddd, 1, J = 1.0, 11.2, 15.2 Hz, CH=C*H*—CH=CH); ^{13}C NMR ($CDCl_3$) δ 13.75, 22.22, 25.59, 27.36, 31.91, 32.33, 32.46, 62.72, 126.16, 128.57, 130.18, 133.80; IR (neat) 3330, 3015, 2920, 2850, 1645, 1465, 1435, 1373, 1050, 1025, 975, 725 cm^{-1}. The ^{1}H NMR,[83] ^{13}C NMR,[82] and IR[83] spectra matched the published data.

Pheromone of the Silkworm Moth: Scheme IV. 1-Pentynyltrimethylstannane (28). Method 1. Using (Diethylamino)trimethylstannane.[13] Under anhydrous conditions, 0.524 g (7.70 mmol) of 1-pentyne (Farchan) was added to 1.65 g (7.00 mmol) of (diethylamino)trimethylstannane.[51,54] Analysis of GLC (OV-17, TCD) indicated complete consumption of the starting stannane after 12 h of stirring at 22–25 °C. Purification was achieved by distillation, bp 25 °C (0.25 mmHg) [lit.[13] bp 172 °C (760 mmHg)], and provided 1.54 g (95.1%) of a colorless liquid: ^{1}H NMR ($CDCl_3$) ($CHCl_3$) δ 0.23 (s, 9), 0.95 (t, 3, J = 7.3 Hz), 1.51 (sept, 2, J = 7.2 Hz), 2.19 (t, 2, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ −7.88, 13.30, 22.12, 22.51, 82.01, 110.86; IR (neat) 2138 cm^{-1}.

Method 2. Using Methyllithium.[57] To a solution of 3.27 g (48.1 mmol) of 1-pentyne (Farchan) in 50 mL of dry ether at −20 °C was added dropwise 28.6 mL (43.7 mmol) of methyllithium. The resulting white mixture was stirred for 1 h at −20 °C and then warmed to 0 °C. At 0 °C, 8.3 g (42 mmol) of trimethyltin chloride in 50 mL of dry ether was added. This mixture was slowly warmed to room temperature while stirring for 12 h. The ether was removed by fractional distillation; then all volatiles were vacuum transferred and collected at liquid nitrogen temperature. The distillate was concentrated at reduced pressure and then bulb-to-bulb distilled, bp 50–60 °C (0.03 mmHg) [lit.[13] bp 170 °C (760 mmHg)], to yield 9.62 g (99.0%) of a colorless liquid. Spectral data were consistent with the previous product.

10-Undecyn-1-ol.[70] This compound was prepared by the alkylation[84] of 1-nonynl (Farchan) with ethylene oxide to yield 3-undecyn-1-ol, followed by isomerization[70,71] with potassium 3-aminopropylamine (KAPA).[72,73]

Tetrahydro-2-[(10-undecynyl)oxy]-2*H*-pyran (25). A solution of 5.02 g (29.8 mmol) of 10-undecyn-1-ol, 3.76 g (44.7 mmol) of dihydropyran, and 0.75 g (3.0 mmol) of PPTS[69] in 250 mL of dry methylene chloride was stirred for 15 h at 22–25 °C. To the reaction mixture was added 650 mL of ether and 50 mL of half-saturated brine. The phases were separated, and the organics were washed with half-saturated brine (1 × 50 mL) and brine (1 × 50 mL) and dried over potassium carbonate. The crude product was purified by column chromatography on silica gel by using hexane–ethyl acetate (9:1). From the column was isolated 4.52 g of product. A second impure fraction yielded 2.56 g after radial chromatography by using hexane–ethyl acetate (95:5). The combine yield was 7.08 g (94.1%) of a colorless liquid. A small sample was purified by bulb-to-bulb distillation, bp 91–92 °C (0.22 mmHg): ^{1}H NMR ($CDCl_3$) δ 1.22–1.89 (m, 20), 1.94 (t, 1, J = 2.4 Hz), 2.17 (dt, 2, J = 2.4, 6.8 Hz), 3.38 (dt, 1, J = 6.8, 9.8 Hz), 3.45–3.56 (m, 1), 3.73 (dt, 1, J = 6.8, 9.3 Hz), 3.80–3.95 (m, 1), 4.58 (t, 1, J = 3.4 Hz); ^{13}C NMR ($CDCl_3$) δ 18.43, 19.72, 25.68, 26.30, 28.60, 28.77, 29.05, 29.41, 29.86, 30.92, 62.27, 67.67, 67.95, 84.70, 98.92; IR (neat) 3310, 2920, 2100, 1020 cm^{-1}. Anal. Calcd for $C_{16}H_{28}O_2$: C, 76.14; H, 11.18. Found: C, 76.04; H, 11.18.

Trimethyl[11-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1-undecynyl]stannane (23). Under anhydrous conditions, 0.812 g (3.22 mmol) of tetrahydro-

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(84) Hiemstra, H.; Sno, M. H. A. M.; Vign, R. J.; Speckamp, W. N. *J. Org. Chem.* **1985**, *50*, 4014.

2-[(10-undecynyl)oxy]-2*H*-pyran was added to 0.764 g (3.24 mmol) of (diethylamino)trimethylstannane.[13] Analysis by GLC (OV-17, TCD) indicated complete consumption of the starting alkyne after 17 h of stirring at 22–25 °C. Purification was accomplished by bulb-to-bulb distillation, bp 133–134 °C (0.23 mmHg), to yield 1.30 g (97.2%) of a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 0.26 (s, 9), 1.23–1.44 (m, 14), 1.44–1.65 (m, 4), 1.66–1.90 (m, 2), 2.23 (t, 2, J = 7.3 Hz), 3.38 (dt, 1, J = 6.3, 9.8 Hz), 3.45–3.56 (m, 1), 3.73 (dt, 1, J = 6.8, 9.8 Hz), 3.81–3.93 (m, 1), 4.58 (t, 1, J = 3.9 Hz); ^{13}C NMR ($CDCl_3$) δ −7.85, 19.69, 20.09, 25.60, 26.26, 28.83, 29.07, 29.41, 29.80, 30.85, 62.24, 67.66, 98.86, 111.09; IR (neat) 2930, 2860, 2150, 1455, 1440, 1135, 1118, 1075, 1032, 770 cm^{-1}. Anal. Calcd for $C_{19}H_{36}O_2Sn$: C, 54.97; H, 8.74. Found: C, 55.03; H, 8.78.

(*Z*)-1-Iodo-1-pentene (24). This compound was prepared by the diimide reduction[19] of 1-iodo-1-pentyne,[85] prepared by the iodination of 1-pentynyltrimethylstannane (**28**)[13] to yield 62.9% of a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 0.95 (t, 3, J = 8.2 Hz), 1.46 (sept, 2, J = 7.3 Hz), 2.05–2.16 (m, 2), 6.13–6.21 (m, 2); ^{13}C NMR ($CDCl_3$) δ 13.60, 21.29, 36.66, 82.12, 141.18; IR (neat) 3058, 2955, 2920, 1620, 680 cm^{-1}.[86]

(*E*)-Tributyl[11-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1-undecenyl]stannane. An ethereal solution of methylmagnesium iodide (1.45 mL, 3.00 mmol, 2.06 M) was added to a THF solution of tributylstannyllithium, prepared from 0.564 g (3.00 mmol) of anhydrous stannous chloride and 3.61 mL (9.00 mmol, 2.49 M) of *n*-butyllithium, at 0 °C under an argon atmosphere.[18] After stirring for 15 min, 0.0134 g (0.150 mmol) of cuprous cyanide and 0.252 g (1.00 mmol) of tetrahydro-2-[(10-undecyn-yl)oxy]-2*H*-pyran (**25**) in 5 mL of dry THF were added, and the reaction mixture was stirred for 1 h at 0 °C. Cautiously, water was added until no further reaction was observed. The reaction mixture was extracted with ether, washed with water and brine, and then dried over potassium carbonate. Purification was achieved by radial chromatography by using hexane–ethyl acetate (9:1). Removal of the solvents under reduced pressure provided 0.220 g (40.5%) of a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 9, J = 7.3 Hz), 1.15–1.88 (m, 20), 2.11 (q, 2, J = 5.9 Hz), 3.38 (dt, 1, J = 6.8, 9.3 Hz), 3.45–3.56 (m, 1), 3.73 (dt, 1, J = 6.8, 9.3 Hz), 3.81–3.94 (m, 1), 4.58 (t, 1, J = 3.9 Hz), 5.87 (s, 1), 5.92 (t, 1, J = 5.4 Hz); ^{13}C NMR ($CDCl_3$) δ 9.54, 13.59, 19.72, 25.65, 26.32, 27.23, 29.15, 29.51, 29.59, 29.86, 30.89, 37.87, 62.27, 67.69, 98.89, 127.09, 149.88; IR (neat) 2929, 2840, 1600, 1465, 1375, 1352, 1135, 1120, 1080, 1035, 990 cm^{-1}. Anal. Calcd for $C_{28}H_{56}O_2Sn$: C, 61.89; H, 10.39. Found: C, 61.49; H, 10.42.

(*E*)-Tetrahydro-2-[(11-iodo-10-undecenyl)oxy]-2*H*-pyran (27, R = THP). Method 1. Hydrozirconation.[35] To a solution of 0.572 g (2.23 mmol) of $Cp_2Zr(Cl)H$[30,80] in 2.2 mL of dry benzene was added 0.534 g (2.10 mmol) of tetrahydro-2-[(10-undecynyl)oxy]-2*H*-pyran at 22–25 °C. The white suspension had turned to a green solution after stirring 7 h in the dark. Sufficient iodine (ca. 0.53 g) was added to maintain the pink color of iodine. This mixture was transferred to a separatory funnel with 100 mL of ether and washed with water (3 × 25 mL), 10% sodium thiosulfate (2 × 25 mL) and brine (1 × 25 mL) and dried over potassium carbonate. The dried extracts were concentrated under reduced pressure, and purification was achieved by MPLC by using hexane–ethyl acetate (95:5). Removal of the solvents provided 0.716 g (89.6%) of a pale yellow liquid: ^{1}H NMR ($CDCl_3$) δ 1.19–1.95 (m, 20), 2.04 (q, 2, J = 6.9 Hz), 3.38 (dt, 1, J = 6.6, 9.6 Hz), 3.45–3.54 (m, 1), 3.73 (dt, 1, J = 6.8, 9.6 Hz), 3.82–3.91 (m, 1), 4.58 (t, 1, J = 2.8 Hz), 5.96 (dt, 1, J = 1.4, 14.4 Hz, CH=C*H*—I), 6.50 (dt, 1, J = 7.1, 14.4, C*H*=CH—I); ^{13}C NMR ($CDCl_3$) δ 19.72, 25.65, 26.26, 28.39, 28.90, 29.25, 29.41, 29.42, 30.89, 35.95, 62.24, 67.63, 73.99, 98.89, 146.74; IR (neat) 3050, 2930, 2860, 1610, 943 cm^{-1}. This compound was carried on to the free alcohol.

Method 2. Hydrostannation.[18] An ethereal solution of methylmagnesium iodide (1.45 mL, 3.00 mmol, 2.06 M) was added to a solution of tributylstannyllithium, prepared from 0.566 g (3.00 mmol) of anhydrous stannous chloride and 3.61 mL (9.00 mmol, 2.49 M) of *n*-butyllithium, at 0 °C under an argon atmosphere. After stirring for 15 min, 0.0134 g (0.150 mmol) of cuperous cyanide and 0.252 g (1.00 mmol) of tetrahydro-2-[(10-undecynyl)oxy]-2*H*-pyran (**25**) in 5 mL of dry THF were added, and the reaction mixture was stirred for 1 h at 0 °C. Cautiously, water was added until no further reaction was observed. The reaction mixture was extracted with ether, washed with water and brine, and then dried over potassium carbonate. Without further purification, the concentrated extract was dissolved in 10 mL of methylene chloride, and sufficient iodine in methylene chloride was added to maintain the pink color of iodine (ca. 0.254 g, 1.00 mmol). This mixture was concentrated under reduced pressure, and to the residue was added 10 mL of saturated potassium fluoride, 10 mL of water, and 25 mL of ether. This mixture was stirred for 1 h at room temperature. The resulting white precipitate was removed by filtration through glass wool, and the phases were separated. The organics were washed with water (3 × 25 mL) and brine (1 × 25 mL) and dried over potassium carbonate. Purification was achieved by radial chromatography by using hexane–ethyl acetate (9:1). Removal of the solvents provided 0.313 g (82.3%) of a colorless liquid. The spectral data was consistent with the previous product.

(*E*)-11-Iodo-10-undecen-1-ol (27, R = H). A solution of 0.386 g (1.02 mmol) of (*E*)-tetrahydro-2-[(11-iodo-10-undecenyl)oxy]-2*H*-pyran and 0.0025 g (0.010 mmol) of PPTS in 8 mL of absolute ethanol[69] was heated for 4 h at 55 °C. Analysis by TLC using hexane–ethyl acetate (8:2) indicated complete removal of the tetrahydropyranyl ether (R_f 0.51). All volatile components were removed under reduced pressure. To the residue was added 100 mL of ether. The organics were washed with water (1 × 25 mL), half-saturated brine (1 × 25 mL), and brine (1 × 25 mL) and dried over potassium carbonate. Further purification was achieved by MPLC on silica gel by using hexane–ethyl acetate at a flow rate of 7 mL/min. Removal of the solvents provided 0.278 g (94.0%) of a white solid, mp = 27–30 °C: ^{1}H NMR ($CDCl_3$) δ 1.26–1.79 (m, 14), 1.56 (t, 1, J = 6.5 Hz, OH), 2.04 (q, 2, J = 7.1 Hz), 3.63 (t, 2, J = 6.6 Hz), 5.96 (dt, 1, J = 0.8, 14.3 Hz, CH=C*H*—I), 6.50 (dt, 1, J = 7.0, 14.3 Hz, C*H*=CH—I); ^{13}C NMR ($CDCl_3$) δ 25.75, 28.35, 28.84, 29.22, 29.35, 29.41, 32.84, 35.90, 62.98, 73.99, 146.70; IR (neat) 3320, 3058, 2930, 2860, 1612, 945 cm^{-1}. This compound was carried on to the 1,3-enyne.

(*Z*)-Tetrahydro-2-[(12-hexadecen-10-ynyl)oxy]-2*H*-pyran (22). To a solution of 0.0135 g (0.0520 mmol) of $(MeCN)_2PdCl_2$ in 10 mL of dry DMF was added 0.196 g (1.00 mmol) of (*Z*)-1-iodo-1-pentene (**24**) and 0.431 g (1.04 mmol) of tetrahydro-2-[(11-(trimethylstannyl)-10-undecynyl)oxy]-2*H*-pyran (**23**). Upon addition of the tin reagent, the yellow solution immediately turned black. Analysis by GLC (DB1, FID) indicated complete consumption of the vinyl iodide, after 1 h at 22–25 °C. The reaction mixture was diluted with 100 mL of ether and washed with 50 mL of water. The aqueous phase was diluted with 50 mL of water and back-extracted with ether (2 × 25 mL). The combined ethereal extracts were washed with water (3 × 25 mL), 10% sodium thiosulfate (1 × 25 mL), and brine (1 × 25 mL) and dried over potassium carbonate. Removal of the ether under reduced pressure provided a liquid which was purified by radial chromatography by using hexane–ethyl acetate (9:1). Removal of the solvents provided 0.266 g (83.1%) of the pure *Z* product **22**. Further purification was achieved by bulb-to-bulb distillation, bp 93–96 °C (0.3 mmHg): ^{1}H NMR ($CDCl_3$) δ 0.93 (t, 3, J = 7.4 Hz), 1.16–1.95 (m, 15), 2.25 (t, 2, J = 7.3 Hz), 2.33 (dt, 2, J = 1.9, 6.7 Hz), 3.38 (dt, 1, J = 6.6, 9.6 Hz), 3.45–3.54 (m, 1), 3.72 (dt, 1, J = 6.9, 9.5 Hz), 3.81–3.91 (m, 1), 4.58 (t, 1, J = 2.8 Hz), 5.44 (dt, 1, J = 1.2, 10.7 Hz, CH=C*H*—C≡C), 5.81 (dt, 1, J = 7.3, 10.7 Hz, C*H*=CH—C≡C); ^{13}C NMR ($CDCl_3$) δ 13.62, 19.56, 19.72, 22.18, 25.68, 26.30, 28.89, 28.99, 29.12, 29.44, 29.50, 29.86, 30.92, 32.09, 62.27, 67.67, 77.61, 94.43, 98.91, 109.80, 141.98; IR (neat) 3020, 2930, 2858, 2205, 1615, 730 cm^{-1}. Anal. Calcd for $C_{21}H_{36}O_2$: C, 78.70; H, 11.32. Found: C, 78.60; H, 11.29.

(*E*)-Tetrahydro-2-[(10-hexadecen-12-ynyl)oxy]-2*H*-pyran (26, R = THP). To a solution of 0.134 g (0.352 mmol) of (*E*)-tetrahydro-2-[(11-iodo-10-undecenyl)oxy]-2*H*-pyran (**27**, R = THP) in 4 mL of DMF was added 0.0046 g (0.018 mmol) of $(MeCN)_2PdCl_2$ and 0.0853 g (0.370 mmol) of pentynyltrimethylstannane (**28**). The yellow solution immediately turned black upon addition of the stannane. This reaction mixture was stirred for 30 min at 22–25 °C. Analysis by GLC (DB1, FID) indicated complete consumption of the vinyl iodide. The reaction mixture was transferred to a separatory funnel with 100 mL of ether and washed with 25 mL of water. The aqueous phase was diluted with 50 mL of water and back-extracted with 25 mL of ether. The combined ethereal extracts were washed with water (3 × 25 mL) and brine (1 × 25 mL) and dried over potassium carbonate. The solvents were removed under reduced pressure, and the remaining liquid was purified by radial chromatography by using hexane–ethyl acetate (98:2). Removal of the solvents provided 0.0976 g (86.4%) of the pure *E* product (**26**, R = THP). Further purification was achieved by bulb-to-bulb distillation, bp 124–125 °C (0.25 mmHg): ^{1}H NMR ($CDCl_3$) δ 0.98 (t, 3, J = 7.3 Hz), 1.05–1.90 (m, 22), 2.05 (q, 2, J = 6.9 Hz), 2.25 (dt, 2, J = 1.7, 6.8 Hz), 3.37 (dt, 1, J = 6.5, 9.6 Hz), 3.45–3.53 (m, 1), 3.72 (dt, 1, J = 6.8, 9.6 Hz), 3.82–3.89 (m, 1), 4.57 (t, 1, J = 2.8 Hz), 5.44 (dt, 1, J = 1.4, 16.1 Hz, CH=C*H*—C≡C), 6.03 (dt, 1, J = 7.0, 15.8 Hz, C*H*=CH—C≡C); ^{13}C NMR ($CDCl_3$) δ 13.36, 19.68, 21.39, 22.32, 25.65, 26.26, 28.90, 29.06, 29.35, 29.42, 29.82, 30.88, 32.84, 62.21, 67.63, 79.50, 88.38, 98.86, 110.09, 142.98; IR (neat) 3205, 2930, 2860, 2210, 955 cm^{-1}. The ^{1}H NMR and IR spectra matched the published data.[86]

(*E*)-10-Hexadecen-12-yn-1-ol (26, R = H). To a solution of 0.249 g (0.840 mmol) of 11-iodo-10-undecen-1-ol in 9 mL of dry DMF was added 0.0151 g (0.0420 mmol) of $(MeCN)_2PdCl_2$ and 0.024 g (0.882

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mmol) of pentynyltrimethylstannane (**28**). The yellow solution immediately turned black upon addition of the stannane. The reaction mixture was stirred for 30 min at 22-25 °C. Analysis by GLC (DB1, FID) indicated complete consumption of the vinyl iodide. The reaction mixture was transferred to a separatory funnel with 100 mL of ether and washed with 25 mL of water. The aqueous phase was diluted with 50 mL of water and back-extracted with 25 mL of ether. The combined ethereal extracts were washed with water (3 × 25 mL) and brine (1 × 25 mL) and dried over potassium carbonate. The solvents were removed under reduced pressure, and the remaining liquid was purified by radial chromatography by using hexane–ethyl acetate (8:2). Removal of the solvents provided 0.180 g (90.6%) of a pale yellow liquid: ^{1}H NMR ($CDCl_3$) δ 0.94 (t, 3, J = 7.4 Hz), 0.98-1.40 (m, 15), 1.50 (q, 2, J = 7.2 Hz), 2.02 (q, 2, J = 7.0 Hz), 2.21 (t, 2, J = 6.9 Hz), 3.56 (t, 2, J = 6.7 Hz), 5.40 (dt, 1, J = 1.6, 15.8 Hz, CH=C*H*—C≡C), 6.00 (dt, 1, J = 7.1, 15.8 Hz, C*H*=CH—C≡C); ^{13}C NMR ($CDCl_3$) δ 13.27, 21.32, 22.22, 25.70, 28.80, 28.96, 29.25, 29.31, 29.40, 32.76, 62.85, 79.44, 88.33, 110.02, 142.88, 146.61; IR (neat) 3350, 3025, 2920, 2860, 2215, 1055, 955 cm^{-1}. The ^{1}H NMR and IR spectra matched the published data.[87]

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Methyl Transfers. 13. Transfers between Aryl Selenide Anions. An Unusual Transition State Charge Distribution[1]

Edward S. Lewis,* Taher I. Yousaf, and Thomas A. Douglas

Contribution from the Department of Chemistry, Rice University, Houston, Texas 77251.
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Abstract: The reaction rates and equilibria for the methylation of the phenyl selenide anion by aryl methyl selenides are reported. The reactions are much faster than the analogous reactions of thiophenoxide ion with aryl methyl sulfides. The Hammett equation is followed for the rates ($\rho^+ = +1.1 \pm 0.1$) and the equilibria ($\rho_{eq} = +2.9 \pm 0.1$) at 90 °C in sulfolane. The identity rate for phenyl can be interpolated, $k = (3.6 \pm 0.5) \times 10^{-4}$ s^{-1} M^{-1}. The identity reactions have a derived $\rho_{xx} = -0.7$, and the charge on the methyl group in the transition state is −0.24. The significance of this unusual negative charge is discussed. The selenium compounds are all characterized by ^{77}Se NMR, and the neutral selenides are fully characterized by ^{13}C and ^{1}H NMR as well.

Rates and equilibria of methyl transfers between nucleophiles differing only by a Hammett substituent can yield information on the charge distribution in the identity rate transition state **1**.[2] For the net negatively charged case shown, the charge on the

$$\left[\begin{matrix} -(1+\delta)/2 & \delta & -(1+\delta)/2 \\ X\text{-----}CH_3\text{-----}X \end{matrix}\right]^-$$

1

transition-state methyl groups, 5, is given by expression 1, in which ρ^+ refers to the Hammett ρ for a variable leaving group.

$$\delta = 2(\rho^+/\rho_{eq}) - 1 \quad (1)$$

The ratio ρ^+/ρ_{eq} is also given by the slope of a plot of log k^+ vs. log K_{eq}, which is a somewhat more general form if the Hammett equation fit is imperfect, or if the choice of σ scales is not obvious. Such a plot can also be used for non-Hammett structural changes.[3] The substituent effect on the identity reaction, ρ_{xx}, is also derivable, and it is given by (2). In the earlier cases that we have studied,

$$\rho_{xx} = 2\rho^+ - \rho_{eq} \quad (2)$$

δ and ρ_{xx} were positive,[2,4] and more or less equivalent statements are that the transition state has some carbocation character or that bond breaking is ahead of bond making. In these cases variation in the leaving group has more effect than variations in the attacking nucleophile on the reaction rate.[5]

Changes of a more drastic nature reveal little correlation of the identity rates with the equilibrium constant for methylating a standard nucleophile. Thus, methyl iodide hardly reacts at all with benzenesulfonate ion, yet its identity rate in sulfolane is more than 10^4 times as fast as that of methyl benzenesulfonate.[4] We have been curious about the charge distribution in reactions of methyl iodide, but our technique of substituent effects cannot be used. In this paper we attempt to model iodide ion (and bromide ion) with nucleophiles capable of systematic substituent changes, but near in the periodic table. The obvious candidate would be substituted phenyl telluride anions. However, the chemistry of low oxidation state tellurium was not well developed, few of the compounds were known, and questions about toxicity and stench put us off.[6] Thus, we have compromised on the phenyl selenide anions and report here on reaction 3, getting both rate and

$$\text{ArSeMe} + \text{PhSe}^- \underset{k^-}{\overset{k^+}{\rightleftharpoons}} \text{ArSe}^- + \text{PhSeMe} \quad (K_{eq} = k^+/k^-) \quad (3)$$

equilibrium data, from which the identity rate of reaction 3 with Ar = Ph can be obtained by interpolation, and as described above the charge on the methyl group and the magnitude and direction of the substituent effect on the identity rate. The approach is closely analogous to that applied to the corresponding thiophenoxide anion case.[7]

Results

The rates of reaction 3 were followed by determining the relative amounts of $ArSeCH_3$ and $PhSeCH_3$ from time to time initially with use of GC, but mostly HPLC. Equilibria were determined

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