1-(H)$_{10}$. FABMS (ONPOE), cluster m/z (peak height) at (M + H)$^+$: 2371 (3.5), 2372 (7), 2373 (9), 2374 (7.5), 2375 (4.5). ^{1}H NMR ($CDCl_3$): 7.23–7.10 (m, 24 H), 7.10–6.70 (m, 60 H), 5.34 (s, 3 H), 5.31 (s, 3 H), 5.27 (s, 4 H), 1.261 (bs, 54 H), 1.253, 1.251 (s, 27 H), 1.233, 1.231 (s, 27 H). ^{13}C NMR ($CDCl_3$): 148.71, 148.67, 148.64, 144.06, 143.96, 143.88, 143.85, 141.18, 141.13, 140.99, 130.83, 130.77, 128.94, 128.88, 127.99, 127.15, 124.99, 124.93, 56.52, 56.24, 55.95, 34.31, 31.40; ^{13}C DEPT (135°) CH, CH_3: 130.83, 130.77, 128.94, 128.88, 127.99, 127.15, 124.99, 124.93, 56.52, 56.24, 55.95, 31.40.

1-(D)$_{10}$. FABMS (ONPOE), cluster m/z (peak height) at (M + H)$^+$: 2381 (7), 2382 (9), 2383 (11), 2384 (9), 2385 (6). ^{1}H NMR ($CDCl_3$): 5.34, 5.31, 5.27 (s, <1 H).

2-(H)$_7$. FABMS (ONPOE), cluster m/z (peak height) at (M + H)$^+$: 1745 (14), 1746 (15), 1747 (11). ^{1}H NMR ($CDCl_3$): 7.25–7.17 (m, 18 H), 7.11–7.00 (m, 6 H), 7.00–6.95 (m, 15 H), 6.94–6.87 (m, 12 H), 6.86–6.80 (m, 6 H), 6.76 (bd, J = 8, 3 H), 5.36 (s, 3 H), 5.32 (s, 3 H), 5.30 (s, 1 H), 1.26 (bs, 54 H), 1.25 (bs, 27 H). ^{13}C NMR ($CDCl_3$): 148.70, 148.69, 148.66, 144.07, 144.02, 143.89, 143.85, 141.17, 141.12, 141.01, 141.00, 130.82, 130.75, 128.94, 128.90, 128.01, 127.94, 127.19, 127.14, 127.10, 124.99, 124.98, 124.93, 56.52, 56.25, 55.93, 34.31, 31.40. ^{13}C DEPT (135°) CH, CH_3: 130.82, 130.75, 128.94, 128.90, 128.01, 127.94, 127.19, 127.14, 127.10, 124.99, 124.98, 124.93, 56.52, 56.25, 55.93, 31.40.

2-(D)$_7$. FABMS (ONPOE), cluster m/z (peak height) at (M + H)$^+$: 1751 (50), 1752 (55), 1753 (45). ^{1}H NMR ($CDCl_3$): 5.4–5.2 (s, <0.3 H). ^{13}C NMR ($CDCl_3$): 56.2–55.3 (m, negligible intensity).

3-(H)$_4$. FABMS (3-NBA/GLY), cluster m/z (peak height) at M$^+$: 1077 (3), 1078 (10), 1079 (9), 1080 (5); (M – C_4H_8)$^+$: 1022 (4), 1023 (3); M$^+$, calc for $C_{82}H_{94}$ 1078.735550, found 1078.7367 and 1078.7339. ^{1}H NMR ($CDCl_3$): 7.21 (d, J = 7, 12 H), 7.09 (t, J = 7, 3 H), 6.94 (d, J = 7, 12 H), 6.91 (bd, J = 8, 3 H), 6.89 (bs, 3 H), 6.81 (bd, J = 7, 3 H), 5.33 (s, 4 H), 1.27 (s, 54 H). ^{13}C NMR ($CDCl_3$): 148.7, 144.1, 143.9, 141.2, 130.8, 128.9, 127.9, 127.21, 127.16, 125.0, 56.5, 56.0, 34.3, 31.4. ^{13}C DEPT (135°): CH, CH_3; 130.8, 128.9, 127.9, 127.22, 127.17, 125.0, 56.5, 56.0, 31.4.

3-(D)$_4$. FABMS (3-NBA/GLY), cluster m/z (peak height) at M$^+$: 1081 (10), 1082 (9), 1083 (8), 1084 (5); (M – C_4H_8)$^+$: 1026 (4), 1027 (3). ^{1}H NMR ($CDCl_3$): 5.33 (s, <0.2 H). ^{13}C NMR ($CDCl_3$): 56.5 (undetected), 56.0 (undetected).

4-(H)$_2$. ^{1}H NMR ($CDCl_3$): 7.175 (d, J = 8, 8 H), 7.094 (t, J = 8, 1 H), 6.974 (s, 1 H), 6.920 (d, J = 8, 8 H), 6.867 (d, J = 8, 2 H), 5.31 (s, 2 H), 1.21 (s, 1 H). ^{13}C NMR ($CDCl_3$): 148.8, 144.2, 141.2, 130.9, 129.0, 128.0, 127.2, 125.0, 56.0, 34.4, 31.4.

4-(D)$_2$. ^{1}H NMR ($CDCl_3$): 5.38 (s, <0.1 H). ^{13}C NMR ($CDCl_3$): 56.0 (s, negligible intensity), 55.5 (t, J_{CD} = 17).

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Supplementary Material Available: Experimental procedure for the preparation of 4,4'-di-*tert*-butylbenzophenone and 3-bromo-4-*tert*-butylbenzophenone; structures and partial COSY spectra for **1-(H)$_{10}$**, **2-(H)$_7$**, **3-(H)$_4$**, **3-(OEt)$_4$**, **7-(OEt)$_2$Br**, **8-(OEt)$_3$Br**, and **11-(OEt$_3$)(OEt)(OEt$_3$)**; and ^{1}H and ^{13}C NMR spectra for selected compounds (43 pages). Ordering information is given on any current masthead page.

Alkylation of Allylic Derivatives. 17. Cross-Coupling Reactions of Diallylic Pivalates with Butyl- and Phenylcopper Reagents

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Cross coupling (*Z*)-1-phenyl-1,4-pentadien-3-yl pivalate (*cis*-1-OPiv) with $LiCuBu_2$, LiCu(CN)Bu, $LiCuPh_2$, and LiCu(CN)Ph gives only the fully conjugated γ-coupling product. With $LiCuBu_2$, substantial loss of double-bond configuration occurs to give primarily the all-trans coupling product. With other cuprates, no detectable loss of double-bond configuration was observed. Cross coupling (*Z*)-3-(2-phenylethenyl)-2-cyclohexen-1-yl pivalate (*cis*-18-OPiv) with $LiCuBu_2$, $LiCuPh_2$, and LiCu(CN)Ph gives only α coupling product; with LiCu(CN)Bu, a mixture of α, γ, and ε coupling product was obtained. Cross coupling with $LiCuBu_2$ results in loss of double-bond configuration in the α-alkylation product. With the other cuprates, no loss of double-bond configuration was detected in the α and γ coupling product. These results have profound mechanistic implications, which are discussed. The relationship between structure and reactivity was also investigated. A variety of diallylic pivalates (1–5-OPiv) were prepared and cross coupled with $LiCuBu_2$, LiCu(CN)Bu, $LiCuPh_2$, and LiCu(CN)Ph. Generally, coupling occurs at the least-substituted allylic system; mechanistic implications are discussed.

In earlier work[1] we investigated the relationship between structure and reactivity for alkylation of allylic carboxylates with $LiCuMe_2$ in ether. In this study a competitive reaction technique[1,2] was used to determine rate constant ratios for pairs of allylic carboxylates. The competitive method, in which pairs of allylic carboxylates compete for a limited amount of cuprate, is foolproof with regard to comparison of two substrates under identical conditions. This method circumvents the problems associated with obtaining absolute rate measurements; for these coupling reactions, reproducing reaction conditions is difficult because of the rapid rate of reaction (typically <10 min at 0 °C) and simultaneous decomposition of cuprate.

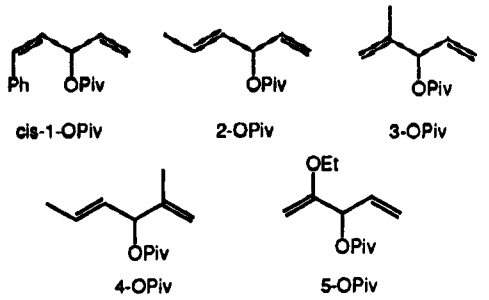
This paper reports an investigation into the relationship between structure and reactivity for the cross coupling diallylic pivalates (1–5-OPiv) with sp^3-copper reagents ($LiCuBu_2$ and LiCu(CN)Bu) and with sp^2-copper reagents ($LiCuPh_2$ and LiCu(CN)Ph) by an internal competitive

(1) Goering, H. L.; Kantner, S. S.; Seitz, E. P., Jr. *J. Org. Chem.* **1985**, *50*, 5495.

(2) Gilliom, R. D. *Introduction to Physical Organic Chemistry*; Addison-Wesley: Reading, MA, 1970; pp 96–99. Melander, L. *Isotope Effects on Reaction Rates*; Ronald Press: New York, 1960; Chapter 3. Walling, C.; Helmreich, W. *J. Am. Chem. Soc.* **1959**, *81*, 1144.

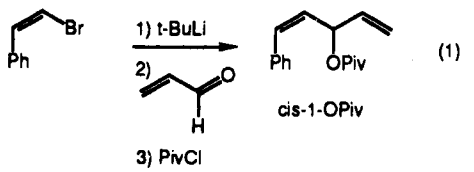
0022-3263/91/1956-2563$02.50/0

reaction technique described below.



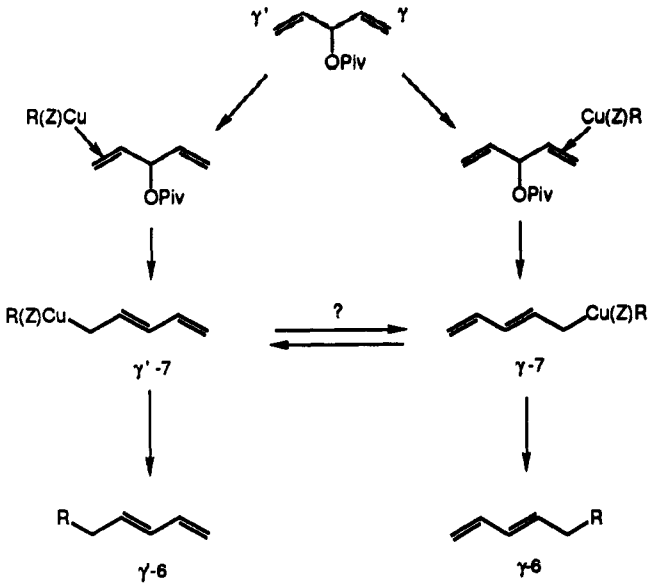
The pivalate leaving group in compounds 1–5-OPiv occupies the allylic position of two allylic systems, each differing in the pattern of double-bond substitution. As shown by Scheme I, cross coupling diallylic pivalates with butylcopper reagents is expected to give conjugated products γ-6 and γ′-6.[3-5] If the γ- and γ′-σ-allylcopper(III) intermediates (γ-7 and γ′-7) do not interconvert, then the product distribution (i.e., the regiochemistry of cross coupling) is a measure of the relative reactivity of each allylic system within each diallylic pivalate. On the other hand, if the copper(III) intermediates (γ-7 and γ′-7) interconvert, then the product distribution is not a true measure of the relative reactivity of each allylic system within the diallylic pivalate, but rather the cross-coupling product distribution depends on both the relative rates of reductive elimination (7 → product) and interconversion (γ-7 ⇌ γ′-7).[6]

cis-1-OPiv was prepared[7] as shown in eq 1 and alkylated in ether with $LiCuBu_2$ and LiCu(CN)Bu to determine if interconversion of intermediates γ-7 and γ′-7 occurs. As

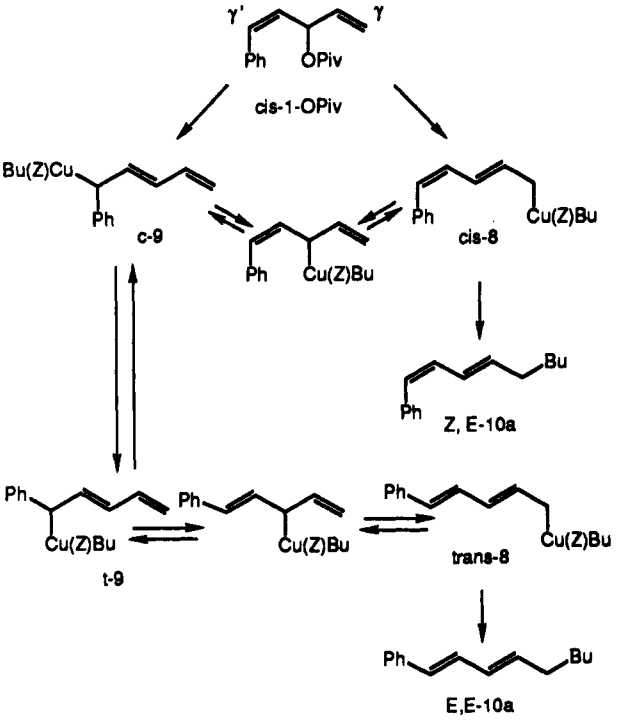


shown in Scheme II, oxidative addition of the diallylic system to the cuprate would give *cis*-8 (γ-addition) and/or c-9 (γ′-addition). If isomerization of 9 → 8 occurs, or alternatively, if partial or full equilibrium of the copper(III) intermediates 8 and 9 occurs, loss of double-bond configuration in the γ-alkylation product 10 is expected since formation of 9 converts the original $C_{\beta'}$–$C_{\gamma'}$ double bond into a single bond; it is at this point that bond rotation can result in loss of configuration as indicated in Scheme II.[3,8] It may be that bond rotation (c-9 → t-9) is slower than isomerization (c-9 → *cis*-8), and then loss of double-bond geometry would not be observed despite formation of 9. However, we have shown that loss of double-bond geometry is observed for cross-coupling reactions of alkylcuprates with *cis*-cinnamyl and (*Z*,*E*)-heptadienyl esters (i.e., bond rotation is faster than isomerization).[3,8] Thus, if 9 is an intermediate, loss of double-bond configuration would be expected. Conversely, if 9 is not an intermediate, the γ-alkylation product should retain original double-bond configuration.

Scheme I. Mechanism for Cross Coupling Diallylic Pivalates with Butylcopper Reagents



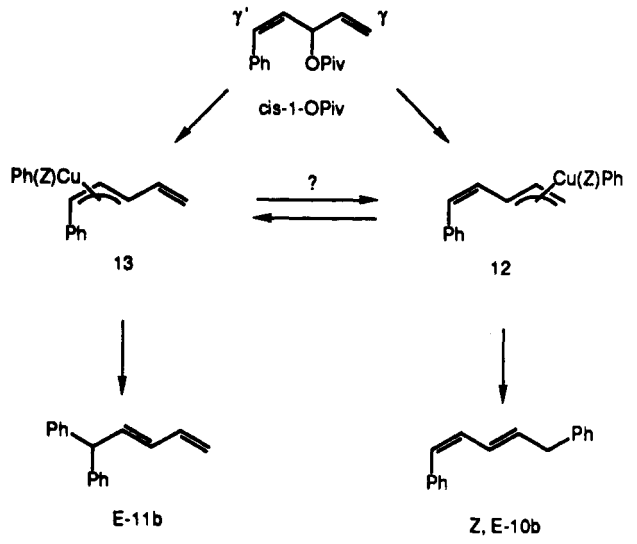
Scheme II. Mechanism for Cross Coupling *cis*-1-OPiv with $LiCuBu_2$ and LiCu(CN)Bu



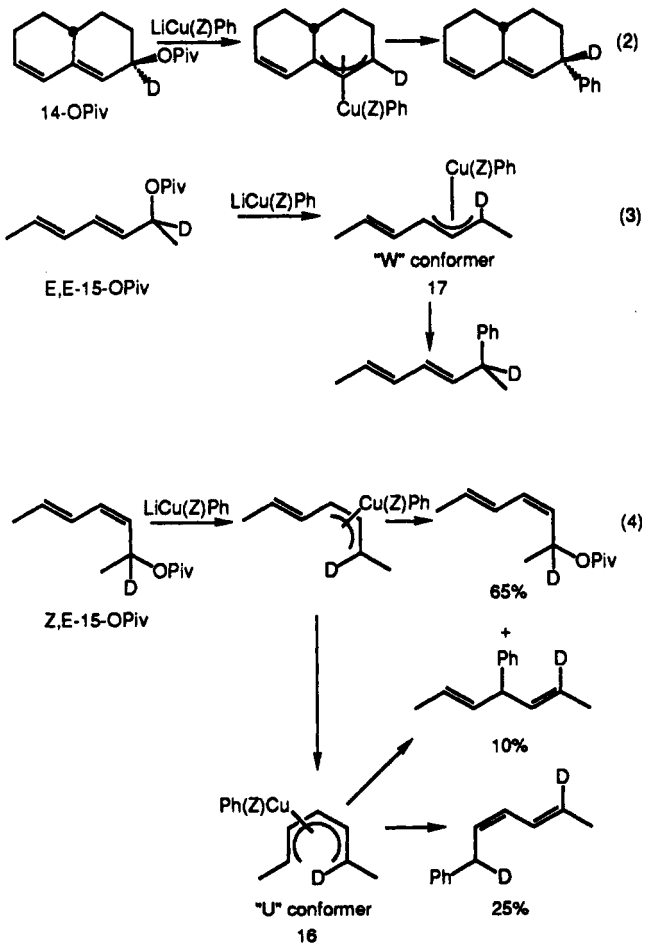
This method is not useful to determine if interconversion of intermediates is involved for cross coupling *cis*-1-OPiv with sp^2-copper reagents (e.g., $LiCuPh_2$ or LiCu(CN)Ph). This reaction presumably proceeds via π-allylcopper(III) intermediates (such as 12 and 13, Scheme III),[3] which retain double-bond character between the β′ and γ′ carbon atoms. Hence, loss of double-bond configuration would not be expected even if the reactive intermediates 12 and 13 interconverted. However, we have shown that cross coupling dienyl systems such as 14,[9] (*E*,*E*)-15,[6a] and (*Z*,-

(3) Underiner, T. L.; Paisley, S. D.; Schmitter, J.; Lesheski, L.; Goering, H. L. *J. Org. Chem.* **1989**, *54*, 2369.
(4) Underiner, T. L.; Goering, H. L. *J. Org. Chem.* **1989**, *54*, 3239.
(5) Tseng, C. C.; Paisley, S. D.; Goering, H. L. *J. Org. Chem.* **1986**, *51*, 2884.
(6) (a) Underiner, T. L.; Goering, H. L. *J. Org. Chem.* **1990**, *55*, 2757. (b) Keinan, E.; Bosch, E. *J. Org. Chem.* **1986**, *51*, 4006. (c) Trost, B. M.; Urch, C. J.; Hung, M.-H. *Tetrahedron Lett.* **1986**, 4949.
(7) Neumann, H.; Seebach, D. *Chem. Ber.* **1978**, *111*, 2785. Neumann, H.; Seebach, D. *Tetrahedron Lett.* **1976**, 4839. Cristol, S. J.; Norris, W. P. *J. Am. Chem. Soc.* **1953**, *75*, 2645.
(8) Goering, H. L.; Kantner, S. S. *J. Org. Chem.* **1983**, *48*, 721.
(9) Underiner, T. L.; Goering, H. L. *J. Org. Chem.* **1988**, *53*, 1140.

Scheme III. Mechanism for Cross Coupling *cis*-1-OPiv with $LiCuPh_2$ and LiCu(CN)Ph



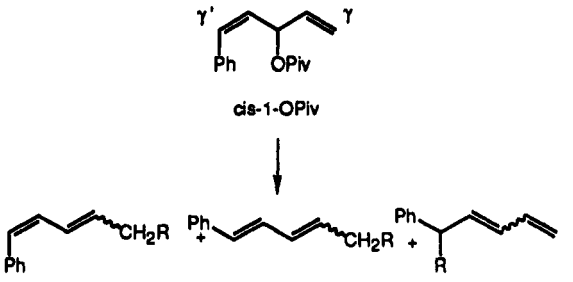
E)-15[3] with phenylcuprates gives primarily, if not exclusively, α coupling products, which indicates that isomerization of π-allylcopper(III) intermediates does not occur in these systems (eqs 2–4). We have shown[3,6a] that in the



latter case, a "U"[10] geometry (**16**) is necessary for isomerization to occur, and although this geometry is possible in diallylic systems, we have found that the reaction prefers to proceed via the "W"[10] geometry (**17**), which gives all-trans product.

(10) Bates, R. B.; Carnighan, R. H.; Staples, C. E. *J. Am. Chem. Soc.* **1963**, *85*, 3031.

Table I. Cross Coupling of *cis*-1-OPiv with LiCu(Z)R[a]



Reagent	T(°C)	Z,E-10	Z,Z-10	E,E-10	E,Z-10	11	Yield[b]
$LiCuBu_2$	-20	32%	10%	58%	0%	0%	50%
	-78	12%	0%	88%	0%	0%	--
LiCu(CN)Bu	-20	80%	20%	0%	0%	0%	74%
	-78	88%	12%	0%	0%	0%	--
$LiCuPh_2$	-20	95%	5%	0%	0%	0%	96%
LiCu(CN)Ph	-20	64%	36%	0%	0%	0%	94%

[a] Determined by capillary GC; average of two runs. [b] Isolated yields.

Experimental results presented in Table I show that cross coupling *cis*-1-OPiv with 2 equiv of LiCu(Z)R in ether gives only γ coupling product **10**. Cross coupling *cis*-1-OPiv with LiCu(CN)Bu occurs with no loss of double-bond geometry when the reaction is carried out at −20 or −78 °C. Similarly, no loss of double-bond configuration is observed in the product from cross coupling *cis*-1-OPiv with either $LiCuPh_2$ or LiCu(CN)Ph; this is expected on the basis of the mechanism outlined by Scheme III. However, significant loss of double-bond geometry is observed in the product arising from reaction of *cis*-1-OPiv with $LiCuBu_2$ at −20 °C, and even greater loss is observed when the reaction is carried out at −78 °C.

That loss of configuration does not result from isomerization of starting pivalate prior to alkylation was established as follows. Alkylation of *cis*-1-OPiv at −78 °C was stopped short of completion, and the unreacted pivalate was isolated by rotary chromatography. Analysis of the ^1H NMR spectrum of the ester showed no detectable *trans*-1-OPiv to be present. Control experiments showed that as little as 1% intercontamination of the isomeric pivalates can be detected by this method. The possibility that *trans*-1-OPiv does not accumulate in the unreacted pivalate because of a high trans/cis rate ratio for the pivalates was ruled out as follows. A synthetic mixture consisting of 85% *cis*- and 15% *trans*-1-OPiv was reacted at −20 °C with 0.5 equiv of $LiCuBu_2$ in ether, and the unreacted pivalates were isolated without fractionation by rotary chromatography. The mixture of pivalates consisted of 80% *cis*- and 20% *trans*-1-OPiv. Thus, if cis → trans isomerization occurs prior to alkylation, *trans*-1-OPiv would accumulate.

Product compositions were determined by capillary GC, which gave base line resolution of all four stereoisomers of **10**. Components of the product mixtures were identified by comparison of capillary GC retention times with those of authentic samples, which were prepared as follows. A mixture of dienes (*E*,*E*)-**10** and (*E*,*Z*)-**10**[11] was prepared by reaction of the ylide derived from triphenylcinnamylphosphonium bromide with either hexanal or phenylacetaldehyde. Likewise, a mixture of dienes (*Z*,*E*)-**10a** and (*E*,*E*)-**10a**[11] was prepared by reaction of the ylide derived

from triphenylbenzylphosphonium bromide with 2-octenal. Diene (*Z,E*)-**10b** was formed nearly stereoisomerically pure (95%) by the cross-coupling reaction and was identified by ^{1}H NMR.

Although dienes (*Z,Z*)-**10a** and (*Z,E*)-**10b** were neither independently synthesized nor isolated from the product mixtures for identification purposes, their presence was determined by a process of elimination. Binary mixtures of (*Z,E*)-**10** and presumably (*Z,Z*)-**10** are obtained by cross coupling *cis*-1-OPiv with LiCu(CN)Bu and LiCu(CN)Ph. Hydrogenation of these mixtures quantitatively yields only one product (1-phenylnonane[12] or 1,5-diphenylpentane[13]) as determined by capillary GC and ^{1}H NMR. This requires the components of each binary mixture to be double-bond stereoisomers (i.e., isomers of **10**). Since the binary mixtures contained (*Z,E*)-**10** but no (*E,E*)- or (*E,Z*)-**10**, the other component must be (*Z,Z*)-**10**.

That **11a** is not produced by cross coupling *cis*-1-OPiv with butylcopper reagents was demonstrated by preparing dienes **11a** by reaction of the ylide derived from triphenylallylphosphonium bromide with 2-phenylhexanal. The GC retention time of **11a** is much shorter than that for all isomers of **10a** and would be readily detected if present. Although **11b**[14] was not prepared, there was no evidence (GC or ^{1}H NMR) for its presence in the product mixtures resulting from reactions of *cis*-1-OPiv with phenylcopper reagents.

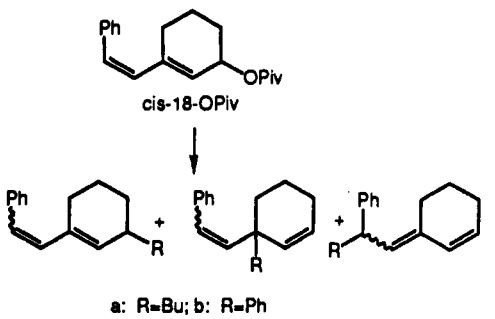
The data in Table I show that for cross coupling of *cis*-1-OPiv with $LiCuBu_2$, the reaction proceeds, at least in part, through intermediate t-**9** (Scheme II). Thus, in this instance, reductive elimination from **9** (to give **11**) is slower than isomerization of **9** → **8**. Hence, the product distribution from this reaction is not indicative of the relative reactivity of each allylic system within *cis*-1-OPiv.

In earlier work, it was shown that the regiospecificity[15] for cross coupling of allylic carboxylates with LiCu(CN)Bu is much higher than reactions with $LiCuBu_2$. Evidently, with LiCu(CN)Bu the initial γ-σ-allylcopper(III) complex undergoes reductive elimination (e.g., **8** → **10**, Scheme II) faster than allylic rearrangement via a $\sigma \rightarrow \pi \rightarrow \sigma$ mechanism (e.g., **8** → **9**).[6a,16]

Reaction of *cis*-1-OPiv with LiCu(CN)Bu gives only coupling products **10a** (Table I). No **11a** was detected in the product mixture. Furthermore, coupling product **10a** is formed with complete preservation of the original double-bond configuration. These results indicate that intermediate **9** is not involved in this reaction (Scheme II). If **9** were involved, the reaction would give predominantly coupling product **11a**, and loss of the original double-bond configuration in **10a** would be observed.[3,8]

Similar behavior has been observed for cross coupling of *cis*-18-OPiv with butyl- and phenylcopper reagents, and the results are presented in Table II. In these experiments, *cis*-18-OPiv was contaminated with 2% *trans*-18-OPiv as determined by ^{1}H NMR. Product distributions

Table II. Cross Coupling of *cis*-18-OPiv[a] with LiCu(Z)R[b]

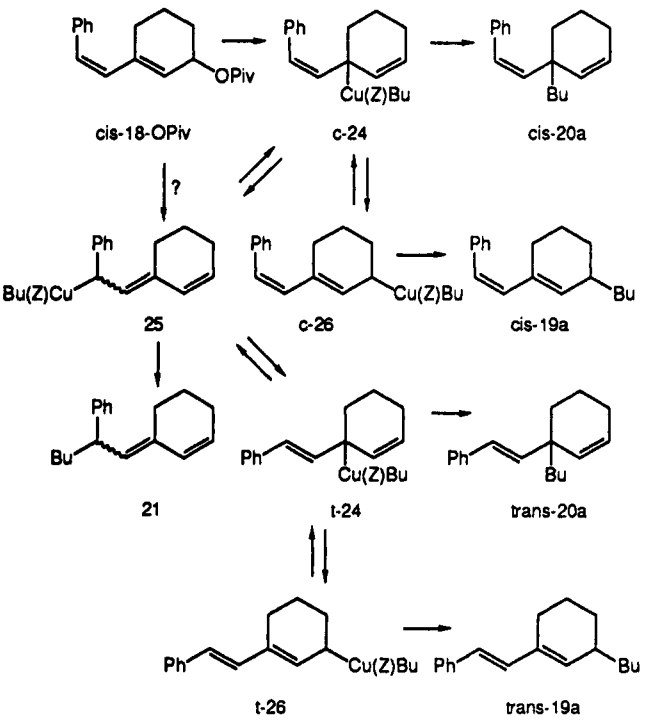


a: R=Bu; b: R=Ph

Reagent	T(°C)	cis-19	trans-19	cis-20	trans-20	21	Yield[c]
$LiCuBu_2$	-20	55%	45%	0%	0%	0%	87%
	-78	2%	98%	0%	0%	0%	--
LiCu(CN)Bu	-20	10%	1%	42%	1%	45%	77%
$LiCuPh_2$	-20	98%	2%	0%	0%	0%	89%
LiCu(CN)Ph	-20	98%	2%	0%	0%	0%	93%

[a] *cis*-18-OPiv was contaminated with 2% *trans*-18-OPiv. [b] Determined by capillary GC; average of two runs. [c] Isolated yields.

Scheme IV. Mechanism for Cross Coupling *cis*-18-OPiv with $LiCuBu_2$ and LiCu(CN)Bu



were determined as described for *cis*-1-OPiv, and components of the reaction mixture were isolated by rotary TLC and identified by comparison with authentic samples or by ^{1}H NMR analysis. Control experiments, similar to those described for *cis*-1-OPiv, indicate that *cis*-18-OPiv is configurationally stable to reaction conditions.

Authentic samples of *cis*- and *trans*-**19a** were prepared from aldehyde **22** and the ylide derived from triphenylbenzylphosphonium bromide (eq 5). Alkylation[17] of *trans*-**23**[4] with $Li_2Cu_3Bu_5$ and $Li_2Cu_3Ph_5$ affords *trans*-

(11) **12a**: Mukaiyama, T.; Shiono, M.; Sato, T. *Chem. Lett.* **1974**, 37. Cainelli, G.; Bertini, F.; Grasselli, P.; Zubiani, G. *Tetrahedron Lett.* **1967**, 1581. **12b**: Brenner, S.; Klein, J. *Isr. J. Chem.* **1969**, *7*, 735. Stetter H.; Reischl, A. *Chem. Ber.* **1960**, *93*, 791.

(12) This sample was spectroscopically and chromatographically identical with an authentic sample (Aldrich).

(13) This sample was spectroscopically and chromatographically identical with that prepared by the method of Borshe, W.; Wollemann, J. *Chem. Ber.* **1912**, *45*, 3713.

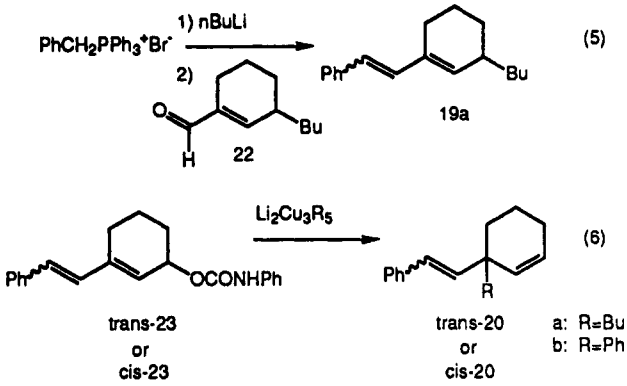
(14) Paquette, L. A.; Henzel, R. P.; Wilson, S. E. *J. Am. Chem. Soc.* **1972**, *94*, 7780.

(15) The terms "regioselective" and "regiospecific" are used as defined in footnote 3 of Goering, H. L.; Singleton, V. D., Jr. *J. Org. Chem.* **1983**, *48*, 1531.

(16) Goering, H. L.; Kantner, S. S. *J. Org. Chem.* **1984**, *49*, 422. Goering, H. L.; Seitz, E. P., Jr.; Tseng, C. C. *J. Org. Chem.* **1981**, *46*, 5304.

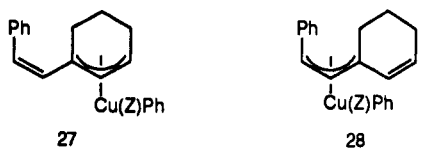
(17) Gallina, C. *Tetrahedron Lett.* **1982**, 3093. Goering, H. L.; Kantner, S. S.; Tseng, C. C. *J. Org. Chem.* **1983**, *48*, 715.

20a,b (eq 6).[4] Likewise, cross coupling *cis*-**23** with $Li_2Cu_3Bu_5$ gives *cis*-**20a** (eq 6).



The mechanism shown in Scheme IV correlates the present results and is consistent with our other work on cross-coupling reactions of dienyl allylic carboxylates with organocopper reagents. Reaction of *cis*-**18**-OPiv with alkylcopper reagents presumably occurs by oxidative addition with allylic rearrangement to give c-**24**. This γ-σ-allylcopper(III) intermediate has three options: it may (a) reductively eliminate to give γ coupling product *cis*-**20**; (b) isomerize to **25**; and/or (c) isomerize to c-**26**. The rate of these individual processes depends on the nontransferred ligand (Z) on copper.[6] When Z = CN, reductive elimination from c-**24** competes with isomerization to **25** and c-**26**. Reductive elimination from the latter two intermediates (to give **21** and *cis*-**19**) evidently occurs faster than reverse isomerization (e.g., **25** → t-**24**) because such a process would lead to loss of double-bond configuration in the α and γ coupling products *trans*-**19** and *trans*-**20** and none is observed. When Z is a second butyl group, reductive elimination from **24** is slow relative to isomerization to **25**. The partial to complete loss of double-bond configuration in the α coupling product in this case indicates that the ϵ-σ-allylcopper(III) complex **25** is an intermediate and it is at this stage that bond rotation can result in loss of configuration as shown in Scheme IV. Evidently, at −78 °C, **25** is a precursor for nearly all of the product. This intermediate accounts for the observed loss of double-bond configuration in the product (*trans*-**19**). An alternative route is also shown in Scheme IV and involves initial formation of **25** (ϵ-addition) without the intermediacy of c-**24** (γ-addition); from the available data, it is not possible to distinguish these two pathways.

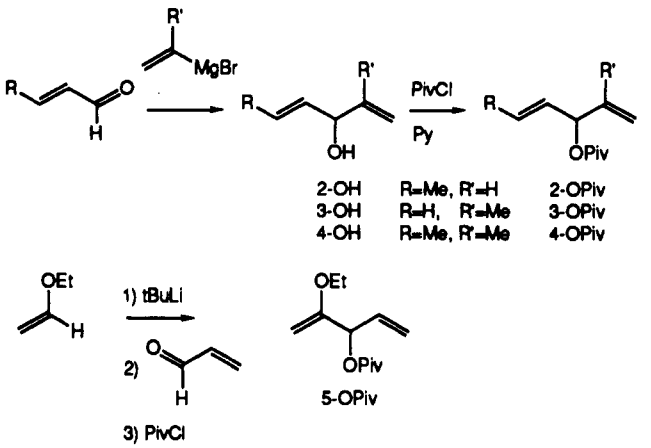
Reaction of *cis*-**18**-OPiv with either $LiCuPh_2$ or LiCu(CN)Ph gives only α coupling product **19b**. No loss of double-bond configuration is detected in either case, suggesting initial formation of π-allylcopper(III) intermediates **27** and/or **28**, which maintain partial or complete C_δ–C_ϵ double-bond character.



27 28

Thus, the groundwork for the structure–reactivity study for cross coupling diallylic pivalates **1–5**-OPiv has been laid. Summarizing, cross-coupling reactions of diallylic pivalates with LiCu(CN)Bu and probably LiCu(Z)Ph proceed with no isomerization of intermediates, and thus the product distribution reflects the rate of the oxidative addition process for each allylic system as illustrated in Schemes I and III. On the other hand, isomerization of intermediates occurs with $LiCuBu_2$. In this case, the product distribution reflects not only the rate of the oxidative addition process but of the isomerization and reductive elimination process as well.[6]

Scheme V. Synthesis of 2–5-OPiv



Cross-Coupling Reactions of Diallylic Pivalates. Diallylic pivalates **2–5**-OPiv were prepared from the corresponding alcohols as shown in Scheme V. Addition of vinylmagnesium bromide to crotonaldehyde gives **2**-OH.[18] Addition of 2-propenylmagnesium bromide to acrolein affords **3**-OH,[18] and addition of the same Grignard reagent to crotonaldehyde affords **4**-OH.[18,19] Synthesis of **5**-OPiv was accomplished by sequentially treating ethyl vinyl ether with *tert*-butyllithium,[20] then acrolein, and finally pivaloyl chloride.[21]

Cross-coupling reactions of the diallylic pivalates (**2–5**-OPiv) with butyl- and phenylcuprates were carried out in ether, and product distributions were determined by capillary GC; if base-line resolution was unobtainable, product ratios were determined by ^1H NMR. Alkylation products were isolated by preparative GC and fully characterized spectrally. Elemental composition was determined by high resolution mass spectroscopy.

The homocuprates used in these experiments were prepared directly from cuprous iodide[22] and 2 equiv of either *n*-BuLi (2.40 M in hexanes) or PhLi (2.0 M in 7:3 cyclohexane/ether). The cyanocuprates were prepared likewise from cuprous cyanide[23] and 1 equiv of either *n*-BuLi or PhLi. An ethereal solution of pivalate was added to a solution of cuprate (2 equiv) at −20 °C, and the solution was allowed to warm to room temperature overnight. The final solutions were approximately 0.1 M in cuprate.

Under these conditions, isomerization of pivalates **2–5**-OPiv to the more stable conjugated isomers apparently does not occur. In other work,[6a] we have found that **29**-OPiv is configurationally stable to lithium cuprate alkylating conditions. In the presence of magnesium salts isomerization of **29**-OPiv to **15**-OPiv occurs rapidly at 0 °C (eq 7).[6a]

Butylation of **2**-OPiv yielded **30a**, and phenylation, **30b**[24]

(18) (a) Boccara, N.; Maitte, P. *Bull. Soc. Chim. Fr.* **1972**, 1448. (b) Oppolzer, W.; Snowden, R. L.; Simmons, D. P. *Helv. Chim. Acta* **1981**, *64*, 2002.

(19) Rautenstrauch, V.; Büchi, G.; Wüest, H. *J. Am. Chem. Soc.* **1974**, *96*, 2576.

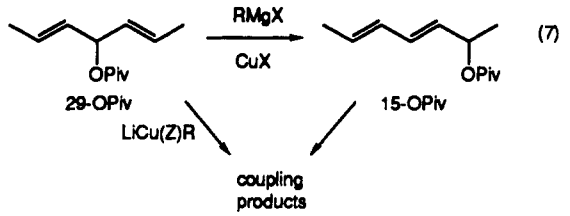
(20) Schöllkoph, U.; Hänssle, P. *Justus Liebig Ann. Chem.* **1972**, *763*, 208. Baldwin, J. E.; Höfle, G. A.; Lever, O. W., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 7125.

(21) Trost, B. M.; Gowland, F. W. *J. Org. Chem.* **1979**, *44*, 3448.

(22) CuI (Aldrich) was purified according to the procedure of Kauffman, G. B.; Tetter, L. A. *Inorg. Synth.* **1963**, *7*, 9.

(23) CuCN was prepared according to the procedure of Barber, H. J. *J. Chem. Soc.* **1943**, 79.

(24) Reich, H. J.; Shah, S. K.; Chow, F. *J. Am. Chem. Soc.* **1979**, *101*, 6648.



(7)

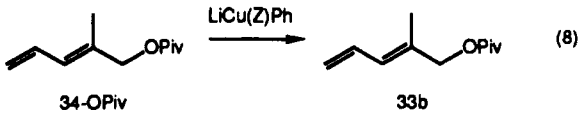
(Table III). These products arise from γ-alkylation at the least-substituted vinyl carbon, and the results are presented in Table III. No α-alkylation, and more significantly, no γ′-alkylation at the substituted vinyl carbon (to yield **31**) was observed. Thus, cross coupling occurs significantly faster at the unsubstituted end (γ coupling) of the allylic system relative to the methyl-substituted end (γ′ coupling).[25]

The ^{1}H NMR spectrum of (*E*)-**30a** is difficult to analyze due to the chemical shift equivalence of the vinyl protons. The product mixture derived from alkylation of 2-OPiv with $LiCuBu_2$ was hydrogenated over 5% palladium on carbon in order to be certain of the assignment of **30a**. The saturated product obtained from hydrogenation was shown to be homogeneous by capillary GC and had the same retention time as an authentic sample of *n*-decane. Thus, alkylation of 2-OPiv with $LiCuBu_2$ gives only one regioisomer.

Butylation or phenylation of 3-OPiv yielded products primarily from γ coupling at the least-substituted double bond (**32**), and the results are presented in Table IV. It appears that a β substituent, in certain instances ($LiCuBu_2$ and LiCu(CN)Ph), is less effective than a γ-substituent in directing the site of coupling; however, high regiospecificity (no detectable γ′-alkylation) was observed with LiCu(CN)Bu and $LiCuPh_2$.

The stereochemistry of the trisubstituted double bond in product **33a** is not readily assigned on the basis of its ^{1}H NMR spectrum. Therefore, *E* and *Z* isomers of **33a** were prepared by Wittig reaction of the ylide derived from triphenylhept-2-ylphosphonium bromide with acrolein. The distinguishing feature in the ^{1}H NMR spectra of these two isomers is that the allylic methylene triplet of the *Z* isomer (δ 2.17) appears downfield of the corresponding signal of the *E* isomer (δ 2.04). This is an effect of steric deshielding.[26]

The stereochemistry of the trisubstituted double bond in **33b** was assigned on the basis of experiments outlined in eq 8. Cross coupling 34-OPiv (prepared from the

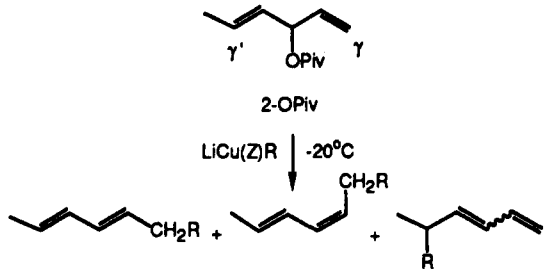


(8)

corresponding alcohol[27] and pivaloyl chloride) with $LiCuPh_2$ (or LiCu(CN)Ph, or PhMgBr/1% CuCN) gives only one product ((*E*)-**33b**), which is identical with the minor product obtained by cross coupling 3-OPiv with LiCu(CN)Ph. In other work,[3] we have shown that the α coupling product derived from cross coupling allylic carboxylates with phenylcuprates retains the double-bond configuration of the starting ester; therefore, the trisubstituted double bond of **33b** most probably has the *E* configuration.

Reaction of 4-OPiv with organocuprates shows directly that a β-methyl substituent has less influence than a γ-methyl substituent over control of the site of cross coupling. Butylation or phenylation of 4-OPiv yields mainly products **35** as a result of γ coupling with the allylic system

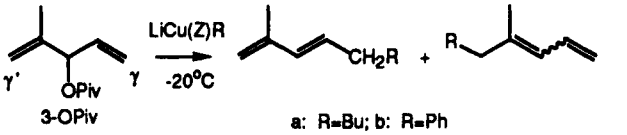
Table III. Cross Coupling of 2-OPiv with LiCu(Z)R[a]



Reagent	E,E-30	E,Z-30	31	Yield[b]
$LiCuBu_2$	93%	7%	0%	93%
LiCu(CN)Bu	73%	27%	0%	96%
$LiCuPh_2$	92%	8%	0%	88%
LiCu(CN)Ph	64%	36%	0%	89%

[a] Determined by capillary GC; average of two runs. [b] Isolated yields.

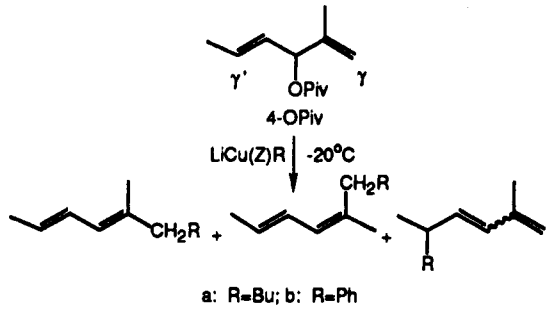
Table IV. Cross Coupling of 3-OPiv with LiCu(Z)R[a]



Reagent	32	33	Yield[b]
$LiCuBu_2$	76%	24%	85%
LiCu(CN)Bu	100%	0%	93%
$LiCuPh_2$	100%	0%	85%
LiCu(CN)Ph	95%	5%	73%

[a] Determined by capillary GC; average of two runs. [b] Isolated yields.

Table V. Cross Coupling of 4-OPiv with LiCu(Z)R[a]



Reagent	E,E-35	E,Z-35	36	Yield[b]
$LiCuBu_2$	50%	46%	4%	79%
LiCu(CN)Bu	18%	65%	17%	96%
$LiCuPh_2$	57%	0%	43%	89%
LiCu(CN)Ph	39%	32%	29%	92%

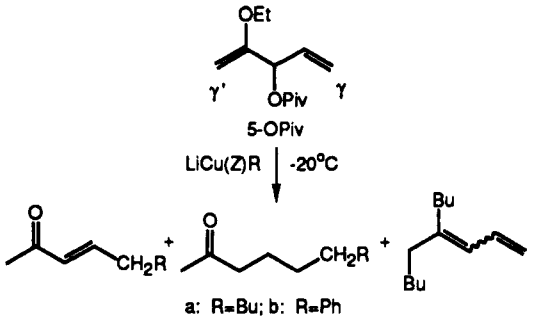
[a] Determined by capillary GC; average of two runs. [b] Isolated yields.

(25) That alkylation product **31a** could be detected if it were present was demonstrated as follows. Wittig reaction of the ylide derived from triphenylallylphosphonium bromide with 2-methylhexanal gives **31a** as a mixture of *E* and *Z* isomers. Coinjection of authentic samples of **31a** with **30a** showed that as little as 0.2% of **31a** could easily be detected by capillary GC.

(26) Jackman, L. M.; Sternhill, S. *Applications of Nuclear Magnetic Resonance*, 2nd ed.; Pergamon Press: New York, 1969; pp 222–5.

(27) Piers, E.; Ruediger, E. H. *J. Org. Chem.* **1980**, *45*, 1725.

Table VI. Cross Coupling of 5-OPiv with LiCu(Z)R[a]



Reagent	37	38	39	Yield[b]
$LiCuBu_2$	63%	16%	21%	70%
LiCu(CN)Bu	100%	0%	0%	93%
$LiCuPh_2$	100%	0%	--	94%
LiCu(CN)Ph	100%	0%	--	96%

[a] Determined by capillary GC (after acidic workup); average of two runs. [b] Isolated yields.

bearing a β-substituent, and the results are presented in Table V. Reaction of 4-OPiv with $LiCuBu_2$ gives ≈96% γ-alkylation, but other reagents are less regiospecific.

Structural assignments of the isomers of **35** are based on chemical shifts of the allylic methylene protons in the ^1H NMR spectra.[26] As observed for the *E* and *Z* isomers of **33a**, the signal due to the methylene protons of (*E,E*)-**35** were upfield (≈0.1 ppm) of the corresponding signal for (*E,Z*)-**35**. Regioisomer **36** is produced as a single stereoisomer and was identified as the *E* double-bond isomer on the basis of its ^1H NMR spectrum.

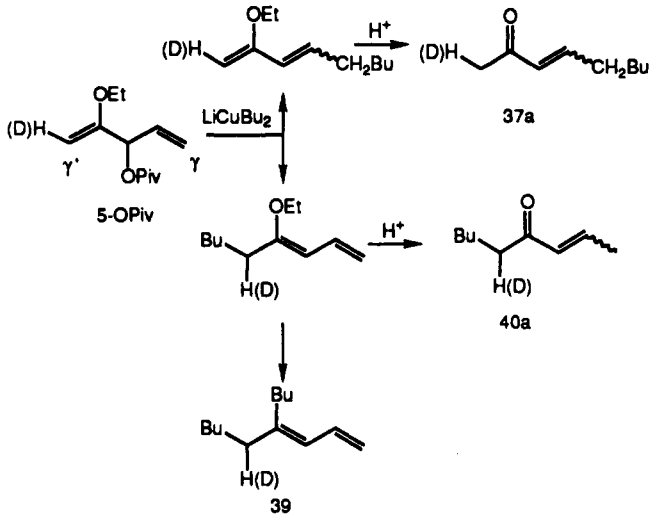
The effect that a β-ethoxy group has on the regiochemistry of cross coupling is demonstrated by reaction of 5-OPiv with organocuprates. Products obtained after acidic workup are shown in Table VI.

Alkylation of 5-OPiv with $LiCuBu_2$ is particularly odd in that besides coupling product **37**, hydride reduction product **38** and dialkylation product **39** are obtained (Table VI). Neither product is observed with LiCu(CN)Bu. The dialkylation product **39** is obtained as a single stereoisomer as determined by capillary GC and ^1H NMR, and its identity was confirmed by independent synthesis. Reaction of the ylide derived from triphenylallylphosphonium bromide with 5-decanone gives **39** as a 4:1 mixture of stereoisomers as determined by capillary GC and ^1H NMR spectroscopy. The stereochemistry of the major isomer could not be assigned from the NMR data, but further experiments (vide infra) indicate that the dialkylation product and the major isomer obtained from the Wittig reaction has the *E* configuration.

If only 1 equiv of $LiCuBu_2$ is used, or if the reaction time is reduced (3 h at room temperature), enone **40a** can be isolated from the product mixture (Scheme VI). Thus, products **37** and **38** result from γ-alkylation, and **39** is evidently produced from initial γ'-alkylation followed by direct displacement of ethoxide[28] by a second equivalent of $LiCuBu_2$ as illustrated in Scheme VI.

Labeled γ-D-5-OPiv was prepared from *cis*-ethyl vinyl ether-β-*d*[29] and alkylated with 2 equiv of $LiCuBu_2$ in order to determine the double-bond configuration of **39** and to

Scheme VI. Alkylation of 5-OPiv and γ-D-5-OPiv with $LiCuBu_2$



support the notion that **39** arises from initial γ'-alkylation. After isolating **39**-*d* from the product mixture, the ^1H NMR spectrum indicated that the most upfield allylic methylene signal (due to the methylene trans to the vinyl group[26]) integrates as only one proton. This establishes that **39** arises from initial γ'-alkylation, and it also confirms that *E* stereochemistry about the double bond.[26]

In conclusion, these experiments support our original mechanistic proposal[3,5,16] for cross-coupling reactions of allylic carboxylates with organocopper reagents as shown in Schemes II and IV. Loss of double-bond configuration in the conjugated coupling product for cross coupling *cis*-1-OPiv (Scheme II) and *cis*-18-OPiv (Scheme IV) with $LiCuBu_2$ is consistent with a low reductive elimination/σ → π isomerization rate ratio. With LiCu(CN)Bu, this ratio is much larger.[6a,9,16] Put another way, cross-coupling reactions of cyanoalkylcuprates are more regiospecific than those of dialkylcuprates.[6a,9,16] On the other hand, cross coupling *cis*-1-OPiv and *cis*-18-OPiv with $LiCuPh_2$ and LiCu(CN)Ph gives a coupling product with complete retention of double-bond configuration. This is consistent with a mechanism involving initial formation of π-allylcopper(III) intermediates **12** or **13** (Scheme III) and **27** or **28**.

Increasing double-bond substitution of an allylic system slows down the rate of cross coupling with phenyl- and butylcuprates. Presumably, with LiCu(CN)Bu and LiCu(Z)Ph, this arises from slowing down the initial oxidative addition step. The regiochemical result of cross coupling pivalates 1–5-OPiv with diphenyl-, cyanophenyl-, and cyanobutylcuprates indicates that a γ-substituted allyl system is less reactive than a β-substituted system which, in turn, is less reactive than an unsubstituted one. The fact that cyanobutylcuprates (sp^3 reagents) and phenylcuprates (sp^2 reagents) give similar product distributions suggests that steric factors are equally important for each reaction mechanism.

Preferential γ coupling (over γ' coupling) for reactions of LiCu(CN)Bu and LiCu(Z)Ph with 1-OPiv, 2-OPiv, 3-OPiv, and 4-OPiv is expected for steric reasons; increasing double-bond substitution is expected to retard both the rate of π-complexation and the rate of formation of σ- or π-allylcopper(III) complex.

The situation is apparently more complicated for cross-coupling diallylic pivalates with $LiCuBu_2$. A number of factors control the regiochemical course of the reaction (namely, rates of oxidative addition, σ → π → σ isomeri-

(28) Fujisawa, T.; Kurita, Y.; Kawashima, M.; Sato, T. *Chem. Lett.* **1982**, 1641. McMurry, J. E.; Scott, W. J. *Tetrahedron Lett.* **1983**, 979. McMurry, J. E.; Scott, W. J. *Tetrahedron Lett.* **1980**, 4313.

(29) Keul, H.; Choi, H.-S.; Kuczkowski, R. L. *J. Org. Chem.* **1985**, *50*, 3365.

zation, and reductive elimination). Generally, however, the product distributions obtained by reaction of diallylic pivalates with $LiCuBu_2$ are similar to those by reaction with LiCu(CN)Bu.

Furthermore, this study demonstrates that cross-coupling reactions of molecules containing two differently substituted allylic systems with an organocopper reagent should occur chemoselectively at the least-substituted end of the allylic system.

Experimental Section

General Methods. Cuprous salts were prepared and purified as described earlier.[22,23] *n*-BuLi (2.5 M in hexanes) and PhLi (2.0 M in 7:3 cyclohexane/ether) were purchased from Aldrich Chemical Company. Proton NMR spectra were obtained at 200 MHz; the instrumentation for this investigation has been reported.[3] Coupling constants are in hertz.

(*Z*)-1-Phenyl-1,4-pentadien-3-yl 2,2-Dimethylpropanoate (*cis*-1-OPiv). Following the procedure of Neumann and Seebach,[7] a solution of 1.83 g (10 mmol) of *cis*-β-bromostyrene in 40 mL of Trapp solvent mixture (4:1:1 THF/ether/pentane) was cooled to −120 °C before 12.5 mL of 1.6 M *t*-BuLi was added over a 5-min period. The reaction was warmed to −110 °C for 1 h and then warmed to −90 °C before 600 mg (15 mmol) of acrolein was added. The reaction mixture was warmed to 0 °C for 30 min, and then 1.33 g (11 mmol) of pivaloyl chloride was added. After stirring for 2 h at room temperature, the reaction was quenched with ice water and the solution was extracted with ether. The organic phase was washed with saturated $NaHCO_3$ and brine and dried over $MgSO_4$. After filtration, removal of solvent by rotary evaporation, and purification by rotary TLC (silica gel), 1.76 g (72%) of pure *cis*-1-OPiv was obtained: NMR (δ, $CDCl_3$) 7.4–7.2 (m, 5 H), 6.66 (d, 1 H, J = 11.9), 6.13 (app ddq, 1 H, J = 8.9, 5.0, 1.3), 5.93 (ddd, 1 H, J = 17.2, 10.3, 5.0), 5.62 (dd, 1 H, J = 11.9, 8.9), 5.33 (app dt, 1 H, J = 17.2, 1.3), 5.23 (app dt, 1 H, J = 10.3, 1.3), 1.20 (s, 9 H); high resolution mass spectrum, calcd for $C_{16}H_{20}O_2$ m/e 244.1464, found 244.1466.

(*E*)-1-Phenyl-1,4-pentadien-3-yl 2,2-dimethylpropanoate (*trans*-1-OPiv) was prepared from the corresponding alcohol[30] and pivaloyl chloride in the usual way:[31] bp 95–99 °C (0.02 mm); NMR (δ, $CDCl_3$) 7.4–7.2 (m, 5 H), 6.64 (d, 1 H, J = 15.6), 6.17 (dd, 1 H, J = 15.6, 6.4), 5.90 (ddd, 1 H, J = 16.0, 12.4, 5.9), 5.85 (app br t, 1 H, J = 5.9), 5.24 (dd, 1 H, J = 16.0, 1.1), 5.25 (dd, 1 H, J = 12.4, 1.1), 1.24 (s, 9 H); high resolution mass spectrum, calcd for $C_{16}H_{20}O_2$ m/e 244.1464, found 244.1466.

General Procedure for Cross Coupling Diallylic and Dienyl Allylic Pivalates with $LiCuR_2$ and LiCu(CN)R. An ethereal solution of the pivalate (0.5 mmol in 2 mL) was added to a solution of cuprate, which was prepared by adding slightly less[31] than a stoichiometric amount of *n*-BuLi or PhLi to a cold (−20 °C) suspension of CuI[22] or CuCN[23] in 8 mL of ether. The reaction was slowly warmed to room temperature overnight. After standard workup,[9] coupling products were isolated by rotary TLC (silica gel). Coupling products derived from 5-OPiv (ethyl vinyl ethers) were first hydrolyzed to the corresponding ketones by stirring with 10 mL of THF containing 2 mL of 2 M HCl before isolation by rotary TLC. Spectral properties of coupling products are listed below.

(*E*,*E*)-1-Phenyl-1,3-nonadiene ((*E*,*E*)-10a): NMR (δ, $CDCl_3$) 7.5–7.2 (m, 5 H), 6.76 (dd, 1 H, J = 15.6, 10.2), 6.43 (d, 1 H, J = 17.0), 6.20 (dd, 1 H, J = 15.1, 10.2), 5.83 (dt, 1 H, J = 15.1, 7.0), 2.14 (app q, 2 H, J = 7.0), 1.5–1.2 (m, 6 H), 1.0–0.8 (m, 3 H); high resolution mass spectrum, calcd for $C_{15}H_{20}$ m/e 200.1566, found 200.1565.

(*E*,*Z*)-1-Phenyl-1,3-nonadiene ((*E*,*Z*)-10a): NMR (δ, $CDCl_3$) 7.5–7.1 (m, 5 H), 7.06 (ddd, 1 H, J = 15.6, 11.1, 1.1), 6.65 (d, 1 H, J = 15.6), 6.16 (dd, 1 H, J = 11.1, 10.7), 5.53 (dt, 1 H, J = 10.7, 7.5), 2.28 (app q, 2 H, J = 7.5), 1.5–1.2 (m, 6 H), 1.0–0.8 (m, 3 H); high resolution mass spectrum, calcd for $C_{15}H_{20}$ m/e 200.1566, found 200.1565.

(*Z*,*E*)-1-Phenyl-1,3-nonadiene ((*Z*,*E*)-10a) was contaminated with 25% of (*Z*,*Z*)-**10a**: NMR (δ, $CDCl_3$) 7.4–7.1 (m, 5 H), 6.60 (ddt, 1 H, J = 14.5, 10.0, 1.5), 6.32 (d, 1 H, J = 11.0), 6.22 (app t, 1 H, J = 10.0), 5.90 (dt, 1 H, J = 14.5, 7.0), 2.11 (app q, 2 H, J = 7.0), 1.4–1.1 (m, 6 H), 0.9–1.0 (m, 3 H); residual peaks due to (*Z*,*Z*)-**10** appear at δ 5.48, δ 5.6, and an app p at δ 2.26 (J = 7.0).

(*Z*,*E*)-1,5-Diphenyl-1,3-pentadiene ((*Z*,*E*)-10b) was contaminated with 20% (*Z*,*Z*)-**10b**: NMR (δ, $CDCl_3$) 7.4–7.1 (m, 10 H), 6.68 (ddt, 1 H, J = 15.2, 10.8, 1.1), 6.36 (d, 1 H, J = 11.6), 6.23 (app t, 1 H, J = 11.0), 5.99 (dt, 1 H, J = 15.2, 7.1), 3.65 (d, 2 H, J = 7.1); residual peaks due to (*Z*,*Z*)-**10b** appear at δ 6.55, δ 5.75 and a doublet at δ 3.62 (J = 7.7).

(*E*,*Z*)- and (*E*,*E*)-1,5-diphenyl-1,3-pentadiene ((*E*,*Z*)- and (*E*,*E*)-10b) were prepared by Wittig reaction: 460 mg of triphenylcinnamylphosphonium bromide was slurried in 10 mL of ether and cooled to 0 °C before addition of 0.4 mL of 2.4 M *n*-BuLi. After stirring for 10 min, 120 mg of phenylacetaldehyde was added, and the reaction mixture was warmed to room temperature and stirred overnight. Filtration of the reaction mixture followed by solvent removal by rotary evaporation gave a crude diene, which was purified by rotary TLC to give 133 mg (60%) of product that was a 1:1 mixture of stereoisomers. **(*E*,*Z*)-10b**: NMR (δ, $CDCl_3$) 7.5–7.1 (m, 11 H), 6.61 (d, 1 H, J = 15.5), 6.30 (app br t, 1 H, J = 11.2), 5.69 (dt, 1 H, J = 11.2, 8.2), 3.65 (d, 2 H, J = 8.2); high resolution mass spectrum, calcd for $C_{17}H_{16}$ m/e 220.1253, found 200.1253. **(*E*,*E*)-10b**: NMR (δ, $CDCl_3$) 7.4–7.1 (m, 10 H), 6.77 (dd, 1 H, J = 15.6, 10.2), 6.46 (d, 1 H, J = 15.6), 6.25 (dd, 1 H, J = 15.0, 10.2), 5.96 (app dt, 1 H, J = 15.0, 6.9), 3.48 (d, 2 H, J = 6.9); high resolution mass spectrum, calcd for $C_{17}H_{16}$ m/e 220.1253, found 220.1253.

(*E*,*Z*)- and (*E*,*E*)-1-phenyl-1,3-nonadiene ((*E*,*Z*)- and (*E*,*E*)-10a) were prepared (as described for (*E*,*Z*)- and (*E*,*E*)-**10b**) as a 34:66 mixture of respective stereoisomers from triphenylcinnamylphosphonium bromide and hexanal in 90% yield.

(*Z*,*E*)- and (*E*,*E*)-1-phenyl-1,3-nonadiene ((*Z*,*E*)- and (*E*,*E*)-10a) were prepared (as described for (*E*,*Z*)- and (*E*,*E*)-**10b**) as a 3:7 mixture of respective stereoisomers from triphenylbenzylphosphonium bromide and 2-octenal in 90% yield.

(*E*)- and (*Z*)-5-phenyl-1,3-nonadiene ((*E*)- and (*Z*)-11a) were prepared (as described for (*E*,*Z*)- and (*E*,*E*)-**10b**) as a 60:40 mixture of respective stereoisomers from triphenylallylphosphonium bromide and 2-phenylhexanal in 51% yield. **(*E*)-11a**: NMR (δ, $CDCl_3$) 7.4–7.1 (m, 5 H), 6.31 (app dt, 1 H, J = 16.8, 10.2), 6.10 (dd, 1 H, J = 15.1, 10.2), 5.81 (dd, 1 H, J = 15.1, 7.8), 5.09 (d, 1 H, J = 16.8), 4.98 (d, 1 H, J = 10.2), 3.26 (app q, 1 H, J = 7.8), 1.6–1.8 (m, 2 H), 1.4–1.1 (m, 4 H), 1.0–0.8 (m, 3 H); high resolution mass spectrum, calcd for $C_{15}H_{20}$ m/e 200.1565, found 200.1566. **(*Z*)-11a**: NMR (δ, $CDCl_3$) 7.4–7.1 (m, 5 H), 6.73 (app dt, 1 H, J = 17.8, 10.8), 6.00 (app t, 1 H, J = 10.8), 5.55 (app t, 1 H, J = 10.8), 5.20 (d, 1 H, J = 17.8), 5.10 (d, 1 H, J = 10.8), 3.72 (app q, 1 H, J = 10.8), 1.6–1.8 (m, 2 H), 1.4–1.1 (m, 4 H), 0.8–1.0 (m, 3 H); high resolution mass spectrum, calcd for $C_{15}H_{20}$ m/e 220.1566, found 200.1566.

Hydrogenation of (*Z*,*Z*)- and (*Z*,*E*)-1-Phenyl-1,3-nonadiene. A 0.1 M ethereal solution of 100 mg of a 4:1 mixture of (*Z*,*E*)- and (*Z*,*Z*)-**10a** (obtained by reaction of *cis*-1-OPiv with LiCu(CN)Bu) was hydrogenated over 50 mg of 5% Pd on carbon while under 40 psi of H_2. After 1 h, the catalyst was filtered off and solvent was removed by rotary evaporation to give 100 mg (100%) of 1-phenylnonane.[12]

Hydrogenation of (*Z*,*Z*)- and (*Z*,*E*)-1,5-Diphenyl-1,3-pentadiene. A 0.1 M ethereal solution of 110 mg of a 2:1 mixture of (*Z*,*E*)- and (*Z*,*Z*)-**10b** (obtained by reaction of *cis*-1-OPiv with LiCu(CN)Ph) was hydrogenated as described above to give 110 mg (100%) of 1,5-diphenylpentane.[13]

(*Z*)-3-(2-Phenylethenyl)-2-cyclohexen-1-yl 2,2-Dimethylpropanoate (*cis*-18-OPiv). A solution of 1.51 g of *trans*-3-styryl-2-cyclohexenone was irradiated with black light in a Rayonet apparatus for 4 h.[32] Removal of solvent by rotary evaporation followed by rotary TLC (silica gel) afforded 1.19 g of *cis*- (R_f = 0.8) and 0.28 g of *trans*-3-styryl-2-cyclohexenone (R_f = 0.5). Reduction of the cis isomer with $NaBH_4$ gave the corresponding

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alcohol,[33] which was converted to *cis*-18-OPiv in the usual way[31] and purified by rotary TLC (silica gel): NMR (δ, $CDCl_3$) 7.4–7.2 (m, 5 H), 6.45 (d, 1 H, J = 12.1), 6.10 (d, 1 H, J = 12.1), 5.70 (br s, 1 H), 5.27 (br s, 1 H), 1.98 (br s, 2 H), 1.9–1.6 (m, 4 H), 1.18 (s, 9 H); high resolution mass spectrum, calcd for $C_{19}H_{24}O_2$ m/e 284.1777, found 284.1779.

(*E*)-3-(2-Phenylethenyl)-2-cyclohexen-1-yl 2,2-dimethylpropanoate (*trans*-18-OPiv) was prepared in the usual way[31] from the corresponding alcohol[33] and pivaloyl chloride and was purified by rotary TLC: NMR (δ, $CDCl_3$) 7.5–7.2 (m, 5 H), 6.78 (d, 1 H, J = 16.0), 6.58 (d, 1 H, J = 16.0), 5.84 (br s, 1 H), 5.37 (br s, 1 H), 2.1–2.4 (m, 2 H), 1.9–1.5 (m, 4 H), 1.18 (s, 9 H); high resolution mass spectrum, calcd for $C_{19}H_{24}O_2$ m/e 284.1777, found 284.1779.

(*Z*)-1-(2-Phenylethenyl)-3-butylcyclohexene (*cis*-19a): NMR (δ, $CDCl_3$) 7.4–7.1 (m, 5 H), 6.32 (d, 1 H, J = 12.3), 6.07 (d, 1 H, J = 12.3), 5.65 (br s, 1 H), 2.0–2.2 (m, 1 H), 1.9–1.8 (m, 2 H), 1.8–1.6 (m, 2 H), 1.5–1.0 (m, 8 H), 0.87 (br t, 3 H, J = 6.9); high resolution mass spectrum, calcd for $C_{18}H_{24}$ m/e 240.1879, found 240.1879.

(*E*)-1-(2-Phenylethenyl)-3-butylcyclohexene (*trans*-19a): NMR (δ, $CDCl_3$) 7.39 (d, 2 H, J = 8.0), 7.30 (app t, 2 H, J = 8.0), 7.18 (t, 1 H, J = 8.0), 6.78 (d, 1 H, J = 16.1), 6.44 (d, 1 H, J = 16.1), 5.80 (s, 1 H), 2.1–2.4 (m, 3 H), 2.0–1.8 (m, 2 H), 1.7–1.5 (m, 1 H), 1.4–1.0 (m, 7 H), 0.91 (br t, 3 H, J = 6.8); high resolution mass spectrum, calcd for $C_{18}H_{24}$ m/e 240.1879, found 240.1879.

(*Z*)-1-(2-Phenylethenyl)-3-phenylcyclohexene (*cis*-19b): NMR (δ, $CDCl_3$) 7.4–7.1 (m, 10 H), 6.42 (d, 1 H, J = 12.1), 6.15 (d, 1 H, J = 12.1), 5.76 (br s, 1 H), 3.42 (br s, 1 H), 2.1–1.9 (m, 2 H), 1.8–1.2 (m, 4 H); high resolution mass spectrum, calcd for $C_{20}H_{20}$ m/e 260.1566, found 260.1563.

3-Butyl-1-cyclohexene-1-carboxaldehyde (22) was prepared in three steps according to the general method of Seifert and Schinz.[34] **A. 3-Butyl-2-oxocyclohexane-1-carboxaldehyde.** To a cold (0 °C) suspension of 4.00 g (74 mmol) of NaOMe in 300 mL of ether was rapidly added mixture of 10.14 g (66 mmol) of 2-butylcyclohexanone and 5.20 g (70 mmol) of ethyl formate. The reaction was warmed to room temperature and stirred overnight before it was poured into 300 mL of water. The ether portion was separated from the aqueous layer and washed with 100 mL of 5% NaOH. The combined aqueous washings were acidified with 5% HCl and then extracted with ether. The organic phase was dried over $MgSO_4$ and filtered, and solvent was removed by rotary evaporation. Distillation of residue gave a small forerun (<1 g, 65–80 °C, 1 mm) followed by the main fraction (9.65 g, 80%, 95–96 °C, 1 mm): NMR (δ, $CDCl_3$) 14.67 (d, 1 H, J = 3.5), 8.61 (d, 1 H, J = 3.5), 2.32 (app br t, 3 H, J = 6.3), 1.9–1.7 (m, 3 H), 1.6–1.2 (m, 7 H), 0.90 (br t, 3 H, J = 6.8); high resolution mass spectrum, calcd for $C_{11}H_{18}O_2$ m/e 182.1307, found 182.1307. **B. 2-[(1-Propyloxy)ethylidene]-6-butyl-1-cyclohexanone.** To a solution of 2.49 g (13.7 mmol) of the above dione in 10 mL of benzene containing 1.1 mL of *n*-PrOH was added ≈10 mg of TsOH. The reaction was heated to reflux for 3 h with simultaneous removal of water using a Dean–Stark trap. At this time, the reaction was cooled, taken up in ether, and washed with 10% NaOH and brine before being dried over $MgSO_4$. Solvent was removed by rotary evaporation, and distillation (90–93 °C, 0.05 mm) of the residue gave 2.38 g (77%) of enol ether: NMR (δ, $CDCl_3$) 7.31 (br s, 1 H), 3.95 (t, 2 H, J = 6.6), 2.6–2.4 (m, 1 H), 2.4–2.0 (m, 2 H), 2.0–1.2 (m, 12 H), 0.95 (t, 3 H, J = 6.8), 0.80 (t, 3 H, J = 6.8); high resolution mass spectrum, calcd for $C_{14}H_{24}O_2$ m/e 224.1777, found 224.1776. **C. 3-Butyl-1-cyclohexene-1-carboxaldehyde (22).** A solution of 2.30 g (10.3 mmol) of the above enol ether in 10 mL of ether was added to a suspension of 480 mg (12.6 mmol) of $LiAlH_4$ in 10 mL of ether. The reaction was refluxed for 15 min before being cooled to 0 °C and addition of 30 mL of 10% H_2SO_4. After warming to room temperature, the aqueous phase was extracted twice with ether and the combined ether extracts were washed with water, saturated aqueous $NaHCO_3$, and brine and then dried over $MgSO_4$. Solvent was removed by rotary evaporation and distillation (86–89 °C, 0.75 mm) of the residue gave 1.68 g (98%) of **22**: NMR (δ, $CDCl_3$) 9.41 (s, 1 H), 6.68 (br s, 1 H), 2.4–2.2 (m, 2 H), 2.2–2.0 (m, 1 H), 2.0–1.7 (m, 2 H), 1.6–1.1 (m, 8 H), 0.93 (br t, 3 H, J = 6.8); high resolution mass spectrum, calcd for $C_{11}H_{18}O$ m/e 166.1358, found 166.1355.

1-(2-Phenylethenyl)-3-butylcyclohexene (19a) was prepared (as described for (*E*,*Z*)- and (*E*,*E*)-**10b**) as an 86:14 mixture of *E*:*Z* isomers from triphenylbenzylphosphonium bromide and 3-butylcyclohexene-1-carboxaldehyde (**22**).

(*Z*)-3-(2-Phenylethenyl)-2-cyclohexenyl phenylcarbamate (*cis*-23) was prepared in the standard way[4] from the corresponding alcohol[33] and phenyl isocyanate in 94% yield. After purification by rotary TLC, *cis*-**23** was isolated as a viscous oil: NMR (δ, $CDCl_3$) 7.5–7.2 (m, 9 H), 7.04 (t, 1 H, J = 6.9), 6.55 (br s, 1 H), 6.46 (d, 1 H, J = 12.3), 6.11 (d, 1 H, J = 12.3), 5.80 (br s, 1 H), 5.33 (br s, 1 H), 2.0–1.4 (m, 6 H); high resolution mass spectrum, calcd for $C_{21}H_{21}NO_2$ m/e 319.1572, found 319.1572.

(*Z*)-1-(2-Phenylethenyl)-1-butyl-2-cyclohexene (*cis*-20a). Reaction of *cis*-**23** with $Li_2Cu_3Bu_5$ according to the procedure reported earlier[4,17] gave *cis*-**20a** in 88% yield after isolation by rotary TLC: NMR (δ, $CDCl_3$) 7.4–7.1 (m, 5 H), 6.32 (d, 1 H, J = 12.3), 6.07 (d, 1 H, J = 12.3), 5.65 (br s, 1 H), 2.2–2.0 (m, 1 H), 1.9–1.8 (m, 2 H), 1.8–1.6 (m, 2 H), 1.5–1.0 (m, 8 H), 0.87 (br t, 3 H, J = 6.9); high resolution mass spectrum, calcd for $C_{18}H_{24}$ m/e 240.1879, found 240.1879.

(*E*)-1-(2-Phenylethenyl)-1-butyl-2-cyclohexene (*trans*-20a). Reaction of *trans*-**23**[4] with $Li_2Cu_3Bu_5$ according to the procedure reported earlierr[4,17] gave *trans*-**20a** in 86% yield after isolation by rotary TLC: NMR (δ, $CDCl_3$) 7.36 (d, 2 H, J = 7.6), 7.28 (app t, 2 H, J = 7.6), 7.17 (t, 1 H, J = 7.6), 6.25 (d, 1 H, J = 16.1), 6.09 (d, 1 H, J = 16.1), 5.82 (dt, 1 H, J = 10.2, 3.5), 5.58 (d, 1 H, J = 10.1), 1.9 (m, 2 H), 1.7–1.2 (m, 10 H), 0.89 (br t, 3 H, J = 6.8); high resolution mass spectrum, calcd for $C_{18}H_{24}$ m/e 240.1879, found 240.1879.

(2-Phenylhexylidene)-2-cyclohexene (21a) was isolated as a 7:3 mixture of *Z*:*E* isomers: NMR (δ, $CDCl_3$) 7.4–7.1 (m, 5 H), 6.49 (d, 0.7 H, J = 10.1), 6.04 (d, 0.3 H, J = 10.1), 5.84 (dtd, 0.7 H, J = 10.1, 4.5, 1.8), 5.70 (dt, 0.3 H, J = 10.1, 4.0), 5.36 (d, 0.3 H, J = 9.5), 5.2 (d, 0.7 H, J = 9.5), 2.4–1.2 (m, 13 H), 0.88 (br t, 3 H, J = 6.8); high resolution mass spectrum, calcd for $C_{18}H_{24}$ m/e 240.1879, found 240.1879. The major isomer was assigned the *Z* configuration on the basis of comparison with model compounds.[35]

(*E*)-1,4-Hexadien-3-yl 2,2-dimethylpropanoate (2-OPiv) was prepared in the standard way[31] from the corresponding alcohol[18b] and pivaloyl chloride in 95% yield: bp 65–68 °C (20 mm); IR (neat) 3090 (w), 2970 (s), 2930 (m), 2870 (m), 1735 (s), 1480 (m), 1280 (s), 1160 (s), 960 (m), 935 (m); NMR (δ, $CDCl_3$) 5.83 (ddd, 1 H, J = 17.4, 10.4, 5.7), 5.76 (dqd, 1 H, J = 15.4, 6.2, 0.9), 5.64 (app br t, 1 H, J = 6.0), 5.46 (ddq, 1 H, J = 15.4, 6.5, 1.4), 5.25 (app dt, 1 H, J = 17.4, 1.2), 5.16 (app dt, 1 H, J = 10.4, 1:2), 1.71 (ddd, 3 H, J = 6.2, 1.4, 0.7), 1.21 (s, 9 H); high resolution mass spectrum, calcd for $C_{11}H_{18}O_2$ m/e 182.1307, found 182.1306.

2-Methyl-1,4-pentadien-3-ol (3-OH)[18b] was prepared from 2-propenylmagnesium bromide and acrolein in 35% yield according to the general procedure of Boccara et al.:[18a] bp 52–55 °C (20 mm); NMR (δ, $CDCl_3$) 5.86 (ddd, 1 H, J = 17.1, 10.3, 6.0), 5.3 (app dt, 1 H, J = 17.1, 1.5), 5.17 (app dt, 1 H, J = 10.3, 1.5), 5.04 (br s, 1 H), 4.88 (br s, 1 H), 4.54 (br d, 1 H, J = 6.0), 1.77 (s, 3 H), 1.65 (br s, 1 H).

2-Methyl-1,4-pentadien-3-yl 2,2-dimethylpropanoate (3-OPiv) was prepared in the usual manner[31] from the above **3-OH** and pivaloyl chloride in 92% yield: bp 79–82 °C (22 mm); IR (neat) 3100 (w), 2980 (s), 2880 (m), 1740 (s), 1660 (m), 1490 (s), 1460 (m), 1400 (m), 1370 (m), 1280 (s), 1155 (s), 1035 (m), 990 (m), 960 (m), 930 (m), 910 (m); NMR (δ, $CDCl_3$) 5.80 (ddd, 1 H, J = 17.2, 10.4, 5.8), 5.58 (br d, 1 H, J = 5.8), 5.30 (app dt, 1 H, J = 17.2, 1.5), 5.20 (app dt, 1 H, J = 10.4, 1.5), 5.02 (br s, 1 H), 4.92 (br s, 1 H), 1.72 (br s, 3 H), 1.23 (s, 9 H); high resolution mass spectrum, calcd for $C_{11}H_{18}O_2$ m/e 182.1307, found 182.1307.

(*E*)-2-Methyl-1,4-hexadien-3-yl 2,2-dimethylpropanoate (4-OPiv) was prepared in the standard way[31] from the corresponding alcohol[18a,19] and pivaloyl chloride in 94% yield: bp 64–67 °C (4 mm); IR (neat) 3030 (w), 2980 (s), 2880 (m), 1735 (s), 1650 (m), 1480 (m), 1450 (m), 1280 (m), 1150 (s), 960 (m), 910 (m); NMR

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(δ, $CDCl_3$) 5.75 (dq, 1 H, J = 15.2, 6.6), 5.52 (br d, 1 H, J = 6.9), 5.44 (ddq, 1 H, J = 15.2, 6.9, 1.6), 4.99 (br s, 1 H), 4.86 (br s, 1 H), 1.75 (m, 6 H), 1.21 (s, 9 H); high resolution mass spectrum, calcd for $C_{12}H_{20}O_2$ m/e 196.1464, found 196.1465.

2-Ethoxy-1,4-pentadien-3-yl 2,2-dimethylpropanoate (5-OPiv) was prepared from ethyl vinyl ether and acrolein in 69% yield according to the general procedure of Trost et al.:[21] bp 77–80 °C (1 mm); IR (neat) 2970 (s), 2945 (m), 2880 (w), 1730 (s), 1460 (m), 1310 (m), 1270 (s), 1150 (s), 1050 (w), 980 (w), 940 (w); NMR (δ, $CDCl_3$) 5.94 (ddd, 1 H, J = 16.4, 10.1, 6.0), 5.58 (br d, 1 H, J = 6.0), 5.33 (app dt, 1 H, J = 16.4, 1.5), 5.22 (app dt, 1 H, J = 10.1, 1.5), 4.17 (d, 1 H, J = 2.5), 4.02 (d, 1 H, J = 2.5), 3.76 (q, 2 H, J = 7.1), 1.28 (t, 3 H, J = 7.1), 1.24 (s, 9 H); high resolution mass spectrum, calcd for $C_{12}H_{20}O_3$ m/e 212.1413, found 212.1413.

(*E*,*E*)-2,4-Decadiene ((*E*,*E*)-30a): NMR (δ, $CDCl_3$) 6.1–5.9 (m, 2 H), 4.8–4.5 (m, 2 H), 2.03 (t, 2 H, J = 6.9), 1.74 (d, 3 H, J = 7.1), 1.4–1.2 (m, 6 H), 0.9 (t, 3 H, J = 7.1).

(*E*,*Z*)-2,4-Decadiene ((*E*,*Z*)-30a): NMR (δ, $CDCl_3$) 6.34 (dd, 1 H, J = 14.1, 10.8), 5.97 (dd, 1 H, 10.9, 10.8), 5.60 (dd, 1 H, J = 14.1, 6.8), 5.30 (dt, 1 H, 10.9, 6.9), 2.18 (app q, 2 H, J = 6.9), 1.8 (d, 3 H, J = 6.8), 1.4–1.2 (m, 6 H), 0.9 (t, 3 H, J = 7.1).

(*E*)-5-Methyl-1,3-nonadiene ((*E*)-31a) was prepared (as described for (*E*,*Z*)- and (*E*,*E*)-**10b**) from triphenylallylphosphonium bromide and 100 mg (0.88 mmol) of 2-methyl hexanal. Purification of the crude reaction mixture by rotary TLC gave 56 mg (57%) of starting aldehyde and 35 mg (28%) of (*E*)-**31a**: NMR (δ, $CDCl_3$) 6.31 (app dt, 1 H, J = 16.5, 10.0), 6.02 (dd, 1 H, J = 15.4, 10.0), 5.58 (dd, 1 H, J = 15.4, 7.8), 5.09 (d, 1 H, J = 16.5), 4.96 (d, 1 H, J = 10.0), 2.2–2.1 (m, 1 H), 1.4–1.2 (m, 6 H), 1.00 (d, 3 H, J = 6.8), 0.88 (t, 3 H, J = 6.9); high resolution mass spectrum, calcd for $C_{10}H_{18}$ m/e 138.1409, found 138.1410.

(*E*)-2-Methyl-1,3-nonadiene (32a): IR (neat) 3090 (w), 3020 (m), 2960 (s), 2930 (s), 2870 (s), 1650 (w), 1610 (m), 1460 (m), 1440 (m), 1380 (m), 960 (s), 880 (s); NMR (δ, $CDCl_3$) 6.14 (d, 1 H, J = 15.6), 5.66 (dt, 1 H, J = 15.6, 6.9), 4.85 (s, 2 H), 2.14 (app q, 2 H, J = 6.9), 1.82 (s, 3 H), 1.4–1.2 (m, 6 H), 0.9 (t, 3 H, J = 7.0); high resolution mass spectrum, calcd for $C_{10}H_{18}$ m/e 138.1409, found 138.1410.

(*E*)-4-Methyl-1-phenyl-2,4-pentadiene (32b): NMR (δ, $CDCl_3$) 7.4–7.1 (m, 5 H), 6.21 (d, 1 H, J = 15.6), 5.79 (dt, 1 H, J = 15.6, 6.9), 4.91 (br s, 2 H), 3.44 (d, 2 H, J = 6.9), 1.83 (app t, 3 H, J = 1.0; high resolution mass spectrum, calcd for $C_{12}H_{14}$ m/e 158.1096, found 158.1098.

(*E*)-4-Methyl-1,3-nonadiene (33a): NMR (δ, $CDCl_3$) 6.58 (app dt, 1 H, J = 15.9, 10.0), 6.14 (d, 1 H, J = 10.0), 6.08 (dd, 1 H, J = 15.9, 2.0), 5.96 (dd, 1 H, J = 10.0, 2.0), 2.02 (t, 2 H, J = 7.1), 1.75 (s, 3 H), 1.5–1.2 (m, 6 H), 0.90 (t, 3 H, J = 7.1); high resolution mass spectrum, calcd for $C_{10}H_{18}$ m/e 138.1409, found 138.1410.

(*E*)- and (*Z*)-4-methyl-1,3-nonadiene ((*E*)- and (*Z*)-33a) were prepared (as described for (*E*,*Z*)- and (*E*,*E*)-**10b**) from triphenylhept-2-ylphosphonium bromide and 100 mg (1.8 mmol) of acrolein. Purification of the residue by rotary TLC afforded 186 mg (86%) of **33a** as a 1:1 mixture of *E* and *Z* isomers. **(*Z*)-33a**: NMR (δ, $CDCl_3$) 6.56 (app dt, 1 H, J = 15.9, 10.0), 6.14 (d, 1 H, J = 10.0), 6.06 (d, 1 H, J = 15.9), 5.94 (d, 1 H, J = 10.0), 2.16 (t, 2 H, J = 7.0), 1.77 (s, 3 H), 1.5–1.2 (m, 6 H), 0.90 (t, 3 H, J = 7.1); high resolution mass spectrum, calcd for $C_{10}H_{18}$ m/e 138.1409, found 138.1410.

(*E*)-2-Methyl-1-phenyl-2,4-pentadiene (33b): NMR (δ, $CDCl_3$) 7.5–7.1 (m, 5 H), 6.58 (app dt, 1 H, J = 15.8, 9.6), 5.94 (d, 1 H, J = 9.6), 5.13 (dd, 1 H, J = 15.8, 2.0), 5.02 (dd, 1 H, J = 9.6, 2.0), 3.36 (s, 2 H), 1.70 (s, 3 H); high resolution mass spectrum, calcd for $C_{12}H_{14}$ m/e 158.1096, found 158.1097.

(*E*)-2-Methyl-2,4-pentadien-1-yl 2,2-dimethylpropanoate ((*E*)-34-OPiv) was prepared in the usual manner[31] from (*E*)-2-methyl-2,4-pentadien-1-ol[27] and pivaloyl chloride: bp 108–110 °C (20 mm); NMR (δ, $CDCl_3$) 6.59 (app dt, 1 H, J = 16.8, 10.4), 6.07 (br d, 1 H, J = 10.4), 5.23 (br d, 1 H, J = 16.8), 5.15 (d, 1 H, J = 10.4), 4.52 (s, 2 H), 1.79 (s, 3 H), 1.22 (s, 9 H); high resolution mass spectrum, calcd for $C_{11}H_{18}O_2$ m/e 182.1307, found 182.1307.

(*E*,*E*)-5-Methyl-2,4-decadiene ((*E*,*E*)-35a): IR (neat) 3020 (m), 2960 (s), 2940 (s), 2850 (s), 1460 (m), 1445 (m), 1360 (w), 960 (s); NMR (δ, $CDCl_3$) 6.27 (ddq, 1 H, J = 15.0, 10.4, 2.0), 5.79 (br d, 1 H, 10.4), 5.78 (dq, 1 H, J = 15.0, 6.4), 2.01 (t, 2 H, J = 6.6), 1.76 (d, 3 H, J = 6.4), 1.72 (s, 3 H), 1.5–1.2 (m, 6 H), 0.90 (t, 3 H, J = 6.9); high resolution mass spectrum, calcd for $C_{11}H_{20}$ m/e 152.1566, found 152.1566.

(*E*,*E*)-2-Methyl-1-phenyl-2,4-hexadiene ((*E*,*E*)-35b): IR (neat) 3085 (w), 3075 (w), 3020 (s), 2990 (m), 2920 (s), 2860 (m), 1605 (w), 1490 (s), 1450 (s), 1380 (m), 1040 (w), 970 (s), 940 (w), 920 (m), 740 (s), 700 (s); NMR (δ, $CDCl_3$) 7.4–7.1 (m, 5 H), 6.27 (ddq, 1 H, J = 14.8, 10.7, 1.6), 5.88 (br d, 1 H, J = 10.7), 5.63 (dq, 1 H, J = 14.8, 6.9), 3.33 (s, 2 H), 1.78 (d, 3 H, J = 6.9), 1.67 (s, 3 H); high resolution mass spectrum, calcd for $C_{13}H_{16}$ m/e 172.1253, found 172.1254.

(*E*,*Z*)-5-Methyl-2,4-decadiene ((*E*,*Z*)-35a): IR (neat) 3020 (m), 2960 (s), 2940 (s), 2850 (s), 1440 (m), 1360 (m), 960 (s); NMR (δ, $CDCl_3$) 6.24 (ddq, 1 H, J = 14.4, 10.0, 2.0), 5.78 (d, 1 H, J = 10.0), 4.56 (dq, 1 H, J = 14.4, 6.2), 2.13 (t, 2 H, J = 6.9), 1.74 (d, 3 H, J = 6.2), 1.72 (s, 3 H), 1.5–1.2 (m, 6 H), 0.90 (t, 3 H, J = 6.9); high resolution mass spectrum, calcd for $C_{11}H_{20}$ m/e 152.1566, found 152.1566.

(*Z*,*E*)-2-Methyl-1-phenyl-2,4-hexadiene ((*E*,*Z*)-35b): IR (neat) 3100 (w), 3070 (w), 3020 (s), 2980 (m), 2910 (s), 2870 (m), 1600 (w), 1495 (s), 1450 (s), 1380 (m), 1030 (m), 960 (s), 740 (s), 700 (s); NMR (δ, $CDCl_3$) 7.6–7.1 (m, 5 H), 6.42 (ddq, 1 H, J = 14.8, 10.9, 1.8), 5.96 (d, 1 H, J = 10.9), 5.68 (dq, 1 H, J = 14.8, 7.0), 3.48 (s, 2 H), 1.79 (d, 3 H, J = 7.0), 1.66 (s, 3 H); high resolution mass spectrum, calcd for $C_{13}H_{16}$ m/e 172.1253, found 172.1255.

(*E*)-2,5-Dimethyl-1,3-nonadiene (36a): NMR (δ, $CDCl_3$) 6.10 (d, 1 H, J = 15.8), 5.52 (dd, 1 H, J = 15.8, 7.9), 4.87 (s, 2 H), 2.15 (app p, 1 H, J = 6.7), 1.83 (app t, 3 H, J = 1.1), 1.25 (m, 6 H), 1.00 (d, 3 H, J = 6.7), 0.87 (br t, 3 H, J = 6.8); high resolution mass spectrum, calcd for $C_{11}H_{20}$ m/e 152.1566, found 152.1566.

(*E*)-2-Methyl-5-phenyl-1,3-hexadiene (36b): IR (neat) 3090 (w), 3020 (m), 2960 (s), 2910 (m), 2890 (w), 1610 (m), 1500 (m), 1450 (s), 1380 (w), 1020 (w), 970 (s), 880 (s), 760 (m), 700 (s); NMR (δ, $CDCl_3$) 7.4–7.2 (m, 5 H), 6.17 (dd, 1 H, J = 15.8, 1.2), 5.81 (dd, 1 H, J = 15.8, 6.9), 4.91 (s, 2 H), 3.54 (app p, 1 H, J = 7.0), 1.83 (app t, 3 H, J = 1.0), 1.39 (d, 3 H, J = 7.0); high resolution mass spectrum, calcd for $C_{13}H_{16}$ m/e 172.1253, found 172.1253.

(*E*)-4-Butyl-1,3-nonadiene (39): NMR (δ, $CDCl_3$) 6.59 (app dt, 1 H, J = 16.6, 10.3), 5.83 (d, 1 H, J = 10.3), 5.08 (dd, 1 H, J = 16.6, 1.9), 4.95 (dd, 1 H, J = 10.3, 1.9), 2.15 (t, 2 H, J = 7.5), 2.04 (t, 2 H, J = 7.4), 1.5–1.2 (m, 10 H), 0.92 (m, 6 H); high resolution mass spectrum, calcd for $C_{13}H_{24}$ m/e 180.1879, found 180.1879.

(*E*)- and (*Z*)-4-butyl-1,3-nonadiene ((*E*)- and (*Z*)-39) were prepared (as described for (*E*,*Z*)- and (*E*,*E*)-**10b**) from triphenylallylphosphonium bromide and 300 mg (1.92 mmol) of 5-decanone. The residue was purified by rotary TLC to yield 203 mg (68%) of starting ketone and 104 mg (30.1%) of **39** as a 4:1 mixture of *E* and *Z* isomers: NMR (δ, $CDCl_3$) 6.59 (app dt, 1 H, J = 16.6, 10.3), 5.83 (d, 1 H, J = 10.6), 5.08 (dd, 1 H, J = 16.6, 1.9), 4.95 (dd, 1 H, J = 10.3, 1.9), 2.2–2.1 (m, 2 H), 2.1–2.0 (m, 2 H), 1.5–1.2 (m, 10 H), 0.8–1.0 (m, 6 H).

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