in 5 mL of CH_2Cl_2 was added *N*-iodosuccinimide (10.6 mg, 0.47 mmol) in one portion at −78 °C, and the mixture was stirred at 0 °C for 2 h in the dark. The reaction mixture was diluted with 20 mL of CH_2Cl_2, washed with 10 mL of saturated $Na_2S_2O_3$ and saturated $NaHCO_3$, dried over Na_2SO_4, and concentrated. Analysis of the crude product by ^1H NMR indicated that **11** and three other isomers were present in a 10:1:1:1 ratio. Purification by flash chromatography (hexane) gave 97 mg (61% yield) of **11** as a colorless oil: IR 2980, 1640, 1460, 1110, 1020, 990, 920 cm^{-1}; ^1H NMR δ 5.89 (ddd, 1, *J* = 8.3, 10.2, 17.3), 5.01 (dd, 1, *J* = 1.8, 10.2), 4.95 (dd, 1, *J* = 1.8, 17.3), 4.06 (dd, 1, *J* = 2.1, 11.5), 3.21 (dd, 1, *J* = 2.4, 10.1), 2.34 (m, 1), 2.10 (ddd, 1, *J* = 7.4, 11.5, 19.2), 1.90–2.02 (m, 3), 1.62–1.76 (m, 3), 1.48–1.60 (m, 1), 1.42–1.48 (m, 1), 1.31 (s, 3), 1.12–1.22 (m, 1), 1.01 (t, 3, *J* = 7.2), 0.93 (d, 3, *J* = 6.9), 0.85 (d, 3, *J* = 6.7), 0.79 (d, 3, *J* = 6.6); ^{13}C NMR δ 144.0, 113.1, 109.1, 86.3, 78.4, 52.7, 40.0, 38.9, 38.1, 36.4, 33.9, 32.4, 28.8, 20.6, 17.2, 16.4, 14.7, 12.2. Anal. Calcd for $C_{18}H_{31}O_2I$: C, 53.21; H, 7.69; I, 31.23. Found: C, 52.95; H, 7.57; I, 30.88.

[2a(*R),3b,5b,6b(8*S**,9*R**)]-8-Ethyl-3,5,9-trimethyl-2-[(1*R**)-1-methyl-2-propenyl]-1,7-dioxaspiro[5.5]undecan-9-ol (12).** To a solution of iodoketal **11** (77 mg, 0.19 mmol) in 5 mL of acetone and 0.25 mL of water was added $AgBF_4$ (44 mg, 0.23 mmol). After being stirred for 3 h at room temperature in the dark, the reaction mixture was diluted with 20 mL of ether, and 0.1 g of $NaHCO_3$ and 1 g of $MgSO_4$ were added. The mixture was filtered and concentrated. Analysis of the crude product by ^1H NMR indicated that **12** and an isomer were present in a 10:1 ratio. Purification by chromatography (5% ethyl acetate/hexane) gave 42 mg (75% yield) of **12** as a colorless oil: IR 3400, 2990, 1640, 1460, 1380, 1110, 980, 920 cm^{-1}; ^1H NMR δ 6.02 (ddd, 1, *J* = 7.7, 10.3, 17.6), 5.00 (dd, 1, *J* = 17.6, 1.1), 4.98 (dd, 1, *J* = 10.3, 1.1), 3.28 (dd, 1, *J* = 1.7, 10.6), 3.24 (dd, 1, *J* = 2.5, 10.1), 2.40 (m, 1), 1.79–1.92 (m, 2), 1.66–1.70 (m, 1), 1.50–1.58 (m, 3), 1.39–1.46 (m, 2), 1.22–1.35 (m, 2), 1.10 (s, 3), 1.09 (b s, 1), 0.97 (d, 3, *J* = 6.9), 0.96 (t, 3, *J* = 7.4), 0.88 (d, 3, *J* = 6.7), 0.80 (d, 3, *J* = 6.6); ^{13}C NMR δ 143.9, 112.8, 96.6, 76.9, 76.0, 67.9, 38.6, 31.1, 37.3, 35.7, 32.2, 30.6, 21.4, 19.1, 17.2, 16.0, 11.9, 11.3. Anal. Calcd for $C_{18}H_{32}O_3$: C, 72.93; H, 10.88. Found: C, 72.76; H, 10.77.

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Cross Coupling of Allylic Derivatives. 15. Regio- and Stereospecific Cross-Coupling Reactions of Dienyl Allylic *N*-Phenylcarbamates with Phenylcopper Reagents

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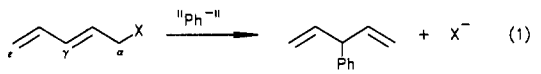
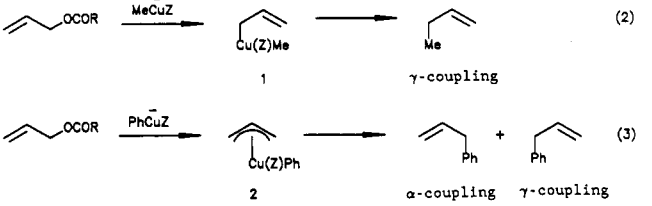
In connection with another study, we required a method to regiospecifically[1] γ-phenylate an allylic dienyl system. Such a transformation would yield an unconjugated diene as illustrated by eq 1.

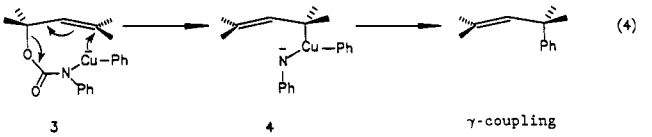


(1)

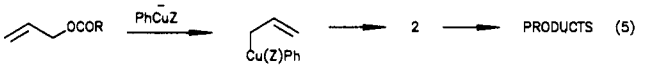
We have recently reported that the mechanism of cross coupling allylic carboxylates with phenyl(sp^2)copper reagents is remarkably different than similar reactions using alkyl(sp^3)copper reagents.[2] Cross coupling allylic carboxylates with alkyl(sp^3)copper reagents can be highly regiospecific (γ-alkylation) and evidently proceeds via a σ-allylcopper(III) intermediate (**1**) as shown by eq 2,[3] but cross coupling with phenyl(sp^2)copper reagents is nonregiospecific and evidently proceeds via a π-allylcopper(III) complex **2** as shown by eq 3.[2] The most compelling evidence for intermediate **2** is that in unbiased systems (such as α-deuterio-2-cyclohexenyl mesitoate) cross coupling with phenylcopper reagents is entirely nonregiospecific,[2,3] and in cis allylic systems (such as *cis*-cinnamyl pivalate), cross coupling gives only cis-α-coupling product (i.e., the original β,γ-double-bond configuration is preserved).[2]



We now report that reaction of allylic dienyl carbamates with phenylcopper reagents according to Gallina's method[4] or a modification that we reported earlier[5] occurs with complete regio- and stereospecificity (syn-γ-coupling) and evidently occurs by a cyclic mechanism illustrated by eq 4. This mechanism involves conversion of the carbamate to a mixed cuprate **3**, which undergoes a cyclic intramolecular oxidative addition of the γ-carbon to give a σ-allylcopper(III) complex **4**.[5] Reductive elimination converts the latter to the syn γ-coupling product.[5] This mechanism parallels that proposed earlier for alkylation of allylic carboxylates with alkyl(sp^3)copper reagents (eq 2).[2,5,6] This is apparently the first instance in which a phenylcopper reagent regiospecifically cross couples with an allylic system; evidently, a σ-allylcopper(III) complex (**4**) is involved in this transformation.



This result is significant in connection with the mechanistic details of cross-coupling reactions of phenyl(sp^2)copper reagents with allylic carboxylates. Heretofore, we were unable to distinguish between (a) direct formation of a π-allylcopper(III) complex (**2**, eq 3) or (b) initial formation of a σ-allylcopper(III) complex (**5**, eq 5) with subsequent complete isomerization to π-allyl complex **2**.[2] The present results indicate that a σ-allylcopper(III) complex (**4**), when formed, undergoes reductive elimination to give the corresponding cross-coupled product. Thus, nonregiospecific cross-coupling reactions of allylic carboxylates with phenyl(sp^2)copper reagents (eq 3) evidently involve direct formation of a π-allylcopper(III) complex **2**.



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

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(4) Gallina, C. *Tetrahedron Lett.* **1982**, *23*, 3093.

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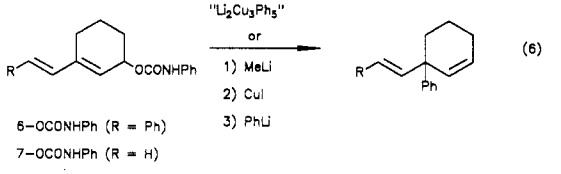
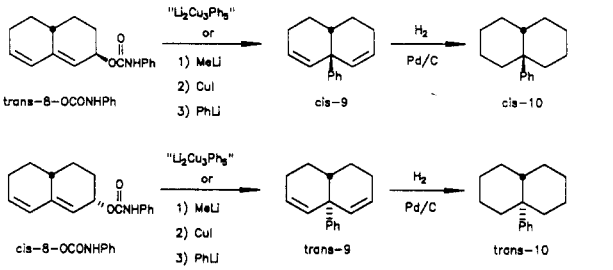
The Gallina procedure[4] involves adding an organocopper reagent "$Li_2Cu_3R_5$" (prepared by adding 5 equiv of RLi to 3 equiv CuI) to 1 equiv of carbamate in ether. Although the method is wasteful of lithium reagent, yields (with respect to carbamate) are very good and exclusive syn-γ-coupling occurs. Our procedure[5] is a three-step, one-pot process and involves initial deprotonation of the carbamate with 1 equiv of MeLi followed by complexation of the lithium carbamate with 1 equiv of CuI. The final step is the addition of 1 equiv of lithium reagent (coupling agent). Thus, only 1 equiv of coupling agent is necessary. In order to obtain good yields and to insure high regio- and stereospecificity, complete complexation (step 2) is critical.

The following examples illustrate how either method can be used to generate phenyl-substituted quaternary carbon centers regio- and stereospecifically.[7] Phenylation of 6-OCONHPh and 7-OCONHPh by either method is regiospecific and gives excellent yields of γ-coupling product (eq 6).



(6)

Phenylation of *cis*- or *trans*-8-OCONHPh[8] by either method is regio- and stereospecific (syn-γ-coupling) and yields *trans*- or *cis*-**9**, respectively (eq 7 and 8). The



(7)

(8)

stereochemistry of *cis*- and *trans*-**9** was determined by hydrogenation of each isomer to the corresponding decalin (**10**) and obtaining ^{13}C NMR spectra at room temperature and at −50 °C. The 10 ring carbons of the conformationally flexible *cis*-**10** give six signals at room temperature and ten signals at −50 °C.[9] *trans*-**10** gives six signals for the 10 ring carbons regardless of the temperature.[9]

Experimental Section

General Methods. All reagents were prepared and purified, and lithium reagents were standardized as reported earlier.[2] The high-resolution mass spectrometer and the 200-MHz NMR spectrometer used in this work have also been described.[2] General procedures for alkylation of allylic *N*-phenylcarbamates have been reported;[4,5,8] the Gallina method[4] gave comparable yields to our method[5] and ranged from 75% to 93%.

3-((*E*)-2-Phenylethenyl)-2-cyclohexenyl *N*-phenylcarbamate (6-OCONHPh) was prepared from the corresponding alcohol[10] and phenyl isocyanate in the usual manner[5,11] and recrystallized from hexane (95% yield). The carbamate had the following properties: mp 148–149 °C dec; NMR ($CDCl_3$) δ 7.0–7.4 (m, 10 H), 6.80 (d, 1 H, J = 16.1 Hz), 6.60 (d, 1 H, J = 16.1 Hz), 6.56 (m, 1 H), 5.94 (br s, 1 H), 5.42 (br s, 1 H), 2.2–2.5 (m, 2 H), 1.7–2.0 (m, 4); high-resolution mass spectrum calcd for $C_{21}H_{21}NO_2$ m/e 319.1573, found m/e 319.1568.

3-Ethenyl-2-cyclohexenyl *N*-phenylcarbamate (7-OCONHPh) was prepared as above from the corresponding alcohol[12] (94% yield) and had the following properties: mp 59–60 °C; NMR ($CDCl_3$) δ 7.2–7.4 (m, 4 H), 7.06 (t, 1 H, J = 6.6 Hz), 6.63 (br s, 1 H), 6.37 (dd, 1 H, J = 17.6, 10.8 Hz), 5.80 (br s, 1 H), 5.40 (br s, 1 H), 5.26 (d, 1 H, J = 17.6 Hz), 5.09 (d, 1 H, J = 10.8 Hz), 2.0–2.4 (m, 2 H), 1.5–2.0 (m, 4 H); high-resolution mass spectrum calcd for $C_{15}H_{17}NO_2$ m/e 243.1260, found m/e 243.1255.

3-Phenyl-3-((*E*)-2-phenylethenyl)cyclohexene: NMR ($CDCl_3$) δ 7.1–7.5 (m, 10 H), 6.42 (s, 2 H), 5.98 (dt, 1 H, J = 10.1, 3.5 Hz), 5.80 (d, 1 H, J = 10.1 Hz), 2.0–2.1 (m, 4 H), 1.4–1.8 (m, 2 H); high-resolution mass spectrum calcd for $C_{20}H_{20}$ m/e 260.1566, found m/e 260.1566.

3-Ethenyl-3-phenylcyclohexene: NMR ($CDCl_3$) δ 7.2–7.4 (m, 5 H), 6.02 (dd, 1 H, J = 17.3, 10.6 Hz), 5.94 (dt, 1 H, J = 10.1, 3.6 Hz), 5.72 (br d, 1 H, J = 10.1 Hz), 5.15 (dd, 1 H, J = 10.6, 1.3 Hz), 5.09 (dd, 1 H, 17.3, 1.3 Hz), 2.0–2.1 (m, 2 H), 1.9–2.0 (m, 2 H), 1.4–1.7 (m, 2 H); high-resolution mass spectrum calcd for $C_{14}H_{16}$ m/e 184.1253, found m/e 184.1255.

***cis*-3,4,4a,5,6,8a-Hexahydro-8a-phenylnaphthalene (*cis*-9)**: NMR ($CDCl_3$) δ 7.1–7.4 (m, 5 H), 5.90 (dt, 2 H, J = 10.0, 3.7 Hz), 5.53 (dt, 2 H, J = 10.0, 2.0 Hz), 2.1–2.2 (m, 4 H), 1.89 (m, 1 H), 1.5–1.7 (m, 4 H); high-resolution mass spectrum calcd for $C_{16}H_{18}$ m/e 210.1409, found m/e 210.1408.

***trans*-3,4,4a,5,6,8a-Hexahydro-8a-phenylnaphthalene (*trans*-9)**: NMR ($CDCl_3$) δ 7.2–7.4 (m, 5 H), 5.94 (dt, 2 H, J = 9.8, 3.7 Hz), 5.67 (dt, 2 H, J = 9.8, 2.2 Hz), 2.2–2.4 (m, 4 H), 1.8–2.0 (m, 1 H), 1.2–1.4 (m, 4 H); high-resolution mass spectrum calcd for $C_{16}H_{18}$ m/e 210.1409, found m/e 210.1410.

***cis*-9-Phenyldecalin (*cis*-10)** had the following properties: ^1H NMR ($CDCl_3$) δ 7.46 (d, 2 H, J = 7.9 Hz), 7.36 (app t, 2 H, J = 7.9 Hz), 7.17 (t, 1 H, J = 7.9 Hz), 2.32 (m, 1 H), 1.2–2.0 (m, 16 H); ^{13}C NMR (−50 °C, $CDCl_3$) δ 150.2, 128.8, 126.5, 125.5, 44.5, 42.0, 37.3, 28.4, 27.4, 27.1, 26.8, 26.7, 22.9, 20.9; high-resolution mass spectrum calcd for $C_{16}H_{22}$ m/e 214.1722, found m/e 214.1720.

***trans*-9-Phenyldecalin (*trans*-10)**: ^1H NMR ($CDCl_3$) δ 7.52 (d, 2 H, J = 7.4 Hz), 7.26 (app t, 2 H, J = 7.4 Hz), 7.10 (t, 1 H, J = 7.4 Hz), 0.9–2.1 (m, 17 H); ^{13}C NMR ($CDCl_3$) δ 146.0, 129.7, 127.5, 124.7, 47.6, 44.5, 43.6, 29.8, 27.7, 22.3; high-resolution mass spectrum calcd for $C_{16}H_{22}$ m/e 214.1722, found m/e 214.1722.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-8406480).

(7) The same methods have been used to stereospecifically generate methyl-substituted quaternary carbons (see ref 8), and butyl-substituted quaternary carbon centers (unpublished results by T. L. Underiner).
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Synthesis of 3′-Cyano-2′,3′-dideoxyadenosine and 2′,3′-Dideoxy-3′-formyladenosine

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Despite the growing recognition that unnatural 2′-deoxynucleosides modified in the sugar portion often exhibit powerful antiviral properties,[1] synthetic methods to replace the natural C–O bond at the 3′-position of the deoxynucleoside with a C–C bond are scarce. The principal synthetic problems have been (1) the instability of 3′-keto-2′-deoxynucleosides, which undergo rapid elimination of the heterocyclic base,[2] precluding the use of traditional C–C bond forming methods such as the aldol

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