Stereospecific Substitution of Silylated Bromoallenes with Organocopper Reagents

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Recently, we reported that chiral bromoallene **3**, obtained from N,O-diprotected serine aldehyde **1**, underwent an S_N2' alkylation with organocopper reagents.[1] Accordingly, the propargylic adduct **4** was formally obtained through direct alkylation of the intermediate propargylic tosylate **2** with retention of configuration (Scheme 1).

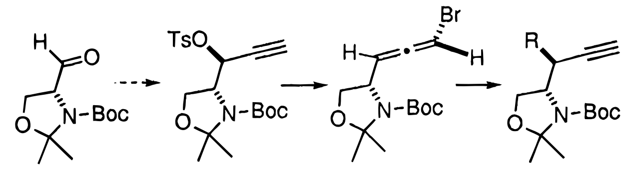
As part of our continuing interest in the application of allene chemistry to organic synthesis, we sought a route for producing the reverse reactivity, i.e., the direct substitution of the bromine atom on the allene. Several examples of direct alkylation of bromoallenes proceeding with retention or inversion of configuration have been reported, depending on the nature of the organometallic reagent.[2−5]

We report here the results observed in the reaction of silabromoallenes **7b** with various organocopper reagents, which show that the presence of the silicon on the allenic frame controls not only the regiochemistry but also the stereochemistry of the addition of the cuprate, independent of the nature of the organocopper reagent. The oxazolidine derived from serine was chosen as the starting material for its capability to serve as an internal probe for the stereochemical assignment and for possible entry to the synthesis of non-natural amino acids.

The preparation of compounds **7** is outlined in Scheme 2. Starting from Garner's aldehyde (**1**),[6] the two epimeric propargylic alcohols **5a,b** are i.e., accessible in high diastereomeric excess. The addition of lithiated (trimethylsilyl)acetylene to aldehyde **1** in the presence of HMPA gave the *anti* product adduct **5a**, whereas reaction with the magnesium salt of (trimethylsilyl)acetylene gave the *syn* product **5b**.[7] The corresponding tosylates (**6a,b**) were converted to the bromoallenes **7a,b** using a slight modification of the Gore procedure.[8] To reach maximal conversion, the reaction was performed at 60 °C for 6 h without loss of stereoselectivity, as determinated by the ^{1}H NMR spectra and the values of optical rotation of silabromoallenes **7**.

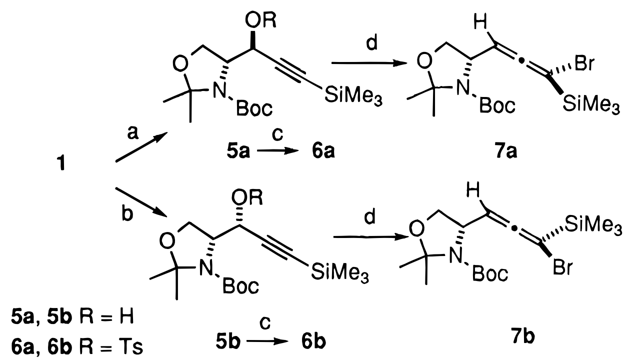
First we examined the reactivity of silabromoallene **7a** with various organocopper reagents (see Table 1). The

Scheme 1[a]



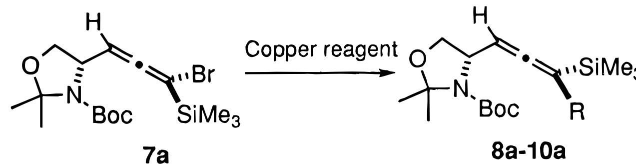
1 2 3 4

Scheme 2



[a] (a) TMS-acetylene, BuLi, THF, HMPA, −78 °C; (b) TMS-acetylene, EtMgBr, CuI, Me_2S, THF, rt; (c) TsCl, TEA, DMAP, CH_2Cl_2; (d) CuBr, LiBr, THF, 60 °C.

Table 1. Alkylation of Silabromoallene



8a R= Ph; **9a** R = Me; **10a** R = Bu

entry	copper reagent	temp, °C	solvent	$[\alpha]_D$[c]	adduct	yield, %[d]
1	PhCuCNLi[a]	−78	THF/Et_2O	+118	**8a**	84
2	$Ph_2CuCNLi_2$[b]	−78 to rt	THF/Et_2O	+120	**8a**	70
3	$PhCuMgBr_2LiBr$[a]	−78 to rt	THF	+115	**8a**	75
4	Ph_2CuLi[b]	−78 to rt	THF/Et_2O	+119	**8a**	65
5	MeCuCNLi[a]	−78	THF/Et_2O	+216	**9a**	78
6	$MeCuMgBr_2LiBr$[a]	−78 to rt	THF	+218	**9a**	80
7	BuCuCNLi[a]	−78 to rt	THF/Et_2O	+188	**10a**	78
8	$Bu_2CuCNLi_2$[a]	−78 to rt	THF/Et_2O	+182	**10a**	80

[a] Reaction carried in the presence of 8 equiv of cuprate. [b] Reaction carried in the presence of 4 equiv of cuprate. [c] Values obtained at temperature of 23 °C (c = 3, EtOH). [d] After purification by column chromatography, all the silaallenes are oils.

alkylation was carried out either in THF or in a mixture of THF/ether at −78 °C, reaching completion after 1 h at −78 °C. Purification by column chromatography on silica gel gave the diastereomerically pure adducts **8a**−**10a**, fully characterized by ^{1}H and ^{13}C NMR. It is noteworthy that, in all cases, no traces of the corresponding propargylic adducts were detected. The fact that structurally different copper reagents, bearing identical transferable groups (entries 1−4, 5,6, and 7,8 in Table 1), produced the same alkylallenes was in contrast with other findings involving non-sililated allenes.[2−5] This result suggests that a common mechanism for the substitution of bromine in bromoallene **7a** might be operating and highlights the strong directing effect of the TMS group during alkylation. Interestingly, a similar

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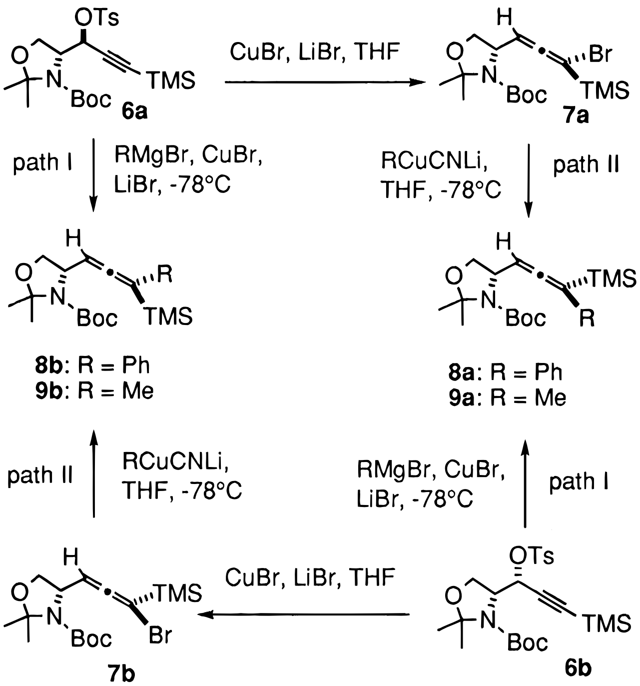
Scheme 3



effect has been reported by Hudrlik et al. in the reaction of α-silaepoxides with cuprates.[9]

To establish the stereochemical trend observed in this reaction, we planned a cross experiment (paths I and II in Scheme 3). We prepared the epimeric silaallenes **8a,9a** and **8b,9b** via a stereochemically defined S_N2' displacement (path I), performed on the epimeric tosylates **6a,b** with soft copper reagents $PhCuMgBr_2{\cdot}LiBr$ and $MeCuMgBr_2{\cdot}LiBr$. The diastereomeric silaallenes exhibit significant differences in their ^1H and ^{13}C spectra. A diagnostic is provided by the proton resonance (^1H NMR) of the allenic C−H at δ 5.44 and 5.39 ppm for **8a** and **8b**, respectively, and by the carbon resonance (^{13}C NMR) of the allenic carbon at δ 202.5 and 206.5 ppm for **8a** and **8b**, respectively. Those differences allowed us also to estimate that the diastereomeric purity of the single allenes was >95%. Therefore, we have in hand the reference compounds necessary to identify the adducts arising from the alkylation of silabromoallenes **7** in path II. To realize this alkylation, we used the low-order organocuprates PhCuCNLi and MeCuCNLi (path II). After purification by column chromatography, the physical data of each adduct were compared to those of reference compounds **8** and **9**. Scheme 3 summarizes our results: the silabromoallene **7a** gave the adduct **8a** or **9a**, and the allene **7b** gave **8b** or **9b**. Examination of the stereochemistry of the substituents at the terminal position of the allene indicates that the alkylating agent entered in path II from the side opposite, i.e., with inversion of configuration. Therefore, this correlation confirmed that, in the presence of a silicon group, (i) the substitution of the bromine does not depend on the structure of the organocopper reagent and (ii) the net result of the alkylation of silabromoallenes **7** with organocopper reagents is substitution of the bromine with inversion of the configuration on the allenic system. The selectivity of this alkylation is rather unexpected when compared with the results obtained in the reaction of

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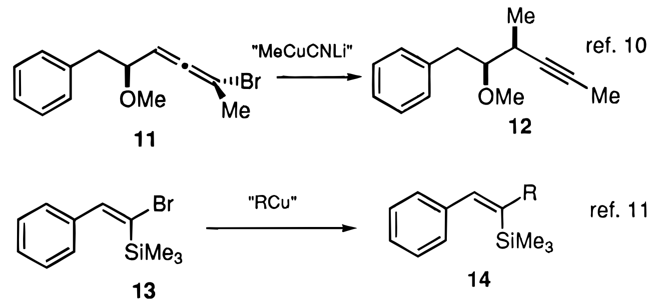
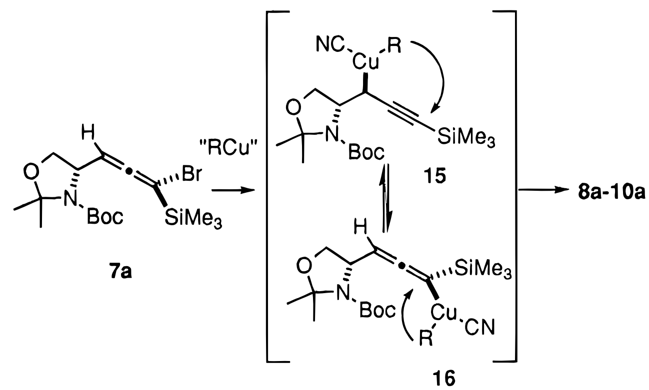
Scheme 4



Scheme 5



alkyl-substituted bromoallene **11**, which gave the alkynyl derivative **12** with methylcyanocuprate. In addition, reaction of the simple 1-bromo-1-silaalkene **13** with organocuprates gave **14** with retention of the double-bond geometry (Scheme 4).[3,10,11]

To tentatively rationalize the results obtained with silabromoallenes **7**, we propose an explanation based on the work of Corey and Boaz on alkylbromoallenes.[3] In the first step, displacement of the bromine in **7a** (or **7b**) by nucleophilic copper via an *anti* bias yields a propargylic Cu(III) intermediate (**15**). According to Corey and Boaz, this transient species can evolve in three different directions: one yielding alkynes via 1,2 *syn* reductive elimination, and two others, allenes via 1,4 reductive elimination or a 1,3-π-slide, followed by a 1,2 reductive elimination. In our work, to account for the regio- and stereoselective formation of allenes **8a**−**10a**, only the two last pathways have to be considered. It can be conjectured that the presence of an electron-donating silicon atom on the acetylene terminus in **15** favors the abovementioned 1,3-π-slide pathway via intermediate **16**. But an other explanation emerges if, according to Houk et al., the bending distorsion of the acetylene function during nucleophilic attack is considered.[12] For instance, in **15**, the stereoelectronic effect of silicon may enlarge this bending, producing a geometry favorable for the intramolecular 1,4 alkyl transfer (Scheme 5).

In conclusion, we have shown that the presence of a silicon nucleus controls the regiochemistry of the addition of alkyl cuprates to chiral silabromoallenes. A formal S_N2 nucleophilic substitution of the bromine on an sp^2 carbon is observed to give the corresponding polysubstituted chiral silaalkylallenes. This methodology should be of

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(12) Strozier, R. W.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 1340.

value for the synthesis of various homochiral compounds.[13]

Experimental Section

^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ and at room temperature (unless otherwise noted); coupling constant *J* values are in hertz. Mass spectra were recorded on a low-resolution instrument by CI at 70 eV, unless otherwise noted. IR spectra were recorded in CCl_4 and measured in cm^{-1}. Air- and/or moisture-sensitive reactions were conducted under an atmosphere of dry argon using oven-dried glassware and standard syringe/septum techniques. THF and ether were distilled from sodium benzophenone and methylene chloride from CaH_2 prior to use. The organic extracts of crude products were dried over anhydrous Na_2SO_4. The organic solvents were removed by evaporation under reduced pressure with a rotary evaporator. The column chromatographies were performed by using a flash chromatography technique.

General Procedure for the Synthesis of Tosylates 6. To a solution of the corresponding alcohol **5a** or **5b** (4.47 g, 13.6 mmol), triethylamine (2.86 mL, 20.4 mmol), and (dimethylamino)pyridine (2.49 g, 20.4 mmol), in dichloromethane (91 mL) at 0 °C was added *p*-toluenesulfonyl chloride (3.24 g, 17 mmol). The reaction mixture was stirred at room temperature overnight, quenched with a saturated aqueous solution of NH_4Cl (30 mL), and extracted with CH_2Cl_2 (3 × 50 mL). After drying and evaporation of the solvent, purification by chromatography (hexane/ether 90/10) gave the final product.

***tert*-Butyl (1′*S*,4*R*)-4-[1′-(Tosyloxy)-3′-(trimethylsilyl)-2′-propynyl]oxazolidine-3-carboxylate (6a).** Yield: 88%, oil. ^{1}H NMR (50 °C): δ 0.01 (s, 9H), 1.47 (s, 3H), 1.51 (s, 9H), 1.60 (s, 3H), 2.41 (s, 3H), 3.96−4.19 (m, 3H), 5.60 (br s, 1H), 7.28 (d, *J* = 8, 2H), 7.8 (d, *J* = 8, 2H). ^{13}C NMR (50 °C): δ −0.6, 21.4, 24.8, 26.2, 28.4, 60.7, 63.3, 69.6, 80.8, 81.3, 96.0, 98.1, 128.2, 129.5, 134.5, 144.4, 154.7. $[\alpha]^{23}_{D}$ = +92 (*c* = 1.4, $CHCl_3$). Anal. Calcd for $C_{23}H_{35}NO_6SSi$: C, 57.35; H, 7.32; N, 2.90. Found: C, 57.26; H, 7.12; N, 2.77.

***tert*-Butyl (1′*R*,4*R*)-4-[1′-(Tosyloxy)-3′-(trimethylsilyl)-2′-propynyl]oxazolidine-3-carboxylate (6b).** Yield: 89%, oil. ^{1}H NMR (50 °C): δ 0.04 (s, 9H), 1.47 (s, 3H), 1.49 (s, 9H), 1.56 (s, 3H), 2.42 (s, 3H), 3.98−4.13 (m, 3H), 5.60 (br s,1H), 7.30 (d, *J* = 8.4, 2H), 7.80 (d, *J* = 8.3, 2H). ^{13}C NMR (50 °C): δ −0.5, 21.4, 23.2, 27.5, 28.3, 59.5, 64.4, 65.9, 81.1, 95.1, 97.0, 110.4, 126.2, 128.2, 129.9, 140.6, 156.2. $[\alpha]^{23}_{D}$ = +56 (*c* = 1.4, $CHCl_3$). Anal. Calcd for $C_{23}H_{35}NO_6SSi$: C, 57.35; H, 7.32; N, 2.90. Found: C, 57.23; H, 7.27; N, 2.88.

General Procedure for the Synthesis of Silabromoallenes 7. To a solution of dry LiBr (2.42 g, 27.9 mmol) and CuBr·Me_2S (5.73 g, 27.9 mmol) in THF (126 mL) was added a solution of the corresponding tosylate **6a** or **6b** (4.5 g, 9.3 mmol) in THF (40 mL). After the solution was stirred at 60 °C for 6 h, the reaction was quenched with a saturated solution of NH_4Cl and extracted with ether (3 × 50 mL). The organic layer was washed with brine and dried. After evaporation of the solvent, chromatography (hexane/ether 95/5) gave the final product as a single diastereomer.

***tert*-Butyl (3′*S*,4*R*)-4-[3′-Bromo-3′-(trimethylsilyl)-1′,2′-propanedienyl]oxazolidine-3-carboxylate (7a).** Yield: 70%, oil. ^{1}H NMR: δ 0.15 (s, 9H), 1.46 (s, 9H), 1.56 (s, 3H), 1.61 (s, 3H), 4.06−4.28 (m, 2H), 4.89 (m, 1H), 5.11 (d, *J* = 3.2, 1H). ^{13}C NMR: δ −0.4, 24.9, 26.3, 28.2, 61.9, 65.1, 80.8, 81.2, 95.0, 100.0, 152.4, 205.0. IR: 2985, 2937, 1958, 1705, 1477, 1369, 1091, 847. MS: *m/z* 390 (M^+, 92), 334 (49), 312 (38), 290 (39), 254 (17), 200 (91). $[\alpha]^{23}_{D}$ = +134 (*c* = 5, EtOH). Anal. Calcd for $C_{16}H_{28}NO_3Si$: C, 49.23; H, 7.23; N, 3.59. Found: C, 49.00; H, 7.10; N, 3.69.

***tert*-Butyl (3′*R*,4*R*)-4-[3′-Bromo-3′-(trimethylsilyl)-1′,2′-propanedienyl]oxazolidine-3-carboxylate (7b).** Yield: 75%. ^{1}H NMR: δ 0.12 (s, 9H), 1.43 (s, 3H), 1.46 (s, 9H), 1.60 (s, 3H), 4.01−4.26 (m, 3H), 5.19 (d, *J* = 1.8, 1H). ^{13}C NMR: δ −0.4, 24.8, 26.2, 28.2, 61.0, 65.0, 80.8, 81.2, 94.8, 101.0, 152.4, 205.1. IR: 2985, 2937, 1958, 1705, 1477, 1369, 1091, 847. MS: *m/z* 390 (M^+, 55), 334 (35), 290 (23), 200 (100), 100 (84). $[\alpha]^{23}_{D}$ = +44 (*c* = 1.4, $CHCl_3$). Anal. Calcd for $C_{16}H_{28}NO_3Si$: C, 49.23; H, 7.23; N, 3.59. Found: C, 49.37; H, 7.15; N, 3.51.

General Procedure for the Addition of Organocopper Reagents on Silabromoallene 7a. Reaction of the Lower Order Organocuprates Derived from Methyl-, Butyl-, and Phenyllithium. A suspension of copper(I) cyanide (8 equiv) in ether at 0 °C was treated dropwise with the corresponding lithium derivative (8 equiv). The mixture was stirred for 30 min at 0 °C. After the mixture was cooled to −78 °C, a solution of silabromoallene **7a** (1 equiv) in dry THF was added. After being stirred for 2 h at −78 °C, the mixture was quenched with a saturated NH_4Cl solution and extracted with ether. The organic layer was dried (Na_2SO_4) and concentrated *in vacuo*. The crude product was purified by chromatography (hexane/ether 90/10) to give the final product as a single diastereomer.

(ii) Reaction of the Higher Order Organocuprates Derived from Methyl-, Butyl-, and Phenyllithium. The procedure is the same as the one above, except that 2 equiv of the lithium derivative was added for each equivalent of copper(I) cyanide. Moreover, the reaction mixture was allowed to warm to room temperature before being quenched.

(iii) Reaction with Methyl and Phenyl Organocuprates Derived from Grignard Reagents. To a solution of dry LiBr (8 equiv) and CuBr·Me_2S (8 equiv) in THF was added at −30 °C the corresponding Grignard reagent (8 equiv). The mixture was stirred for 30 min at −30 °C. After the mixture was cooled to −78 °C, a solution of silabromoallene **7a** (1 equiv) in dry THF was added. The reaction mixture was stirred for 10 min at −78 °C before being allowed to warm to room temperature. After being stirred for 1 h at room temperature, the mixture was quenched with saturated NH_4Cl, extracted with ether, and dried. Chromatography (hexane/ether 90/10) gave the final product as a single diastereomer.

***tert*-Butyl (3′*S*,4*R*)-4-[3′-Phenyl-3′-(trimethylsilyl)-1′,2′-propanedienyl]oxazolidine-3-carboxylate (8a).** ^{1}H NMR (50 °C): δ 0.27 (s, 9H), 1.47 (s, 9H), 1.52 (s, 3H), 1.59 (s, 3H), 3.94−4.08 (m, 2H), 4.48-4.55 (m, 1H), 5.44 (d, *J* = 5.2, 1H), 7.16−7.36 (m, 5H). ^{13}C NMR (50 °C): δ −0.4, 24.5, 26.9, 28.4, 55.5, 67.8, 79.9, 81.2, 88.5, 94.4, 126.2, 127.8, 128.3, 137.2, 151.7, 202.5. IR: 3063, 2983, 2876, 1927, 1695, 1597, 1491, 1387, 1093, 844. $[\alpha]^{23}_{D}$ = +118 (*c* = 3, EtOH). Anal. Calcd for $C_{22}H_{33}NO_3Si$: C, 68.17; H, 8.81; N, 3.61. Found: C, 68.10; H, 8.96; N, 3.81.

***tert*-Butyl (3′*S*,4*R*)-4-[3′-Methyl-3′-(trimethylsilyl)-1′,2′-propanedienyl]oxazolidine-3-carboxylate (9a).** ^{1}H NMR (50 °C): δ 0.98 (s, 9H), 1.49 (s, 9H), 1.51 (s, 3H), 1.57 (s, 3H), 1.71 (d, *J* = 7.8, 3H), 3.82−4.02 (m, 2H), 4.32−4.38 (m, 1H), 5.02−5.04 (m, 1H). ^{13}C NMR (50 °C): δ −2.05, 15.25, 24.59, 26.77, 28.52, 55.50, 68.10, 79.64, 81.20, 85.82, 96.40, 151.79, 205.00. IR: 2983, 2873, 1936, 1693, 1453, 1383, 1095, 847. $[\alpha]^{23}_{D}$ = +216 (*c* = 3, EtOH). Anal. Calcd for $C_{17}H_{31}NO_3Si$: C, 62.72; H, 9.60; N, 4.31. Found: C, 62.98; H, 9.32; N, 4.51.

***tert*-Butyl (3′*S*,4*R*)-4-[3′-Butyl-3′-(trimethylsilyl)-1′,2′-propanedienyl]oxazolidine-3-carboxylate (10a).** ^{1}H NMR (50 °C): δ 0.79−0.90 (m, 3H), 0.98 (s, 9H), 1.23−1.49 (m, 4H), 1.54 (s, 9H), 1.62 (s, 6H), 1.69−1.71 (m, 2H), 3.90−4.05 (m, 2H), 4.51−4.56 (m, 1H), 5.02−5.04 (m, 1H). $[\alpha]^{23}_{D}$ = +188 (*c* = 3, EtOH). Anal. Calcd for $C_{20}H_{37}NO_3Si$: C, 65.34; H, 10.12; N, 3.80. Found: C, 65.41; H, 10.01; N, 3.76.

General Procedure for the Preparation of Allenes 8 and 9 from Tosylates 6. To a solution of dry LiBr (5 equiv) and CuBr·Me_2S (5 equiv) in THF was added at −30 °C the corresponding phenyl or methyl Grignard reagent (5 equiv). The mixture was stirred for 30 min at −30 °C. After the mixture was cooled to −60 °C, a solution of tosylate **6a** or **6b** (1 equiv) in THF was added. The reaction mixture was stirred for 10 min at −60 °C before being allowed to warm to room temperature. After being stirred for 1 h at room temperature, the mixture was quenched with saturated NH_4Cl, extracted with ether, and dried. Chromatography (hexane/ether 90/10) gave the final product as a single diastereomer. The physiscal data of compounds **8a** and **9a** obtained from **6a** are not reported again.

***tert*-Butyl (3′*R*,4*R*)-4-[3′-Phenyl-3′-(trimethylsilyl)-1′,2′-propanedienyl]oxazolidine-3-carboxylate (8b).** Yield: 76%, oil. ^{1}H NMR (50 °C): δ 0.26 (s, 9H), 1.45 (s, 9H), 1.52 (s, 3H), 1.60 (s, 3H), 3.92 (dd, *J* = 2 and 8.7, 1H), 4.04 (dd, *J* = 5.7 and 8.7, 1H), 4.49−4.55 (m, 1H), 5.39 (d, *J* = 5.8, 1H), 7.17−7.35 (m, 5H). ^{13}C NMR (50 °C): δ −0.3, 23.6, 27.2, 28.4, 55.7, 67.7, 81.2, 88.5, 93.7, 103.1, 126.3, 127.8, 128.4, 138.0, 152.9, 206.5.

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IR: 3063, 2983, 2876, 1927, 1695, 1597, 1491, 1387, 1093, 8446. $[\alpha]^{23}_D = +173$ ($c = 3$, EtOH). Anal. Calcd for $C_{22}H_{33}NO_3Si$: C, 68.17; H, 8.81; N, 3.61. Found: C, 68.38; H, 8.62; N, 3.41.

***tert*-Butyl (3′*R*,4*R*)-4-[3′-Methyl-3′-(trimethylsilyl)-1′,2′-propanedienyl]oxazolidine-3-carboxylate (9b).** Yield: 82%, oil. ^{1}H NMR (50 °C): δ 0.11 (s, 9H), 1.49 (s, 9H), 1.50 (s, 3H), 1.58 (s, 3H), 1.73 (d, J = 2.8, 3H), 3.82 (dd, J = 2.5 and 8.6, 1H), 3.99 (dd, J = 5.7 and 8.6, 1H), 4.34−4.41 (m, 1H), 4.96−4.99 (m, 1H). ^{13}C NMR (50 °C): δ −1.9, 15.6, 23.7, 26.5, 28.4, 56.0, 67.9, 79.6, 81.2, 85.9, 93.8, 151.8, 203.6. IR 2983, 2873, 1936, 1693, 1453, 1383, 1095, 847. $[\alpha]^{23}_D = +63$ ($c = 3$, EtOH). Anal. Calcd for $C_{17}H_{31}NO_3Si$: C, 62.72; H, 9.60; N, 4.31. Found: C, 62.98; H, 9.32; N, 4.51.

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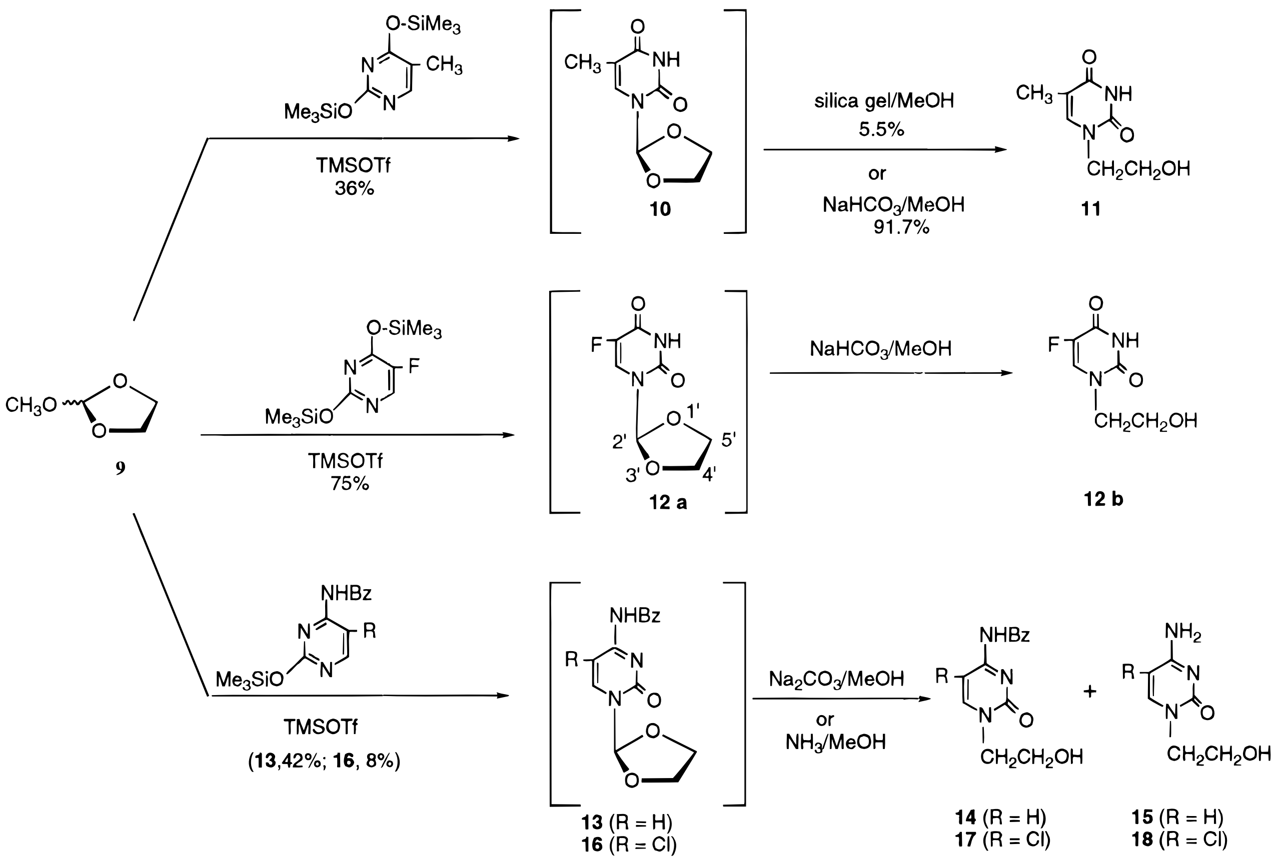
Additions and Corrections

Vol. 60, 1995

Chengyi Liang, Doo Won Lee, M. Gary Newton, and Chung K. Chu*. Synthesis of L-Dioxolane Nucleosides and Related Chemistry.

Page 1547. In view of a recent publication by Samuelsson *et al.* (*J. Org. Chem.* **1996**, *61*, 3599−3603), we would like to make corrections to Scheme 2. Compounds **10**, **12**, **13**, and **16** are intermediates instead of dioxolanes, for which spectral data has been misinterpreted. However, we would like to emphasize that the structure of compound **25** on p 1549 is still correct on the basis of our NMR studies using SELECTIVE INEPT (three-bond coupling studies).

Scheme 2



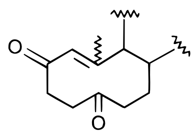
JO964026D

S0022-3263(96)04026-1

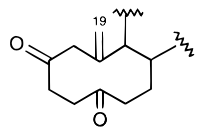
Vol. 60, 1995

Alicia Boto, Rosendo Hernández, Ernesto Suárez,* Carmen Betancor, and María S. Rodríguez. Tandem Carbon-Radical Peroxidation−Addition to Carbonyl Groups Reaction. A New Synthesis of Steroidal β-Peroxy Lactones.

Page 8212. Scheme 4. The correct drawings for structures of compounds **10-*E***, **10-*Z***, and **11** are shown below



10-*E*
10-*Z*



11

JO964015K

S0022-3263(96)04015-7

Vol. 61, 1996

Hiroki Hamada, Mizuho Shiromoto, Makoto Funahashi, Toshiyuki Itoh,* and Kaoru Nakamura. Efficient Synthesis of Optically Pure 1,1,1-Trifluoro-2-alkanols through Lipase-Catalyzed Acylation in Organic Media.

Page 2334, Table 1. Entry 2, column 7, %ee of **3** (config), 83 (*S*) should be 83 (*R*). Entry 4, column 7, %ee of **3** (config), 76 (*S*) should be 76 (*R*). Figure 2 should be corrected as shown.

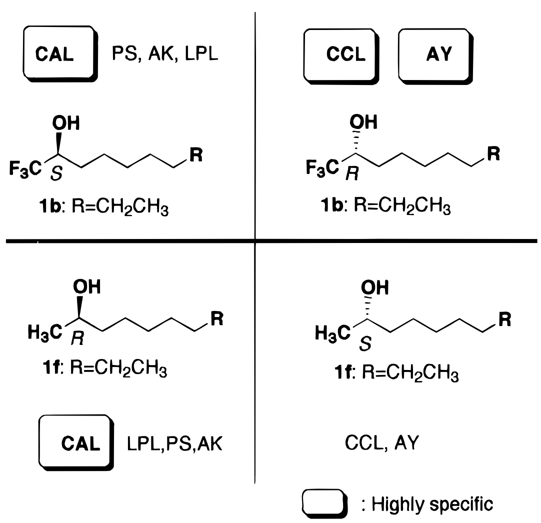


Figure 2. Map of favorite substrates of six types of lipases.

JO9640175

S0022-3263(96)04017-0

Stefan Förster, Anton Rieker, Kazushige Maruyama, Kunihiko Murata, and Akira Nishinaga*. Cobalt Schiff Base Complex-Catalyzed Oxidation of Anilines with *tert*-Butyl Hydroperoxide.

Page 3321. In Table 4, the reaction times are in min and the conversion is in %.

Page 3322, left column, line 17, the number of the compound should be **1j**−**2** instead of **1j**−**8**.

Page 3324, right column, line 5, the reference number should be 16 instead of 17.

JO964018X

S0022-3262(96)04018-2

Alberto Arnone, Pierfrancesco Bravo,* Silvia Capelli, Giovanni Fronza, Stefano V. Meille, Matteo Zanda, Giancarlo Cavicchio, and Marcello Crucianelli. New Versatile Fluorinated Chiral Building Blocks: Synthesis and Reactivity of Optically Pure α-(Fluoroalkyl)-β-sulfinylenamines.

Pages 3383−3387. We failed to include most signs of the $[\alpha]^{20}_{D}$ values of the compounds described in the Experimental Section of the article. The following compounds have positive (+) $[\alpha]^{20}_{D}$ values: (*Z*)-**3b**, (*E*)-**3b**, (*Z*)-**3e**, (*Z*)-**4a**, **9b** (both diastereoisomers), **10a** (both diastereoisomers), **11a** (both diastereoisomers), **12** (both diastereoisomers), (2*S*,R_S)-**14**, (2*S*,R_S)-**15a**, (2*S*,R_S)-**15c**, (*S*)-**16**, (*R*)-**17**, (*R*)-**19**, (*R*)-**21**, (*R*)-**22**, and (*R*)-**24**. The following compounds have negative (−) $[\alpha]^{20}_{D}$ values: (*Z*)-**3a**, (*Z*)-**3c**, (*Z*)-**3d**, (*Z*)-**5d**, (*Z*)-**6a**, (*Z*)-**6b**, (*Z*)-**7a**, (*Z*)-**7b**, (*Z*)-**8a**, (*Z*)-**8b**, and (*R*)-**18**.

JO964014S

S0022-3262(96)04014-5

Christophe Le Roux, Stephanie Mandrou, and Jacques Dubac*. First Catalytic C-Acylation of Enoxysilanes: An Efficient Route to β-Diketones.

Page 3887. In the experimental procedure, replace the first three sentences with the following. 1-Phenyl-2-methyl-1,3-butanedione[20] (**2e**, Table 2, entry 5). To a flame-dried 50 mL flask equipped with a septum inlet and magnetic stir bar was added 10 mL of a mixture of dichloromethane/ether (9/1) by syringe. Bismuth(III) chloride (158 mg, 0.5 mmol) and sodium iodide (225 mg, 1.5 mmol) were transferred to the flask. The flask was removed from the glovebag and connected to an argon line.

JO964024T

S0022-3262(96)04024-8

Angeles Martin, Jose A. Salazar, and Ernesto Suarez*. Synthesis of Chiral Spiroacetals from Carbohydrates.

Page 3999. An article on the synthesis of a chiral 1,7-dioxaspiro[5.5]undecene derivative from D-glucose using a different strategy (Hanessian, S.; Ugolini, A. *Carbohydr. Res.* **1984**, *130*, 261−269) was inadvertently omitted and should be included in ref 10. We thank Professor Hanessian for bringing his paper to our attention and we apologize for this oversight.

JO964021G

S0022-3262(96)04021-2

Saverio Florio*. Generation and Synthetic Applications of (3-Pyridinylchloromethyl)lithium.

Page 4148, column 2, line 26, and in Table 1, *trans*-androsterone must read progesterone.

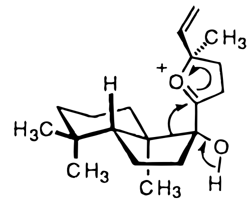
Page 4150, column 1, line 1, must read **2-Methyl-2-(3-oxo-4-androsten-17-yl)-3-(3-pyridinyl)oxirane (2e).** Elemental data are as follows. Anal. Calcd for $C_{27}H_{35}NO_2$: H, 8.70; C, 79.96; N, 3.45. Found: H, 8.80; C, 80.15; N, 3.35.

JO9640229

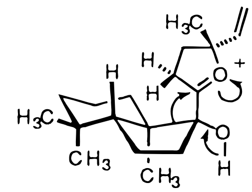
S0022-3262(96)04022-4

Leo A. Paquette* and Hui-Ling Wang. Stereocontrolled Synthesis of *ent*-Grindelic Acid. A Useful Example of Diastereofacial Control in an Oxonium Ion-Initiated Pinacolic Ring Expansion.

Page 5353. Figures A and B incorrectly depict the α-diastereomer and should be replaced by the following representations. The arguments presented in the text were meant to accompany these correct drawings and go unchanged.



A



B

JO964028Y

S0022-3263(96)04028-5

Felix H. Beijer, Rint P. Sijbesma,* Jef. A. J. M. Vekemans, E. W. Meijer, Huub Kooijman, and Anthony L. Spek. Hydrogen-Bonded Complexes of Diaminopyridines and Diaminotriazines: Opposite Effect of Acylation on Complex Stabilities.

Page 6374, caption to Figure 1b should read Hydrogen bonding pattern in the [210] direction.

Page 6375, caption to Figure 2b should read Hydrogen bonding pattern in the (1 $\bar{2}$ 1) plane.

Page 6376, right column, 8th line: Figure 1 should read Figure 2. 21st line: Figure 2 should read Figure 1.

Page 6376, right column. Interchange all occurrences of “the cocrystal of **2** with **11**” and “the cocrystal of **4** with **15**”.

Page 6378, right column. Interchange “Crystal data for complex **2 · 11**” and “Crystal data for complex **4 · 15**”.

JO964029Q

S0022-3262(96)04029-7