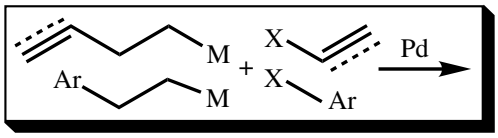

III.2.11.2 Reactions between Homoallyl-, Homopropargyl-, or Homobenzylmetals and Alkenyl or Aryl Electrophiles

EI-ICHI NEGISHI and FANXING ZENG

A. INTRODUCTION AND BACKGROUND

1,5-Dienes, 1,5-enynes, and related compounds have traditionally been synthesized by coupling two allylic, propargyl, and/or benzylic units (**Protocol I** in **Scheme 1**). The availability of some moderately satisfactory procedures for allyl–allyl coupling[1],[2] and propargyl–allyl coupling[3]–[5] and the difficulties associated with Pd-catalyzed reactions of allyl-, propargyl-, or benzylmetals with allyl, propargyl, or benzyl electrophiles are discussed in **Sect. III.2.10**. In the previously developed methodology based on **Protocol I**, homologation by an isoprene unit requires several steps in each cycle. For this reason alone, the conventional methods are not well suited for the construction of oligomeric isoprenoids consisting of more than a few isoprene units. Furthermore, the regio- and stereoselectivities tend to be less than perfect. In particular, the stereoselectivity in the synthesis of (*Z*)-isoprenoids has been limited to less than 90%.[2] Preferably, incorporation of an isoprene unit should require only one or less, that is, the use of controlled oligomerization processes, and the yield, regio- and stereoselectivities, as well as all other critical aspects, such as cross/homo-coupling ratio and so on, should be either perfect or nearly so.

There are at least two alternatives—**Protocols II** and **III** in **Scheme 1**—as routes to the same classes of compounds. Although there have been some reports on Protocol II[6],[7] using Cu as the metal countercation, its generality and overall synthetic value have not yet been well delineated. β-Elimination associated with homoallyl, homopropargyl, and homobenzyl electrophiles is a serious concern. The relative inability of commonly used Pd or Ni complexes to undergo facile oxidative addition to homoallyl, homopropargyl, and homobenzyl electrophiles is a serious barrier to be overcome. On the other hand, **Protocol III**, which can proceed via oxidative addition of Pd or Ni to alkenyl or aryl electrophiles and cross-coupling with homoallyl-, homopropargyl-, or homobenzylmetals, appears promising, especially in view of the highly satisfactory Pd-catalyzed alkylation with alkylmetals discussed in **Sect. III.2.11.1**.

The feasibility of developing **Protocol III** based on Pd- or Ni-catalyzed cross-coupling with homoallyl- or homopropargylmetals containing Zn or Mg was demonstrated in

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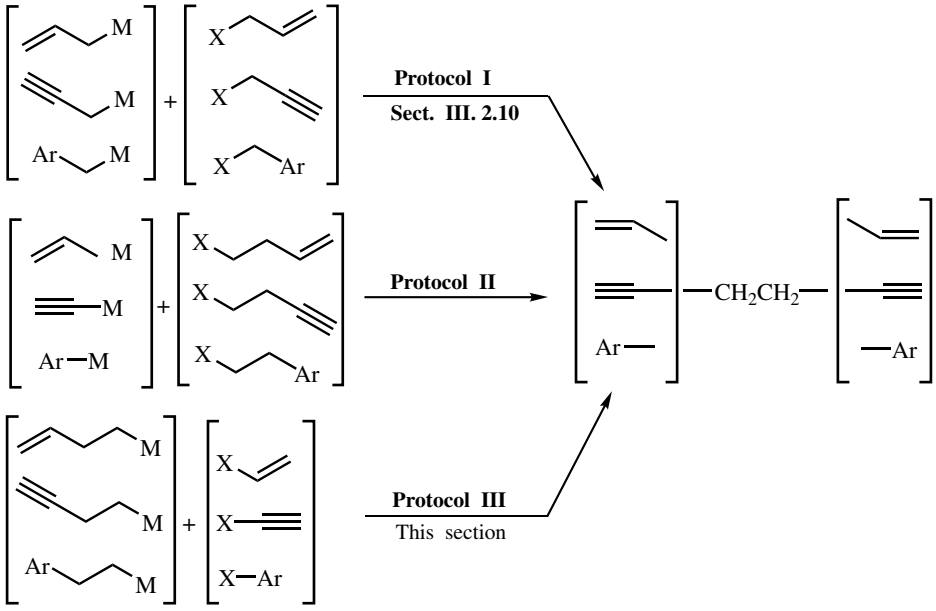
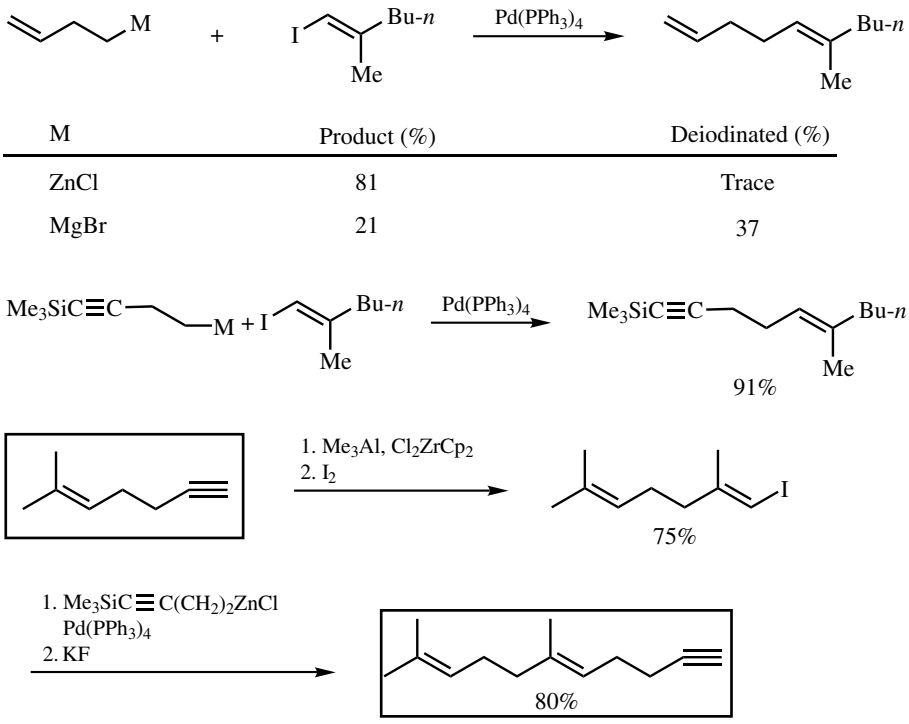


Scheme 1

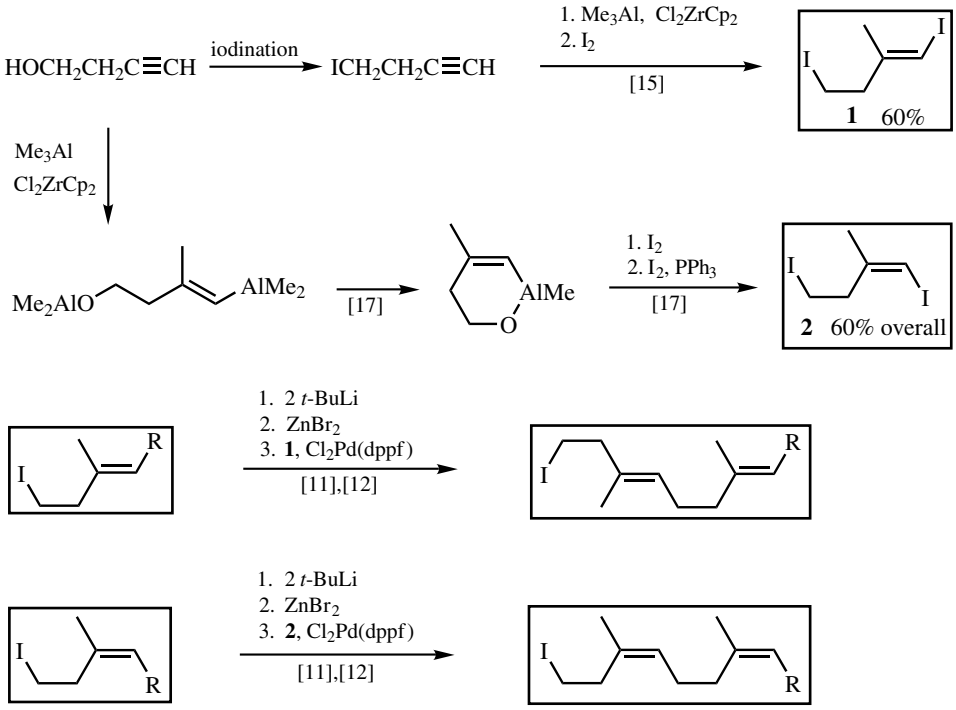
1980[8],[9] (**Scheme 2**). In general, a combination of Pd and Zn appeared most satisfactory, and essentially all of the subsequent studies have been performed using this combination. It is noteworthy that, despite the presence of relatively labile allylic or propargylic H atoms, the extent of dehydrometallation as judged by the yields of deiodinated products was minimal. Little or no regio- and stereoscramblings took place. This investigation led to the development of a very satisfactory iterative protocol for the selective synthesis of oligomeric isoprenoids containing 1,5-diene units,[8],[9] as detailed later. However, this protocol has been associated with a few shortcomings. First, it involves a linear and iterative construction requiring a two-pot homologation by a C_5 isoprene unit. Second, its applicability has been limited to the synthesis of *Z*-isoprenoids. Although carbocupration of alkynes[10] has been applied to the synthesis of simple monoterpenes, its use in the iterative construction of oligomeric isoprenoids has not been demonstrated, and applications of the Zr-catalyzed carboalumination of alkynes to the synthesis of *Z*-isoprenoids resorting to **Protocol III** would require further basic exploration of the carboalumination reaction itself.

In attempts to circumvent these difficulties, a related but conceptually discrete tail-to-head construction protocol has recently been developed.[11],[12] For discussions of some intricate aspects, it is useful to distinguish two modes of oligoisoprenoid construction, that is, head-to-tail (H-to-T hereafter) and tail-to-head (T-to-H hereafter) modes, where the head and tail of the isoprene unit are defined as the disubstituted (head) and monosubstituted (tail) ends of a trisubstituted alkene moiety, respectively. Thus, the protocol developed in 1980[8],[9] represents the H-to-T mode of isoprenoid construction. The recently developed T-to-H construction protocol entails one-pot homologation cycles using (*E*)- and (*Z*)-1,4-diiodo-2-methyl-1-butenes (**1** and **2**, respectively, in **Scheme 3**). More specifically, it involves (i) Pd-catalyzed



Scheme 2

homoallyl–alkenyl coupling using **1** and/or **2** first as an alkenyl iodides, and (ii) *in situ* zincation of homoallylic iodides via lithiation with 2 equiv of *t*-BuLi followed by addition of $ZnBr_2$ or $ZnCl_2$.[13] The invention of this protocol has critically depended on several developments made over the past two decades. First, the preparation of **1** involves Zr-catalyzed carboalumination[14] of homopropargyl iodide[15] followed by iodinolysis.[16] On the other hand, preparation of the *Z*-isomer (i.e., **2**) entails Zr-catalyzed carboalumination of homopropargyl alcohol[15] followed by chelation-assisted stereoisomerization[17] to give, after iodinolysis, (*Z*)-4-iodo-3-methyl-3-buten-1-ol, which is then iodinated to provide **2** as a 98% isomerically pure compound. Second, Pd-catalyzed cross-coupling with **1** or **2** takes advantage of the fact that the alkenyl end preferentially and selectively participates in the coupling reaction.[15] The reactivity ratio of the two ends is estimated to be at least 100. Third, clean and essentially quantitative metallation of homoallyl iodides proceeds with 2 equiv of *t*-BuLi.[13] Treatment of homoallyl or homopropargyl bromides or iodides with a mixture of Mg and ZnX_2 (X = Cl or Br) is very satisfactory in less demanding cases. In more demanding cases, however, it is distinctly less clean than the lithiation of iodides with *t*-BuLi. The difference is further accentuated in the synthesis of oligomeric isoprenoids where iteration of the procedures is required. In such cases, the *t*-BuLi–ZnX_2 protocol appears to provide the only highly satisfactory procedures. As the alkenyl iodide ends of **1** or **2** must react first, the development of T-to-H procedures is required. Some preliminary results pertaining to the above discussion are summarized in **Scheme 3**.



Scheme 3

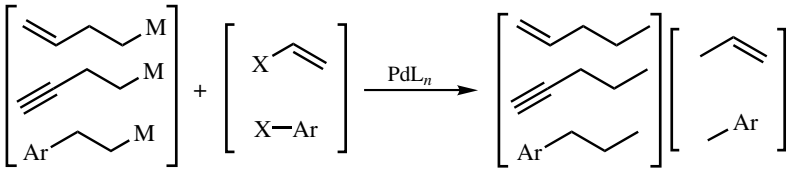
In the following subsections, both the initially developed H-to-T protocol and the T-to-H protocol as well as some related methods involving B are discussed in detail.

B. SCOPE OF Pd-CATALYZED CROSS COUPLING WITH HOMOALLYL-, HOMOPROPARGYL-, AND HOMOBENZYLMETALS CONTAINING Zn AND Mg

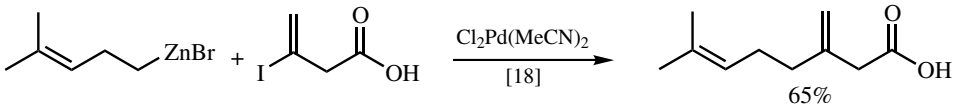
There are six discrete combinations for Pd-catalyzed cross-coupling between homoallyl-, homopropargyl-, or homobenzylmetals and alkenyl or aryl electrophiles (**Scheme 4**). In addition to these processes, those involving alkyl, allyl, benzyl, propargyl, alkynyl, and acyl electrophiles are conceivable, and some have indeed been observed. However, these reactions are discussed in other pertinent sections.

All six combinations shown in **Scheme 4** have been investigated with appropriate alkylzincs and have been shown to be generally favorable. Some specific examples in addition to those shown in **Schemes 2** and **3** are also shown in **Scheme 4**.

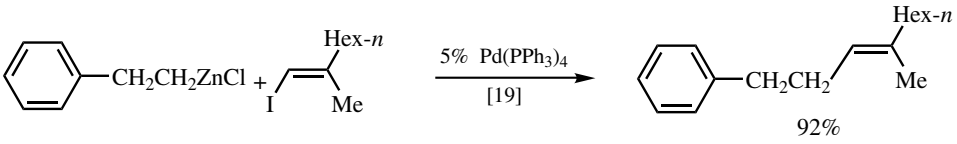
In general, **Protocol III** in **Scheme 1** is far superior to **Protocol II**, as exemplified by comparative results shown in **Scheme 4**. As mentioned earlier, the main difficulties associated with **Protocol II** are β-elimination and the inability of Pd complexes to undergo facile oxidative addition with γ,δ-unsaturated alkyl electrophiles. In some special cases where β-dehydropalladation is not possible, some Pd-catalyzed aryl–homoallyl coupling reactions have been observed[22] (**Scheme 5**).



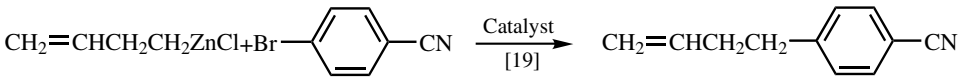
Homoallyl–alkenyl coupling



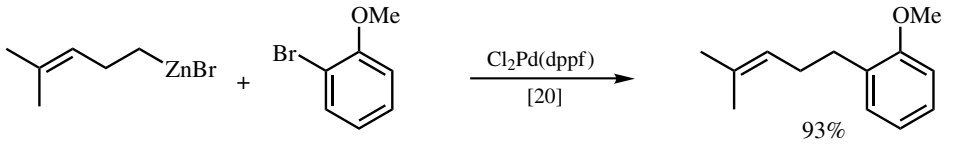
Homobenzyl–alkenyl coupling



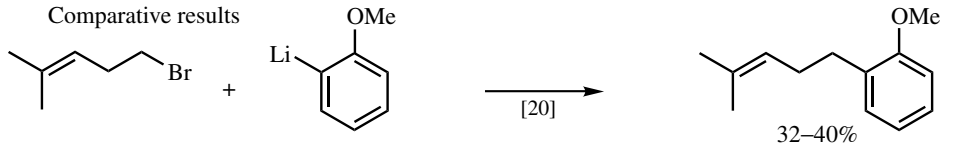
Homoallyl–aryl coupling



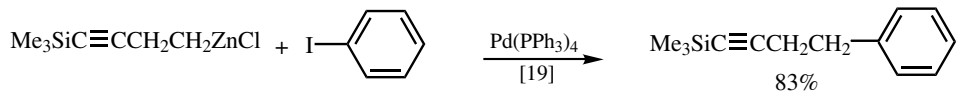
5% Pd(PPh$_3$)$_4$ (78%) 5% Ni(PPh$_3$)$_4$ (82%)

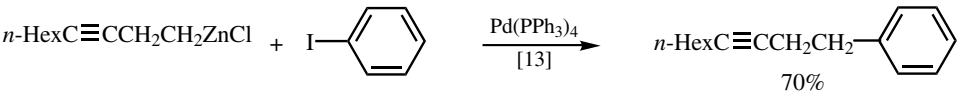


Comparative results

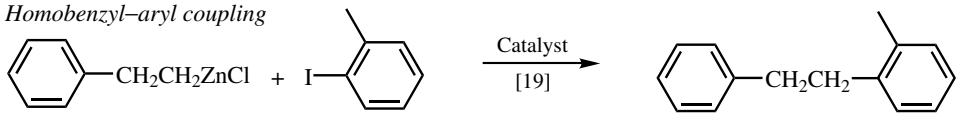


Homopropargyl–aryl coupling



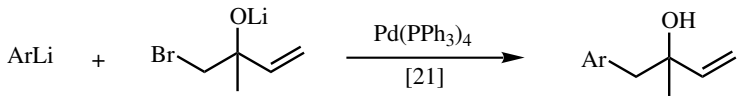


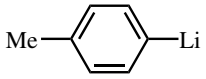
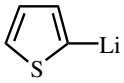
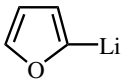
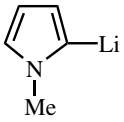
Homobenzyl–aryl coupling



5% Pd(PPh$_3$)$_4$ (73%)
5% Ni(PPh$_3$)$_4$ (70%)

Scheme 4



ArLi	Yield (%)	ArLi	Yield (%)
	86		78
	60		70

Scheme 5

C. SYNTHESIS OF NATURAL PRODUCTS VIA Pd-CATALYZED HOMOALLYL–ALKENYL AND HOMOPROPARGYL–ALKENYL COUPLING REACTIONS

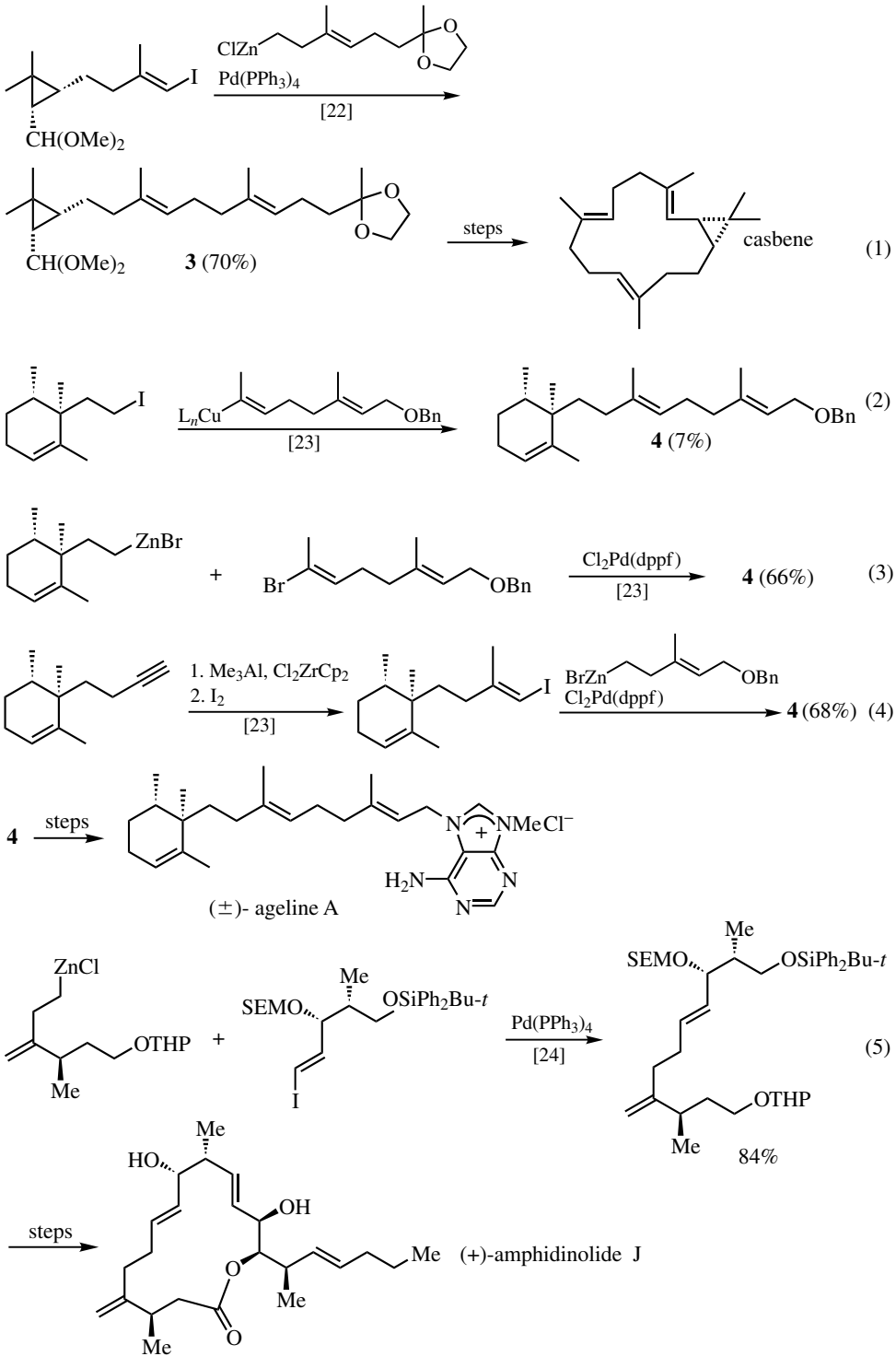
C.i. Applications of Pd-Catalyzed Homoallyl–Alkenyl Coupling to the Synthesis of Natural Products

Pd-catalyzed homoallyl–alkenyl coupling discussed in **Sect. B** has provided a dependable and selective method for the synthesis of stereo- and regiodefined 1,5-dienes of natural origin. In some cases, the Pd-catalyzed cross-coupling reaction is used in conjunction with Zr-catalyzed carboalumination of alkynes.[14]–[16] Some representative results are shown in **Scheme 6**. In a synthesis of casbene, a key intermediate **3** has been prepared by Pd-catalyzed homoallyl–alkenyl coupling[22] (Eq. 1). In the synthesis of (±)-ageline A, synthetic routes to **4** via Pd-catalyzed homoallyl–alkenyl and alkyl–alkenyl coupling reactions with organozincs have been shown to be far superior to that involving the conventional route via Cu-promoted alkenyl–alkyl coupling[23] (Eqs. 2–4). A recent synthesis of (+)-amphidinolide J[24] provides yet another example demonstrating a similar difficulty and its solution by resorting to Pd-catalyzed homoallyl–alkenyl coupling (Eq. 5).

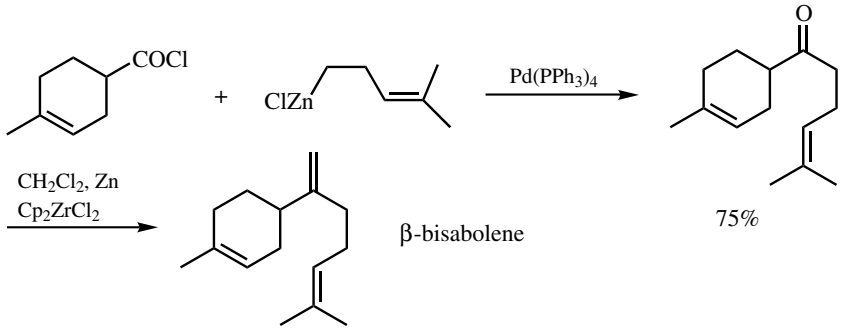
An interesting variant of Pd-catalyzed homoallyl–alkenyl coupling is Pd-catalyzed acylation (**Sect. III.2.12.1**) followed by carbonyl olefination shown in **Scheme 7**.[25]

C.ii. Pd-Catalyzed Head-to-Tail Synthesis of Oligomeric Isoprenoids

In none of the applications presented thus far has the feasibility of repeating the construction of a 1,5-diene unit shown in **Scheme 2** been investigated for the synthesis of oligomeric isoprenoids. The iterative H-to-T protocol for the synthesis of oligomeric isoprenoids was first applied to highly selective syntheses of (*E*,*E*)-farnesol[8] and mokupalide,[8],[9] as shown in **Scheme 8**. All steps are > 98% regio- and stereoselective, and no isomeric separation was necessary throughout these syntheses. The overall efficiency and high stereoselectivity should be compared with the previously known syntheses of oligomeric all-(*E*)-isoprenoids.[1],[3],[26]–[32]

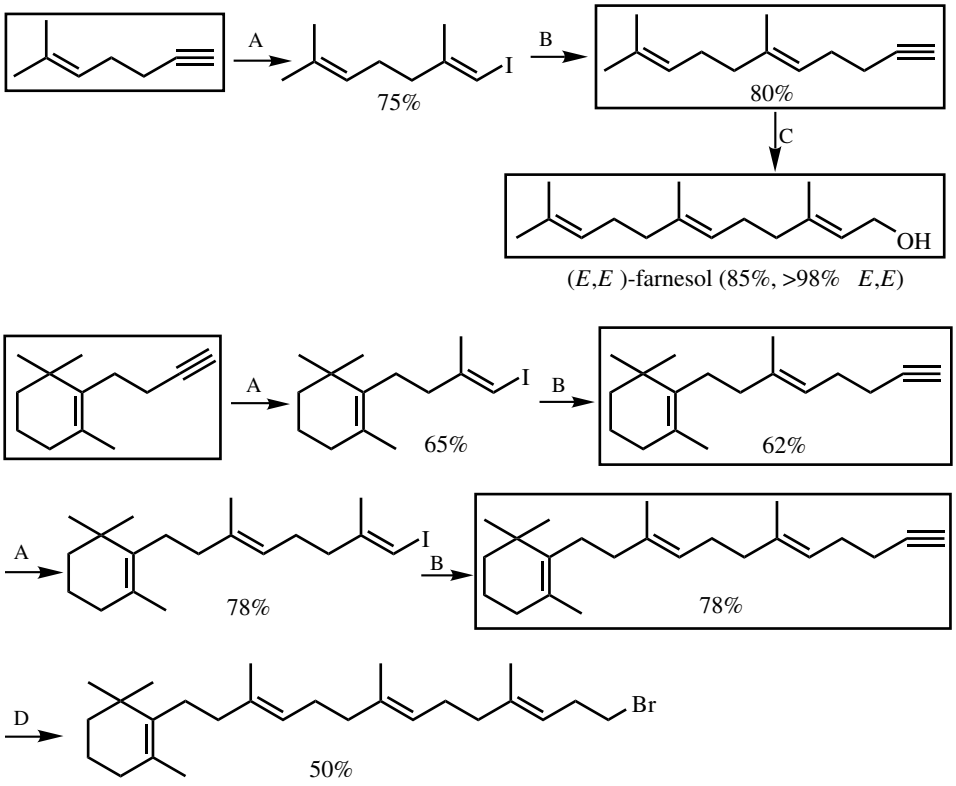

ClZn
Pd(PPh3)4
[22]
CH(OMe)2
3 (70%)
steps
casbene
(1)
L_nCu
OBn
[23]
4 (7%)
(2)
ZnBr
Br
Cl2Pd(dppf)
4 (66%)
(3)
1. Me3Al, Cl2ZrCp2
2. I2
BrZn
Cl2Pd(dppf)
4 (68%)
(4)
4
steps
NMeCl−
H2N
(±)- ageline A
ZnCl
OTHP
Me
SEMO
OSiPh2Bu-t
Pd(PPh3)4
[24]
84%
(5)
HO
OH
O
(+)-amphidinolide J

Scheme 6

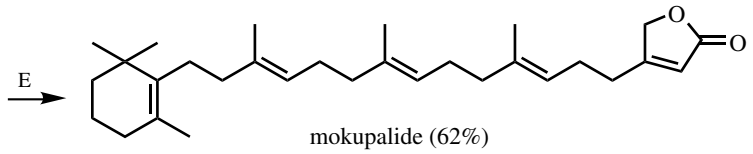


Scheme 7

Homologation of isoprenoid chains by a two-step process consisting of the steps A and B shown in **Scheme 8** currently permits incorporation of only an *E*-C_5 trisubstituted alkene unit. However, capping the tail end of an oligomeric isoprenoid chain with incorporation of a *Z*-trisubstituted alkene can be achieved satisfactorily by resorting to one of the two protocols[12],[33],[34] given in **Scheme 9**. These procedures have provided a couple of ultimately satisfactory methods for the synthesis of (2*Z*,6*E*)-farnesol. Various modifications of these procedures are also conceivable.

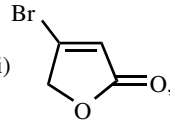


Scheme 8

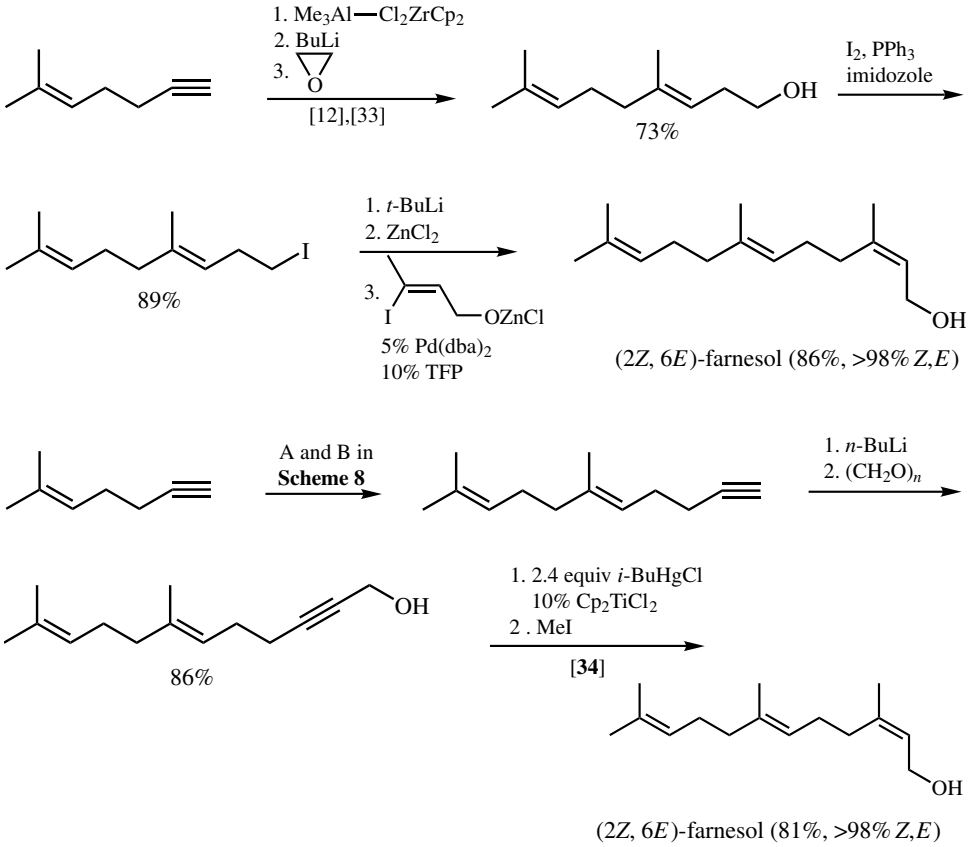


mokupalide (62%)

A = $Me_3Al—Cl_2ZrCp_2$ then I_2.
B = $Me_3SiC\equiv C(CH_2)_2ZnCl$, 5% $Pd(PPh_3)_4$, then $KF\cdot 2H_2O$.
C = (i) $Me_3Al—Cl_2ZrCp_2$, (ii) *n*-BuLi, (iii) $(CH_2O)_n$.
D = (i) $Me_3Al—Cl_2ZrCp_2$, (ii) *n*-BuLi, (iii)  ,
(iv) *p*-TsCl, Py, then LiBr in acetone.

E = (i) Mg, $ZnBr_2$, (ii)  , $Cl_2Pd(PPh_3)_2$ and 2 *i*-Bu_2AlH.

Scheme 8 (*Continued*)



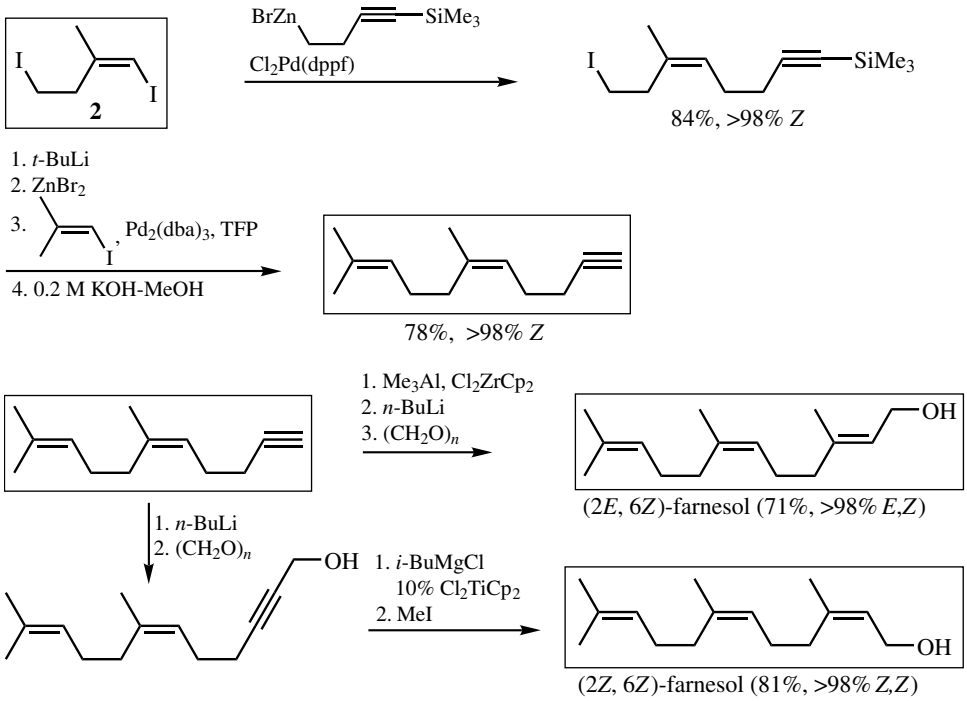
Scheme 9

C.iii. Efficient and Selective Iterative and Convergent Synthesis of Oligomeric Isoprenoids Containing *E*- and/or *Z*-Trisubstituted 1,5-Diene Units

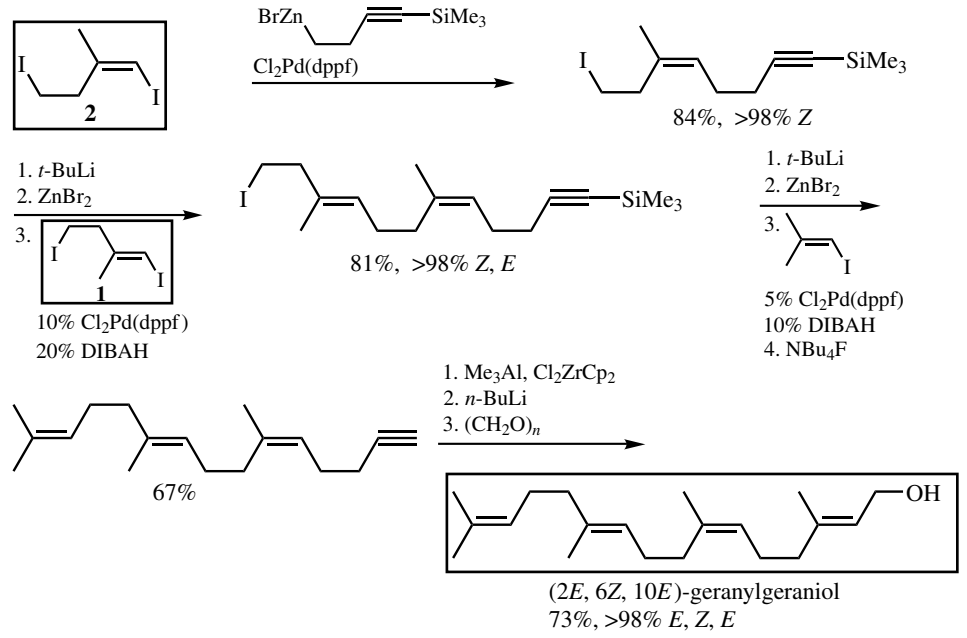
The two-step H-to-T protocol discussed above has provided a highly selective and reasonably efficient route to all-*E*-isoprenoids, and its appropriate modifications have permitted incorporation of the *Z*-end capping isoprene units. However, efficient and highly stereoselective incorporation of the *Z*-trisubstituted alkene unit in the main chain of an oligomeric isoprenoid has remained an elusive synthetic goal.[2] Critically needed were stereo- and regiodefined difunctional trisubstituted C_5 isoprene synthons, permitting stereo- and regiospecific homologation. As presented in **Scheme 3**, (*E*)- and (*Z*)-1,4-diiodo-2-methyl-1-butenes (**1** and **2**, respectively) promised to satisfy all of the above-mentioned requirements. Indeed, the use of **2** has permitted, for the first time, a highly efficient and selective (>98% *Z*) incorporation a (*Z*)-trisubstituted C_5 isoprene unit in the synthesis of the (2*E*,6*Z*)- and (2*Z*,6*Z*)-isomers of farnesol, as shown in **Scheme 10**.[12] The T-to-H mode of synthesis is dictated by the relative reactivities of the two C—I bonds in **1** or **2**. Capping the head with 1-halo-2-methyl-1-propene can readily be achieved by Pd-catalyzed homoallyl–alkenyl coupling. A remarkably higher efficiency and stereoselectivity as compared with the previously available method[2] based on **Protocol I** should be noted.

The synthetic schemes shown in **Scheme 10** do not involve the iterative use of **1** or **2** for isoprenoid chain homologation. As expected, homologation of isoprenoid chains with **1** and/ or **2** by a one-pot cycle consisting of Pd-catalyzed homoallyl–alkenyl coupling and metallation of homoallyl iodides via lithiation with *t*-BuLi followed by zincation has been shown to be highly satisfactory,[12] even though the cross-coupling yield observed with **2** can further be improved. The stereoselectivity observed with either **1** or **2** was >98%. The synthesis of (2*E*,6*Z*,10*E*)-geranylgeraniol[12] further indicates that it is now practical to incorporate at will either the *E*- or *Z*-trisubstituted C_5 isoprene unit with essentially complete control of regio- and stereochemistry in one pot (**Scheme 11**).

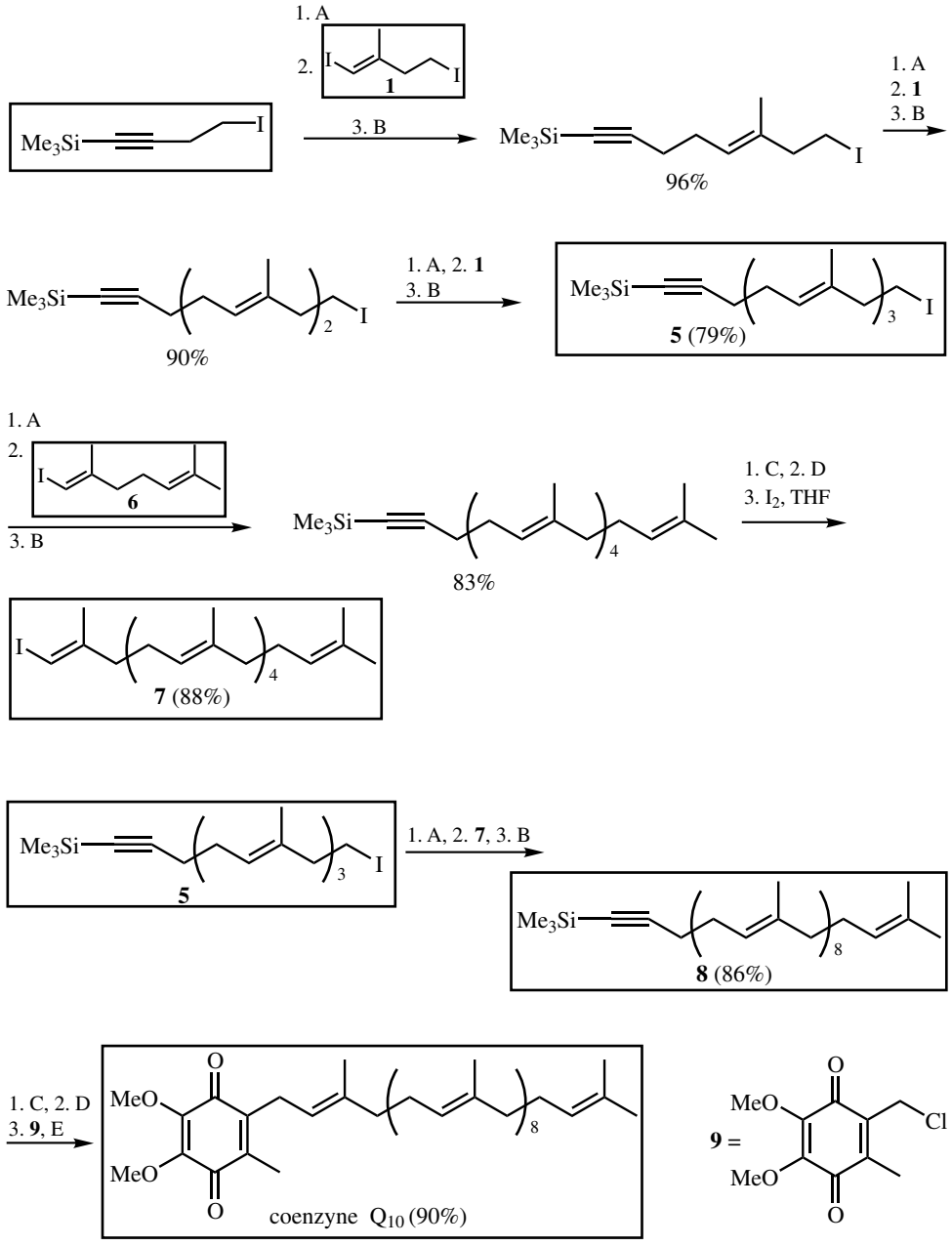
Thus far, only linear syntheses of oligoisoprenoids have been discussed. However, the T-to-H protocol using **1** and/or **2** is readily applicable to convergent syntheses of oligomeric isoprenoids. In practice, a proper mix of iterative and convergent steps may be found for a given target to optimize the overall efficiency of the synthesis. In this respect, it should clearly be noted that essentially any combinations of linear and iterative steps are available with roughly comparable facility. A remarkably efficient and highly selective synthesis of coenzyme Q_{10} shown in **Scheme 12**[12] incorporates all of the desirable features discussed above. Ni-catalyzed alkenyl–benzyl or alkenyl–allyl coupling[35],[36] can be substituted with the Pd-catalyzed procedure, which yields comparable results, as detailed in **Sect. III.2.9**. Once the preparation of 4-iodo-1-(trimethylsilyl)-1-butyne in two steps, **1** in two steps, **6** in two steps, and **9**[37] in four steps from commercially available compounds was possible, the synthesis of coenzyme Q_{10} involving (i) the construction of all nine stereodefined trisubstituted alkene units, (ii) the formation of nine carbon–carbon bonds linking ten trisubstituted C_5-alkene units via Pd-catalyzed homoallyl–alkenyl or homopropargyl–alkenyl coupling, and (iii) coupling of the side chain with the quinone moiety via Ni- or Pd-catalyzed alkenyl–allyl coupling can be achieved in 39% overall yield in seven longest linear steps with essentially full control of regio- and stereochemistry.



Scheme 10



Scheme 11

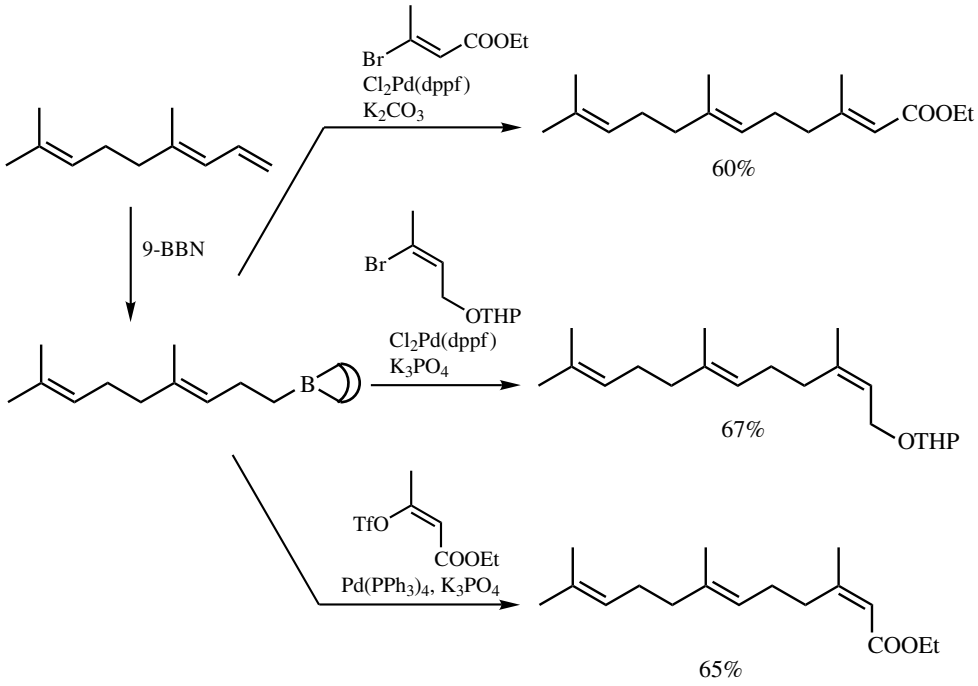


A = (1) 2.2 *t*-BuLi, Et_2O, –78 °C, 0.5 h; (2) $ZnBr_2$, THF.
B = 2% $Cl_2Pd(dppf)$, THF, 23 °C
C = KOH, MeOH, 40 °C, 2 h.
D = Me_3Al, cat. Cl_2ZrCp_2, $(CH_2Cl)_2$, 23 °C, 8 h.
E = $Cl_2Ni(PPh_3)_2$ + 2 *n*-BuLi, $2PPh_3$, THF, 23 °C.

Scheme 12

D. OTHER Pd-CATALYZED CROSS-COUPLING REACTIONS WITH HOMOALLYL-, HOMOPROPARGYL-, AND HOMOBENZYLMETALS

As in the case of Pd-catalyzed alkylation, the only metal currently used in Pd-catalyzed cross-coupling that can potentially compete with Zn is B, and the accessibility of homoallylboranes via hydroboration along with high chemoselectivity associated with B is the main attractive feature associated with B. The results summarized in **Scheme 13** show the feasibility of synthesizing oligomeric isoprenoids via hydroboration of conjugated dienes and Pd-catalyzed homoallyl–alkenyl coupling.[38],[39] Although the yields of 1,5-diene products are moderate (60–70%) the stereospecificity appears to be very high. It should also be noted that all cross-coupling reactions shown in **Scheme 13** fall into the category of intrinsically favorable Pd-catalyzed conjugate substitution (**Sect. III.2.15**). So, it is not clear if the same reaction is applicable to those cases where more usual alkenyl halides are used. The feasibility of iterative homologation of oligomeric isoprenoids has not yet been explored. Clearly, further investigations are necessary to clarify these synthetically important aspects.



Scheme 13

E. SUMMARY

Pd-catalyzed cross-coupling between homoallyl-, homopropargyl-, and homobenzylzincs with alkenyl and aryl iodides, bromides, and related electrophiles can proceed selectively in high yields. All six possible combinations have been shown to be generally satisfactory. Particularly noteworthy are the Pd-catalyzed homoallyl–alkenyl and homopropargyl–alkenyl

coupling reactions that can be applied to some highly efficient and selective syntheses of oligomeric isoprenoids with essentially full control of regio- and stereochemistry, and many natural products of this class have been synthesized using these reactions.

The iterative and convergent protocol using (*E*)- and/or (*Z*)-1,4-diiodo-2-methyl-1-butenes is efficient as well as regio- and stereoselective, requiring hardly any isomeric separation even in the synthesis of a decameric isoprenoid. It permits both iterative and convergent modes of construction of oligomeric isoprenoids in any desired ratio of the two modes of operation to best suit a given synthetic task. At any point of synthesis, either the *E*- or *Z*-trisubstituted C_5-alkene unit can be incorporated. This synthetic method promises to find many additional applications in the area of isoprenoid synthesis.

Magnesium and boron are two other metals besides Zn that can potentially be useful in some cases. Boron is particularly interesting since homoallylboranes can be generated by hydroboration of conjugated dienes and since homallylboranes have been shown to undergo Pd-catalyzed coupling with alkenyl halides. The scope of the B-based homoallylation and related reactions must, however, be investigated further to better define their merits and demerits.

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