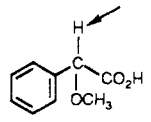
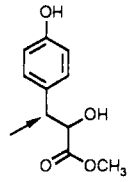
Table II. Chemical Shift Difference for Chiral Substrates with BNPPA•Py-d_5

substrate	$\Delta\delta$	solvent
 9	0.005	$CDCl_3$
 10	0.006	$CDCl_3$

NMR. Measurement of the chiral purity is fast and convenient; simply add BNPPA to the NMR solution and record a proton spectrum. In all cases studied there is at least one proton with high enough chemical shift dispersion to be integrated accurately. The only drawback to using BNPPA was line broadening induced by complexation, presumably due to exchange processes.

Acknowledgment. We would like to acknowledge K. Gunderson for preliminary studies, R. C. Anderson for helpful discussions, V. Parrino for compound **7**, J. Linder for compound **9**, R. Strohschein for compound **10**, and McNeil Laboratories for compounds **5** and **6**. We would also like to thank R. Lomelo for typing the manuscript.

Registry No. (*R*)-**1**, 16078-25-4; (*S*)-**1**, 17305-22-5; (±)-**1**, 53152-98-0; (*R*)-**2a**, 1722-95-8; (*S*)-**2a**, 3197-42-0; (U)-**2a**, 3000-79-1; (*R*)-**3**, 25333-42-0; (*S*)-**3**, 34583-34-1; (±)-**3**, 3684-26-2; (*R*)-**4**, 85-63-2; (*S*)-**4**, 2688-77-9; (±)-**4**, 1699-51-0; **5**, 123409-80-3; **6**, 123409-81-4; (*R*)-**7**, 3886-69-9; (*S*)-**7**, 2627-86-3; (±)-**7**, 618-36-0; (*R*)-**8**, 25137-01-3; (*S*)-**8**, 37675-18-6; (±)-**8**, 71962-74-8; (*R*)-**9**, 3966-32-3; (*S*)-**9**, 26164-26-1; (±)-**9**, 7021-09-2; (*R*)-**10**, 123359-32-0; (*S*)-**10**, 123359-33-1; (±)-**10**, 123409-82-5; (*R*)-BNPPA, 39648-67-4; (*S*)-BNPPA, 35193-64-7.

Palladium-Catalyzed Chemistry of β-Lactam Vinyl Triflates: Coupling with Organostannanes and Alkoxycarbonylation†

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Modification of β-lactam nuclei has been limited only by the stability of the nucleus and the imagination of the medicinal chemist. In our exploration of the enhanced stability provided by the 1-carbacephalosporin over the cephalosporin nucleus,[1] we focused on 3-substituents which exploited this stability difference. Access to 1-carbacepham-3-enol triflate (**1a**)[2,3] prompted methods of development for conversion to the 3-vinyl (**2**), 3-(substituted)-alkyl (**2**), and 3-ester (**4**) analogues. Numerous reports, especially from Stille's group, have demonstrated the utility of the palladium-catalyzed coupling of vinyl halides and triflates with organostannanes.[4] Unfortunately, there have been few attempts to apply this chemistry in areas that demand its selectivity and scope.[5] The mechanistically related palladium-catalyzed conversion of steroidal vinyl triflates to unsaturated esters has been reported by Cacchi et al.,[6] and other reports[7] have utilized this methodology on structurally diverse yet, in general, chemically unreactive substrates. We report[8] here that palladium-catalyzed chemistry upon the complex enol triflates **1** has successfully attained both structural goals, **2** and **4**. Alkenyl groups, as well as a variety of other ligands, can be transferred from tin to C-3 of **1** (3-bromocephalosporin[9] is also a viable substrate). In the presence of carbon monoxide and alcohols, alkoxycarbonylation of **1** (Z = CH_2) provides entry into C-3 esters.

Results and Discussion

The *p*-nitrobenzyl (6*R*,7*S*)-7-(phenoxyacetamido)-1-carba-1-dethia-3-[[(trifluoromethyl)sulfonyl]oxy]-3-cepham-4-carboxylate (**1a**) could be converted to **1b**[10] by reduction (zinc, HCl(aq)/DMF, 0 °C) of the *p*-nitrobenzyl group and esterification (Ph_2CN_2, CH_3CN, 23 °C) in 78% overall yield. Further transformation of **1b** by C-7 sidechain cleavage [(i) PCl_5, CH_2Cl_2, pyridine; (ii) i-BuOH, CH_2Cl_2, −10 °C; (iii) H_2O] and acylation with the 4,6-dimethoxy-1,3,5-triazine active ester of D-(t-Boc)phenylglycine[11] produced **1c** (28% yield).

Attempted vinylation of **1a** under standard conditions[4] (tri-*n*-butylvinylstannane, LiCl) with $(Ph_3P)_4Pd$ as catalyst in a variety of solvents produced only traces of product. Forcing conditions in an attempted carbonylation of **1b** utilizing a stoichiometric amount of $(Ph_3P)_4Pd$ with 1 atm of CO, *n*-Bu_3SnH and LiCl afforded a crystalline material in 16% yield which contained palladium. This same material could be produced in 78% yield from **1a**, omitting the carbon monoxide and tin hydride. The spectral data[12]

† This paper is dedicated to the memory of the late Professor J. K. Stille.

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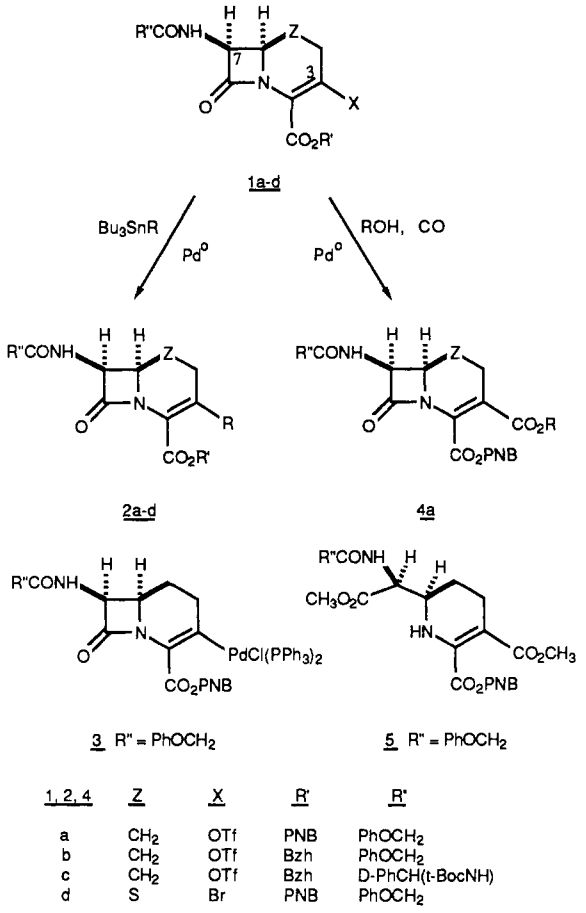

1, 2, 4	Z	X	R'	R"
a	CH_2	OTf	PNB	$PhOCH_2$
b	CH_2	OTf	Bzh	$PhOCH_2$
c	CH_2	OTf	Bzh	D-PhCH(t-BocNH)
d	S	Br	PNB	$PhOCH_2$

for this organometallic complex is consistent with the proposed structure **3**.

In light of these results, considerable experimentation led to the following reaction conditions: a "ligandless" catalyst, bis(acetonitrile)palladium(II) chloride,[13] in DMF containing 2 equiv of LiCl and 1.1 equiv of the organostannane. This ligandless catalyst gave results similar to those of Stille,[4] but the reactions occurred considerably faster and at lower temperatures.[13] The scope of the reaction was indeed very broad as demonstrated in Table I. The unsaturated stannanes consistently gave the highest yields and went at the lowest temperatures. Transfer of vinyl and allylic groups occurred without double bond isomerization in the transferred ligand. Methyl and substituted-alkyl transfer required heating. An undesired reduction product **2a–c**, R = H, was observed in yields as high as 20% during the alkyl transfers. This led to the discovery of a high-yield process for the reduction of **1**. Treatment of **1b,d** with 1.3 equiv of tetra-*n*-butylstannane, 0.1 equiv of $PdCl_2(CH_3CN)_2$, catalytic tetravinylstannane, and BHT gave high yields (80–90%) of **2b,d** (R = H).

This same palladium catalyst ($PdCl_2(CH_3CN)_2$) proved to be quite effective in the alkoxycarbonylation of the 1-carbacephem-3-enol triflate. Subjecting **1a** to the previously cited carbonylation conditions[6] afforded only a moderate yield (30%) of the desired methyl ester **4a**, accompanied by a complex mixture of byproducts including **5**. Attempts to optimize this process by varying catalytic load, amine base, phosphine ligand, or organic cosolvent were nonproductive. However, conditions using the aforementioned "ligandless" palladium catalyst resulted in a remarkable improvement in yield. Treatment of **1a** under these optimum conditions (0.3 equiv of $PdCl_2(CH_3CN)_2$, 3 equiv of LiCl, 2 equiv of Et_3N, 1 atm of CO, 1:1 CH_3OH–DMF, 23 °C) doubled the yield of **4a**. As illustrated in Table II, a wide variety of primary and secondary alcohols successfully participate in this transformation, *tert*-butyl alcohol was not synthetically useful. The greater reactivity of this catalyst (coupled with its relatively high load) greatly shortened the reaction time, helping to minimize product degradation in the basic medium.

In conclusion, we have demonstrated the utility of the palladium-catalyzed chemistry upon vinyltriflates (or halides) derived from complex β-lactam nuclei: couplings with organostannanes,[14] reduction, and alkoxycarbonylations with carbon monoxide and alcohols are all synthetically useful processes. Use of the "ligandless" palladium catalyst has resulted in reaction conditions that are milder than those previously reported. We were able to isolate a presumed organometallic intermediate which is unreactive toward carbonyl insertion/reduction, presumably due to two strongly ligating triphenylphosphine ligands. Modification of the products of this chemistry and the associated biological data will be reported elsewhere.

Table I. Conversion of 1a–d to 2a–d

sm	R	% yield	% 3-H	temp, °C
1b	vinyl	91		25
1b	isobutenyl	76		25
1b	*cis*-propenyl	88		25
1b	2,2-difluorovinyl	78		25
1b	propynyl	66		0
1b	methallyl	46[a]		85
1b	Me[b]	70		35
1b	CH_2OCH_3	58	5–10	40
1b	CH_2OBz	39	5–10	60
1a	CH_2OBz	28	17	60
1a	$CH_2OTBDMS$	25	5–10	65
1a	1-ethoxyvinyl	81		25
1c	isobutenyl	79		25
1d	vinyl	80		25
1d	*cis*-propenyl	64		35

[a] The product was a 3:2 mixture of Δ-3:Δ-2 olefins. [b] Me_4Sn was the stannane used.

Table II. Yield of 4 in Carbacephem-3-enol Triflate Carbonylation

sm	alcohol (ROH)	% 4
1a	Me	58
1a	Et	73
1a	*n*-Pr	60
1a	*n*-Bu	75
1a	$MeOCH_2CH_2$	41
1a	*i*-Pr	63
1a	*t*-Bu	3

Experimental Section

Materials. Reagents were used as supplied unless otherwise noted. Reactions were run under an atmosphere of dry nitrogen or argon unless otherwise noted. Silica gel (E. Merck, 230–400

(12) ^1H NMR (300 MHz, $CDCl_3$): δ 5.00 (1 H, C-7, dd, J = 4.5, 9.0 Hz), 2.92 (1 H, C-6, dt, J = 4.5, 12.0 Hz), 2.82 (1 H, C-2, br d, J = 18 Hz), 1.85 (1 H, C-2, m), 0.90 (1 H, C-1, m), −0.30 (1 H, C-1, ddt, J = 6.0, 12.0, 12.0 Hz). IR ($CHCl_3$): 1754 cm^{-1}. MS m/e (FAB): 1116 (M^+ + 1), 1080 (M^+ − Cl). Anal. Calcd for $C_{59}H_{50}N_3O_7ClP_2Pd$: C, 63.45; H, 4.51; N, 3.76; Cl, 3.17. Found: C, 63.32; H, 4,56; N, 3.75; Cl, 3.37. Attempts to find a suitable crystal for X-ray are ongoing.

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mesh ASTM) was used for flash column chromatography. ^1H NMR spectra were recorded on a General Electric QE-300 instrument. Infrared (IR) spectra were determined on a Nicolet MX-1 FT-IR, ultraviolet (UV) spectra on a Cray 219, and mass spectral data (MS) were obtained on either a CEC-21-110 or a Varian MAT-731 spectrometer.

Benzhydryl (6*R*,7*S*)-7-(Phenoxyacetamido)-1-carba-1-dethia-3-vinyl-3-cephem-4-carboxylate. A solution of triflate **1b** (2.00 g, 3.17 mmol) in 6 mL of anhydrous DMF under N_2 was treated with lithium chloride (0.269 g, 6.34 mmol) and $(CH_3CN)_2PdCl_2$ (0.041 g, 0.16 mmol), and the solution was degassed and purged with N_2. Tributylvinylstannane (1.02 mL, 3.49 mmol) was added dropwise over 1 min. After 10 min the resulting black solution was rinsed into a separatory funnel with ethyl acetate. Ether was added, and the organics were washed with water, dried over $MgSO_4$, filtered, and evaporated. The residue was taken up in CH_3CN, washed three times with hexane, concentrated, and purified by chromatography on silica gel (eluting with CH_2Cl_2, 2% ethyl acetate/CH_2Cl_2, and 5% ethyl acetate/CH_2Cl_2) to give 1.46 g (91%) of olefin **2b** (R = CH=CH_2) as an oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, J = 8 Hz, 2 H), 7.1–7.4 (m, 13 H), 7.00 (t, J = 8 Hz, 1 H), 6.93 (s, 1 H), 6.88 (d, J = 8 Hz, 2 H), 5.44 (m, 1 H), 5.32 (AB, 2 H), 4.53 (AB, 2 H), 3.86 (dt, J = 5, 12 Hz, 1 H), 2.64 (dd, J = 6, 18 Hz, 1 H), 2.22 (m, 1 H), 1.90 (m, 1 H), and 1.20 (m, 1 H); IR ($CHCl_3$) 3023, 3019, 1770, 1718, 1690, 1521, 1496, and 1380 cm^{-1}; UV (EtOH) λ_{max} 298 nm (ϵ 17 000); MS m/e 509 (M^+ + 1). Anal. Calcd for $C_{31}H_{28}N_2O_5$: C, 73.21; H, 5.55; N, 5.50. Found: C, 73.03; H, 5.80; N, 5.32.

Benzhydryl (6*R*,7*S*)-7-(Phenoxyacetamido)-1-carba-1-dethia-3-hydro-3-cephem-4-carboxylate. A solution of triflate **1b** (200 mg, 0.317 mmol) in 0.63 mL of anhydrous DMF under N_2 was treated with lithium chloride (27 mg, 0.634 mmol) and $(CH_3CN)_2PdCl_2$ (8 mg, 0.1 equiv), degassed, and purged with N_2. Finally, the reaction mixture was treated with 7 mg (0.032 mmol) of 2,6-di-*tert*-butyl-4-methylphenol and tetrabutyltin (135 μL, 0.412 mmol). The solution was heated to 70 °C and a 5-μL sample of tetravinylstannane was added. After 1.5 h the reaction mixture was allowed to cool, diluted with ethyl acetate, and filtered through Celite. The filtrate was diluted with ether, washed with water, dried over $MgSO_4$, filtered, and evaporated. The residue was taken up in CH_3CN and washed five times with hexane. The resultant solution was concentrated and purified by chromatography on silica gel (elution with 50% ethyl acetate/hexane) to give 139 mg (91%) of reduction product, **2b** (R = H): ^1H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, J = 8 Hz, 2 H), 7.2–7.4 (m, 13 H), 7.03 (t, J = 8 Hz, 1 H), 6.97 (s, 1 H), 6.91 (d, J = 8 Hz, 2 H), 6.53 (br s, 1 H), 5.45 (m, 1 H), 4.55 (s, 2 H), 3.84 (m, 1 H), 2.2–2.4 (m, 2 H), 1.90 (m, 1 H), and 1.40 (m, 1 H); IR ($CHCl_3$) 3019, 1773, 1726, 1689, 1522, 1496, 1401, 1289, 1279, and 1265 cm^{-1}; UV (EtOH) λ_{max} 264 nm (ϵ 7700); MS m/e 483 (M^+ + 1). Anal. Calcd for $C_{29}H_{26}N_2O_5$: C, 72.19; H, 5.43; N, 5.81. Found: C, 71.91; H, 5.48; N, 5.93.

***p*-Nitrobenzyl (6*R*,7*S*)-7-(Phenoxyacetamido)-3-(*cis*-1-propenyl)-3-cephem-4-carboxylate.** A solution of bromide **1d** (0.274 g, 0.500 mmol) and $(CH_3CN)_2PdCl_2$ (8 mg, 0.031 mmol) in 1.00 mL of anhydrous DMF was degassed and purged with N_2. The *cis*-1-propenyltributylstannane (0.175 g, 0.53 mmol) was added dropwise. The reaction solution was heated briefly with a heat gun, which caused the solution to turn black. TLC showed the reaction to be complete. The reaction was poured into water and extracted with EtOAc/Et_2O. The organic extracts were washed with H_2O and concentrated. The residue was dissolved in acetonitrile and washed three times with hexane. Solvent removal and flash chromatography with 5% EtOAc/CH_2Cl_2 produced 0.162 g (64%) of *cis*-propenyl product, **2d** (R = *cis*-CH=CH(CH_3)): ^1H NMR (300 MHz, $CDCl_3$) δ 8.21 (d, J = 8 Hz, 2 H), 7.58 (d, J = 8 Hz, 2 H), 7.32 (q, J = 8 Hz, 2 H), 7.02 (t, J = 8 Hz, 1 H), 6.93 (d, J = 8 Hz, 2 H), 6.16 (br d, J = 11 Hz, 1 H), 5.91 (q, J = 5 Hz, 1 H), 5.72 (dq, J = 7, 11 Hz, 1 H), 5.3 (m, 1 H), 5.09 (d, J = 5 Hz, 1 H), 3.45 (AB, 2 H), and 1.60 (d, J = 7 Hz, 3 H); IR ($CHCl_3$) 1786, 1730, 1696, 1525, 1495, 1383, 1350, and 1233 cm^{-1}; MS m/e 509 (M^+). Anal. Calcd for $C_{25}H_{23}N_3O_7S$: C, 58.93; H, 4.55; N, 8.25. Found: C, 58.68; H, 4.66; N, 7.97.

***p*-Nitrobenzyl (6*R*,7*S*)-7-(Phenoxyacetamido)-1-carba-1-dethia-3-carbethoxy-3-cephem-4-carboxylate.** Vinyl triflate **1a** (5.89 g, 9.82 mmol) and lithium chloride (1.25 g, 29.5 mmol) were placed under N_2 and dissolved in 180 mL of a 1:1 mixture of anhydrous DMF and anhydrous ethanol. CO was bubbled into the solution by a gas dispersion tube for 5 min, at which time the purging was discontinued and triethyl amine (2.74 mL, 19.6 mmol) and $(CH_3CN)_2PdCl_2$ (0.840 g; 3.24 mmol) were added. A Fisher gas bag filled with CO was attached to maintain a positive pressure of CO. After stirring for 1.5 h the black solution was diluted with 750 mL of ethyl acetate. The organics were washed with 1 N HCl, saturated $NaHCO_3$, 1 N HCl, and brine, dried over $MgSO_4$, and filtered. Upon addition of 500 mL of toluene (to aid the removal of ethanol thereby minimizing β-lactam cleavage during isolation), the mixture was concentrated and purified by chromatography on silica gel (elution with 50% ethyl acetate/hexane) to afford 3.73 g (73%) of the ester **4a** (R = C_2H_5): ^1H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, J = 9 Hz, 2 H), 7.60 (d, J = 9 Hz, 2 H), 7.35 (t, J = 8 Hz, 2 H), 7.05 (m, 2 H), 6.90 (d, J = 6 Hz, 2 H), 5.45 (m, 1 H), 5.40 (AB, 2 H), 4.55 (s, 2 H), 4.15 (m, 2 H), 3.95 (m, 1 H), 2.82 (dd, J = 5, 18 Hz, 1 H), 2.30 (ddd, J = 6, 12, 18 Hz, 1 H), 2.02 (m, 1 H), 1.40 (dq, J = 5, 12 Hz, 1 H), and 1.20 (t, J = 7 Hz, 3 H); IR ($CHCl_3$) 1782, 1746, 1697, 1525, 1350, 1270, and 1223 cm^{-1}; MS m/e 523 (M^+). Anal. Calcd for $C_{26}H_{25}N_3O_9$: C, 59.65; H, 4.81; N, 8.03. Found: C, 59.43; H, 4.86; N, 8.08.

Acknowledgment. We would like to thank R. C. Hoying for providing **1a**. The services of the Physical Chemistry Research Department, especially those of J. W. Paschal and T. K. Elzey, are appreciated.

Registry No. **1a**, 108493-71-6; **1b**, 123078-32-0; **1c**, 123266-29-5; **1d**, 76610-66-7; **2a** (R = CH_2OBz), 123266-38-6; **2a** (R = $CH_2OTBDMS$), 123266-39-7; **2a** (R = 1-ethoxyvinyl), 123289-24-7; **2b** (R = CH=CH_2), 123266-25-1; **2b** (R = H), 123266-26-2; **2b** (R = CH=$C(CH_3)_2$), 123266-31-9; **2b** (R = CH=CF_2), 123289-23-6; **2b** (R = C≡CCH_3), 123266-32-0; **2b** (R = $CH_2C(CH_3)$=CH_2) Δ^3, 123266-33-1; **2b** (R = $CH_2C(CH_3)$=CH_2) Δ^2, 123266-34-2; **2b** (R = Me), 123266-35-3; **2b** (R = CH_2OCH_3), 123266-36-4; **2b** (R = CH_2OBz), 123266-37-5; **2c** (R = CH=$C(CH_3)_2$), 123266-40-0; **2d** (R = *cis*-CH=$CHCH_3$), 123266-27-3; **2d** (R = CH=CH_2), 123266-41-1; **3**, 123266-45-5; **4a** (R = C_2H_5), 120340-15-0; **4a** (R = CH_3), 120340-19-4; **4a** (R = n-Pr), 120340-16-1; **4a** (R = n-Bu), 123266-42-2; **4a** (R = $MeOCH_2CH_2$), 123266-43-3; **4a** (R = i-Pr), 120340-17-2; **4a** (R = t-Bu), 123266-44-4; Bu_3SnCH=CH_2, 7486-35-3; *cis*-Bu_3SnCH=$CHCH_3$, 66680-84-0; Bu_3SnCH=$C(CH_3)_2$, 66680-86-2; Bu_3SnCH=CF_2, 123266-30-8; Bu_3SnC≡CCH_3, 64099-82-7; $Bu_3SnCH_2C(CH_3)$=CH_2, 67883-62-9; Me_4Sn, 594-27-4; $Bu_3SnCH_2OCH_3$, 27490-32-0; Bu_3SnCH_2OBz, 66222-28-4; $Bu_3SnCH_2OTBDMS$, 123061-64-3; $Bu_3SnC(OEt)$=CH_2, 97674-02-7; D-(t-BOC)phenylglycine 4,6-dimethoxy-1,3,5-triazine ester, 123266-28-4.

Supplementary Material Available: Characterization (IR, ^1H NMR, MS, UV, analysis) data for new compounds listed in Tables I and II (5 pages). Ordering information is given on any current masthead page.