Notes

The Stevens [1,2]-Shift of Oxonium Ylides: A Route to Substituted Tetrahydrofuranones[1]

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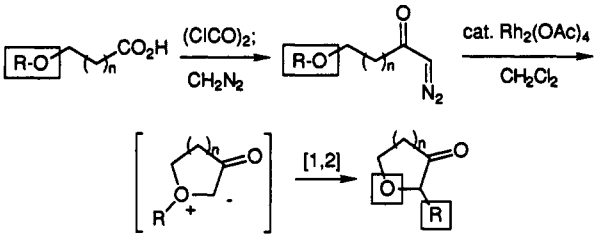
Substituted cyclic ethers are commonly encountered structural subunits in a variety of natural products, such as ionophore antibiotics and marine toxins. The tetrahydrofuran unit is among the most ubiquitous of the naturally occurring cyclic ethers, and a number of elegant approaches to this ring system have been described in recent years.[2] We report here a new approach to substituted tetrahydrofurans using a tandem oxonium ylide generation/Stevens [1,2]-shift protocol.

The [1,2]-shift of ylides has received periodic attention with regard to mechanistic issues[3] but has rarely been applied as a synthetic method. Since this reaction results in the controlled generation of a carbon–carbon bond at the expense of an easily formed carbon–heteroatom bond, we have sought to explore its potential application to target structures of current synthetic interest. In the case of ammonium or sulfonium ylides, ylide formation is most often effected by deprotonation of the corresponding salt; however, such a protocol is not applicable to oxonium ylides in light of the preference by trivalent oxonium salts to donate an alkyl group rather than a proton. Direct ylide formation by intramolecular addition of metal carbenoids to heteroatom lone pairs has recently enjoyed widespread attention[4] and has proven to be a mild and direct route to cyclic ylides.[5]

There have been several reports of cyclic oxonium ylide formation by intramolecular rhodium carbenoid addition to ether oxygen,[6] typically followed by concerted [2,3]-sigmatropic rearrangement involving an allylic moiety. [1,2]-Shifts of rhodium carbenoid derived cyclic sulfonium[7a] and ammonium[7b] ylides are known, and [1,2]-shifts as competing side reactions of allylic oxonium ylides have been reported.[6b,8,9] In contrast to earlier examples involving acyclic ylides or ring contraction of cyclic ylides, in this work we have examined substrates explicitly designed to undergo migration of an exocyclic group on a cyclic oxonium ylide. The net result of such a transformation would be the formal insertion of the carbenoid into a C–O bond with concomitant generation of a cyclic ether from an acyclic ω-alkoxy-α'-diazo ketone precursor.



The requisite diazo ketone substrates were prepared in good yield from the corresponding readily available carboxylic acids via in situ acid chloride formation followed by condensation with diazomethane.[10] Standard conditions for the rhodium-catalyzed carbenoid generation/oxonium ylide formation/[1,2]-shift protocol consisted of stirring 3 mol % $Rh_2(OAc)_4$ in CH_2Cl_2 at ambient temperature followed by dropwise addition of a solution of diazo ketone in CH_2Cl_2 at a rate of 0.5 mmol/h. Starting material was consumed shortly after completion of its addition. Workup consisted of evaporation of solvent followed by immediate chromatography of the residue to give the cyclic ether products shown in Table I. In all but two cases (vide infra), oxonium ylide [1,2]-shift products were formed in good to excellent yield from the corresponding diazo ketones, thus providing access to substituted tetrahydrofuranones in two procedurally simple steps from the carboxylic acid starting materials.

It is interesting to note the degree to which C–H insertion by the rhodium carbenoid intermediate competes with ylide formation. It has been documented that C–H bonds α to ether oxygens are particularly prone to intramolecular carbene insertion.[11] Nonetheless, our results indicate that C–H insertion is competitive only when the choice consists of formation of a five-membered ring via insertion vs formation of a six-membered cyclic oxonium ylide (entry 3). Products derived from five-membered cyclic oxonium ylides were formed to the exclusion of six-membered C–H insertion products,[12] and in the case

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(9) For examples of [1,2]-shifts of oxonium ylides derived from copper or thermally generated carbenes, see: (a) Kirmse, W.; Kund, K. *J. Am. Chem. Soc.* **1989**, *111*, 1465. (b) Nozaki, H.; Takaya, H.; Noyori, R.; *Tetrahedron* **1966**, *22*, 3393.

(10) Hudlicky, T.; Koszyk, F. J.; Kutchan, T. M.; Sheth, J. *J. Org. Chem.* **1980**, *45*, 5020.

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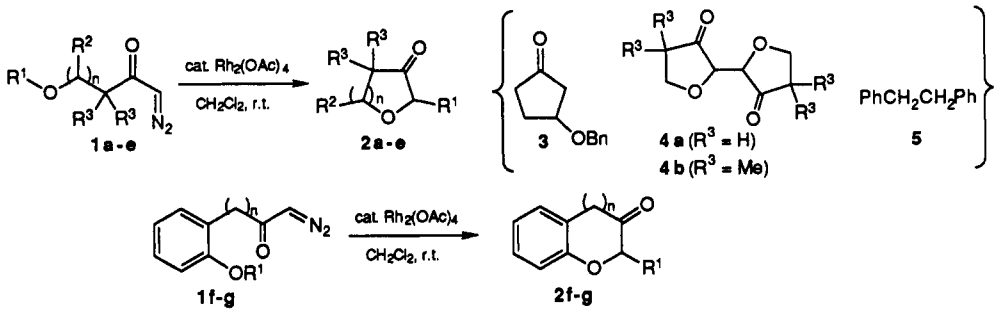
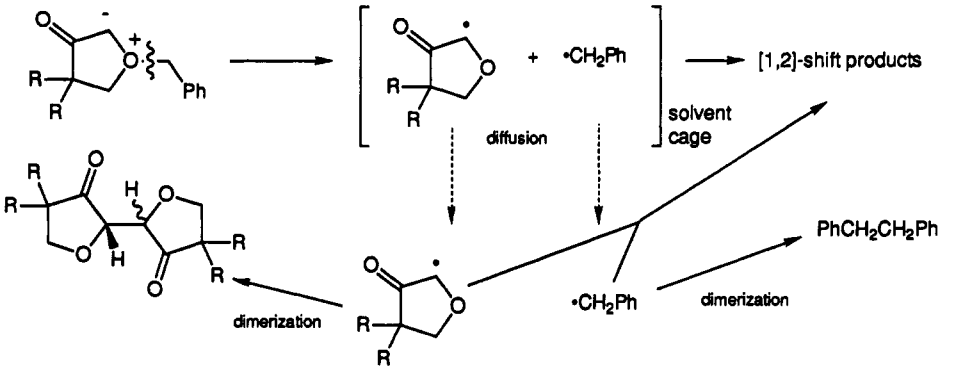
Table I. Stevens [1,2]-Shifts of Cyclic Oxonium Ylides



entry	substrate	R^1	R^2	R^3	n	[1,2]-product	yield[a] (%)	side products
1	**1a**	Bn	H	H	1	**2a**	64	**4a** (27%),[b,c] **5** (16)[c]
2	**1b**	Bn	H	Me	1	**2b**	65	**4b** (17%),[b,c] **5** (16)[c]
3	**1c**	Bn	H	H	2	**2c**	16	**3** (47)
4	**1d**	Bn	Me	H	1	**2d**	52[d]	**5** (11)[c]
5	**1e**	$PhCOCH_2$	H	Me	1	**2e**	17	*e*
6	**1f**	Bn			0	**2f**	70	*e*
7	**1g**	Bn			1	**2g**	67	*e*

[a] All yields reported are isolated yields after chromatography and were averaged over at least three runs. [b] Isolated as a 1:1 mixture of diastereomers. [c] Yields of homodimers 4 and 5 varied considerably. The yields given represent average values. [d] Isolated as a 1.5:1 mixture of diastereomers. [e] No homodimers or C–H insertion products were isolated.

Scheme I



where a five-center α-ether C–H insertion transition state is precluded (entry 7), the six-membered ylide-derived product was formed in good yield. Also notable is the observed migration of a phenacyl substituent (entry 5), albeit in modest yield, which indicates that this transformation is not limited to benzylic migrating groups.

Finally, the isolation of bibenzyl **5** and diastereomeric bis(tetrahydrofurans) **4a,b** in several cases (entries 1, 2, 4) is particularly significant with regard to the mechanism of the [1,2]-shift. These side products are the classic signature of radical-pair intermediates, whose escape from the solvent cage in a relatively nonviscous solvent such as dichloromethane should be facile (Scheme I).[13] Observation of retention of migrating-group stereochemistry[6b] in the ring contraction of related five-membered oxonium ylides has led to the proposal of a concerted, polar [1,2]-shift with rhodium assistance. However, we find the isolation of significant quantities of dimeric byproducts to be compelling evidence for a major portion of the mechanistic pathway in the examples reported in this work to involve homolysis/recombination.

In summary, we have demonstrated a mild, direct (two steps) and procedurally simple approach to functionalized tetrahydrofuranones, generally in good yield. A novel strategy employing the Stevens rearrangement of oxonium ylides permits the use of simple, readily available acyclic β-alkoxycarboxylic acids as precursors. The isolation of homodimers in some cases indicates the likelihood of a radical-pair mechanism for the [1,2]-shift. Further mechanistic studies and application of this overall sequence to cyclic ether substrates[14] will be reported elsewhere.

Experimental Section

Melting points are uncorrected. All ^1H NMR spectra were recorded at 300 MHz and all ^{13}C NMR spectra at 75 MHz. Flash chromatography[15] was carried out using Merck Kieselgel 60 (230–400 mesh), and TLC analysis was performed using Kieselgel 60 F_{254} plates. Diethyl ether was freshly distilled from sodium–benzophenone, and dichloromethane and DMF from CaH_2. Rhodium(II) acetate, purchased from the Aldrich Chemical Co., was used as received.

Representative Procedure: Preparation of 1-Diazo-4-(benzyloxy)-3,3-dimethylbutan-2-one (1b). 3-(Benzyloxy)-2,2-dimethylpropionic acid (179 mg; 0.86 mmol) was dissolved in hexanes (5 mL) along with a catalytic amount of DMF (ca. 0.005 mL), and distilled oxalyl chloride (0.23 mL; 2.6 mmol) was added slowly via syringe. Gas evolution was noted. The mixture was

(12) Tetrahydrofuranone products derived from oxonium ylide [1,2]-shifts were unequivocally distinguished in entries 2 and 6 from the formally possible C–H insertion products by ketone reduction with $NaBH_4$. Structures of the other [1,2]-shift products were assigned by analogy.

(13) We would expect the monomeric captodative radicals shown in the scheme to be reasonably long-lived in analogy to the related 2-oxomorpholin-3-yl radicals reported by Koch: Benson, O., Jr.; Demirdji, S. H.; Haltiwanger, R. C.; Koch, T. H. *J. Am. Chem. Soc.* **1991**, *113*, 8879.

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refluxed for 2 h under N_2 atmosphere. The reflux condenser was then removed and solvent and excess oxalyl chloride removed under reduced pressure (aspirator). The crude acid chloride was diluted with ether (10 mL) and added dropwise via cannula to a solution of diazomethane (4.3 mmol) in ether (30 mL) at 0 °C over 30 min. After an additional 30 min, the reaction was allowed to warm to room temperature and was stirred for an additional 1 h. At this time the residual diazomethane and the solvent were removed under reduced pressure (aspirator) to give a yellow oil, which was purified via flash chromatography (15 g of silica gel; 18-mm i.d. column; 5:95 EtOAc/hexanes) to yield 168 mg (84%) of **1b** as a yellow oil: R_f 0.45 (30:70 EtOAc/hexanes); IR (neat) 2105, 1660 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 7.36–7.26 (m, 5 H), 5.51 (s, 1 H), 4.51 (s, 2 H), 3.41 (s, 2 H), 1.15 (s, 6 H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 199.1, 154.5, 138.0, 128.2, 127.4, 76.7, 73.4, 53.1, 47.0, 22.6; HRMS calcd for $C_{13}H_{17}N_2O_2$ m/e 233.129 00 (M + 1), found m/e 233.126 95 (M + 1).

Preparation of 1-Diazo-4-(benzyloxy)butan-2-one (1a). 3-(Benzyloxy)propionic acid (497 mg; 2.8 mmol) was subjected to the standard conditions to give a yellow oil, which was purified via flash chromatography (27 g of silica gel; 22-mm i.d. column; 20:80 EtOAc/hexanes) to yield 410 mg (73%) of **1a** as a yellow oil: R_f 0.21 (30:70 EtOAc/hexanes); IR (neat) 2095, 1640 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 7.36–7.26 (m, 5 H), 5.33 (br s, 1 H), 4.50 (s, 2 H), 3.74 (t, J = 6 Hz, 2 H), 2.58 (t, J = 6 Hz, 2 H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 192.8, 137.9, 128.3, 127.6 (two overlapping carbons), 73.2, 65.8, 55.0, 41.2; HRMS calcd for $C_{11}H_{13}N_2O_2$ m/e 205.097 70 (M + 1), found m/e 205.097 23 (M + 1).

Preparation of 1-Diazo-5-(benzyloxy)pentan-2-one (1c). 4-(Benzyloxy)butyric acid (326 mg; 1.7 mmol) was subjected to the standard conditions to give a yellow oil, which was purified via flash chromatography (27 g of silica gel; 22-mm i.d. column; 20:80 EtOAc/hexanes) to yield 234 mg (73%) of **1c** as a yellow oil: R_f 0.25 (30:70 EtOAc/hexanes); IR (neat) 2100, 1680 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 7.37–7.25 (m, 5 H), 5.21 (br s, 1 H), 4.49 (s, 2 H), 3.50 (t, J = 6.1 Hz, 2 H), 2.49–2.42 (m, 2 H), 1.98–1.72 (m, 2 H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 194.6, 138.3, 128.3, 127.6, 127.5, 72.8, 69.1, 54.3, 37.4, 25.0; HRMS calcd for $C_{12}H_{15}N_2O_2$ m/e 219.113 35 (M + 1), found m/e 219.112 65 (M + 1).

Preparation of 1-Diazo-4-(benzyloxy)pentan-2-one (1d). 3-(Benzyloxy)butyric acid (440 mg; 2.3 mmol) was subjected to the standard conditions to give a yellow oil which was purified via flash chromatography (27 g of silica gel; 22-mm i.d. column; 15:85 EtOAc/hexanes) to yield 298 mg (60%) of **1d** as a yellow oil: R_f 0.29 (30:70 EtOAc/hexanes); IR (neat) 2090, 1650 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 7.36–7.24 (m, 5 H), 5.31 (br s, 1 H), 4.54 (d, J_{AB} = 11.5 Hz, 1 H), 4.47 (d, J_{AB} = 11.5 Hz, 1 H), 4.05–3.99 (m, 1 H), 2.61 (dd, J = 14.5, 6.8 Hz, 1 H), 2.41 (dd, J = 14.5, 4.8 Hz, 1 H), 1.26 (d, J = 6.2 Hz, 3 H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 192.9, 138.4, 128.4, 127.6, 127.5, 72.2, 70.9, 55.4, 48.2, 19.8; HRMS calcd for $C_{12}H_{15}N_2O_2$ m/e 219.113 35 (M + 1), found m/e 219.113 28 (M + 1).

Preparation of 1-Diazo-3,3-dimethyl-4-(2-phenyl-2-oxoethoxy)butan-2-one (1e). 2,2-Dimethyl-3-(phenacyloxy)-propionic acid (351 mg; 1.5 mmol) was subjected to the standard conditions to give a yellow oil, which was purified via flash chromatography (27 g of silica gel; 22-mm i.d. column; 15:85 EtOAc/hexanes) to yield 329 mg (86%) of **1e** as a yellow oil: R_f 0.27 (30:70 EtOAc/hexanes); IR (neat) 2100, 1700, 1625 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 7.91–7.45 (m, 5 H), 5.87 (s, 1 H), 4.75 (s, 2 H), 3.56 (s, 2 H), 1.17 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 199.1, 196.4, 134.6, 133.4, 128.5, 127.7, 77.8, 74.2, 53.1, 46.8, 22.4; HRMS calcd for $C_{14}H_{17}N_2O_3$ m/e 261.12392 (M + 1), found m/e 261.123 37 (M + 1).

Preparation of 2-Diazo-2′-(benzyloxy)acetophenone (1f). 2-(Benzyloxy)benzoic acid (365 mg; 1.6 mmol) was subjected to the standard conditions to give a yellow oil, which was purified via flash chromatography (27 g of silica gel; 22-mm i.d. column; 5:95 EtOAc/hexanes) to yield 330 mg (82%) of **1f** as a yellow oil: R_f 0.41 (30:70 EtOAc/hexanes); IR (neat) 2095, 1600 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 8.00–7.97 (m, 1 H), 7.46–7.35 (m, 6 H), 7.08–7.00 (m, 2 H), 6.34 (s, 1 H), 5.15 (s, 2 H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 184.9, 157.4, 136.0, 133.4, 130.5, 128.8, 128.4, 127.6, 126.2, 121.2, 112.9, 70.9, 58.0; HRMS calcd for $C_{15}H_{13}N_2O_2$ m/e 253.097 26 (M + 1), found m/e 253.097 70 (M + 1).

Preparation of 1-Diazo-3-[2′-(benzyloxy)phenyl]propan-2-one (1g). 2-(Benzyloxy)phenylacetic acid (584 mg; 2.4 mmol) was subjected to the standard conditions to give 557 mg of a yellow oil, which was purified via flash chromatography (27 g of silica gel; 22-mm i.d. column; 35:65 EtOAc/hexanes) to yield 484 mg (75%) of **1g** as a yellow crystaline solid: mp 49–59 °C; R_f 0.39 (35:65 EtOAc/hexanes); IR (neat) 2100, 1640 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 7.38–7.17 (m, 7 H), 6.94–6.91 (m, 2 H), 5.08 (s, 1 H), 5.06 (s, 2 H), 3.638 (s, 2 H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 193.2, 156.2, 136.6, 131.1, 128.8, 128.6, 128.0, 127.3, 123.7, 121.2, 111.9, 70.1, 54.1, 42.8; HRMS calcd for $C_{16}H_{15}N_2O_2$ m/e 267.113 34 (M + 1), found m/e 267.113 51 (M + 1).

Representative Procedure: Preparation of Tetrahydro-2-benzyl-4,4-dimethylfuran-3-one (2b) via Stevens Rearrangement of 1b. A 0.04 M solution of **1b**: (92 mg; 0.40 mmol) in CH_2Cl_2 (10 mL) was added dropwise (~0.5 mmol/h) to a 4 × 10^{-4} M solution of rhodium acetate (5.3 mg; 0.012 mmol) in CH_2Cl_2 (30 mL) under an inert atmosphere (N_2). After addition was complete the mixture was stirred for an additional 0.5 h. The reaction mixture was then washed with 0.5 M potassium carbonate (50 mL), and the aqueous layer was back-extracted with CH_2Cl_2 (2 × 25 mL). The combined organic extracts were washed with saturated brine (25 mL), dried (Na_2SO_4), and concentrated to produce a yellow oil which was purified using flash chromatography (13 g of silica gel; 15-mm i.d. column; 15:85 EtOAc/hexanes) to yield 49 mg (60%) of **2b** as a colorless oil [R_f 0.41 (15:85 EtOAc/hexanes); IR (neat) 1755 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 7.31–7.24 (m, 5 H), 4.13 (dd, J = 7.3, 3.9 Hz, 1 H), 3.85 (d, J_{AB} = 9.2 Hz, 1 H), 3.75 (d, J_{AB} = 9.2 Hz, 1 H), 3.13 (dd, J = 14.4, 3.9 Hz, 1 H), 2.92 (dd, J = 14.4, 7.3 Hz, 1 H) 1.09 (s, 3 H), 0.85 (s, 3 H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 219.2, 137.0, 129.5, 128.2, 126.5, 81.2, 77.7, 44.4, 37.2, 21.7, 21.2; HRMS calcd for $C_{13}H_{16}O_2$ m/e 204.115 03, found m/e 204.115 82] along with 2 mg of 1,2-diphenylethane **5** (6%) and 3.3 mg of the furan dimer **4b** (7%): HRMS calcd for $C_{12}H_{18}O_4$ m/e 226.12080, found m/e 226.12051.

Preparation of Tetrahydro-2-benzylfuran-3-one (2a). A 0.04 M solution of **1a** (249 mg, 1.2 mmol) in CH_2Cl_2 (30 mL) was treated with rhodium acetate (16.2 mg, 0.037 mmol) in CH_2Cl_2 (60 mL) in the usual manner to produce a yellow oil which was purified using flash chromatography (13 g silica gel; 15-mm i.d. column; 15:85 EtOAc/hexanes) to yield 128 mg (60%) of **2a** as a colorless oil [R_f 0.25 (15:85 EtOAc/hexanes); IR (neat) 1750 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 7.29–7.17 (m, 5 H), 4.17 (td, J = 9.3, 4.2 Hz, 1 H), 3.99 (td, J = 9.2, 7.3 Hz, 1 H), 3.95 (dd, J = 7.7, 3.8 Hz, 1 H), 3.06 (dd, J = 14.4, 3.7 Hz, 1 H), 2.84 (dd, J = 14.5, 7.7 Hz, 1 H), 2.43 (ddd, J = 18.1, 7.1, 4.2 Hz, 1 H), 2.31 (td, J = 18.2, 9.3 Hz, 1 H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 215.2, 137.0, 129.3, 128.2, 126.5, 80.4, 64.3, 37.0, 36.9; HRMS calcd for $C_{11}H_{12}O_2$ m/e 176.083 73, found m/e 176.083 58] along with 18 mg of 1,2-diphenylethane **5** (16%) and 28 mg of the furan dimer **4a** (27%): HRMS calcd for $C_8H_{10}O_4$ m/e 170.058 74, found m/e 170.057 91.

Preparation of Tetrahydro-2-benzylpyran-3-one (2c). A 0.04 M solution of **1c** (185 mg, 0.85 mmol) in CH_2Cl_2 (21 mL) was treated with rhodium acetate (11 mg, 0.025 mmol) in CH_2Cl_2 (63 mL) in the usual manner to produce a yellow oil which was purified using flash chromatography (13 g silica gel; 15-mm i.d. column; 15:85 EtOAc/hexanes) to yield 23 mg (14%) of **2c** as a colorless oil [R_f 0.24 (15:85 EtOAc/hexanes); IR (neat) 1720 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 7.33–7.20 (m, 5 H), 4.10–4.02 (m, 2 H), 3.66 (dt, J = 11.1, 3.7 Hz, 1 H), 3.23 (dd, J = 14.6, 3.7 Hz, 1 H), 2.83 (dd, J = 14.7, 8.6 Hz, 1 H), 2.60–2.39 (m, 2 H), 2.23–1.97 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 208.4, 138.1, 129.4, 128.4, 126.3, 84.2, 65.7, 37.7, 35.8, 26.1; HRMS calcd for $C_{12}H_{14}O_2$ m/e 190.099 38, found m/e 190.098 66] along with 73 mg (45%) of C–H insertion product **3** as a colorless oil: R_f 0.18 (15:85 EtOAc/hexanes); IR (neat) 1740 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 7.35–7.28 (m, 5 H), 4.53 (s, 2 H), 4.30–4.24 (m, 1 H), 2.40 (d, J = 4.6 Hz, 2 H), 2.25–2.09 (m, 4 H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 217.5, 138.4, 128.9, 128.2, 128.0, 76.6, 71.1, 45.4, 36.3, 29.4. Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.67; H, 7.44.

Preparation of Tetrahydro-2-benzyl-5-methylfuran-3-one (2d). A 0.04 M solution of **1d** (216 mg, 0.99 mmol) in CH_2Cl_2 (25 mL) was treated with rhodium acetate (13 mg, 0.03 mmol) in CH_2Cl_2 (75 mL) in the usual manner to produce a yellow oil which was purified using flash chromatography (27 g silica gel; 22-mm

i.d. column; 10:90 EtOAc/hexanes) to yield 100 mg (53%) of **2d** as a colorless oil (inseparable 1.5:1 mixture of diastereomers) [R_f 0.51; (40:60 EtOAc/hexanes); IR (neat) 1755 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) diastereomer A δ 7.39–7.27 (m, 5 H), 4.47–4.27 (m, 2 H), 3.06 (dd, J = 14.2, 4.4 Hz, 1 H), 2.97 (dd, J = 14.4, 7.1 Hz, 1 H) 2.48 (dd, J = 18.0, 6.8 Hz, 1 H), 2.22 (dd, J = 18.0, 7.2 Hz, 1 H), 1.39 (d, J = 6.8 Hz, 3 H); diastereomer B δ 7.39–7.27 (m, 5 H), 4.29–4.23 (m, 1 H) 4.10 (dd, J = 7.1, 3.7 Hz, 1 H), 3.17 (dd, J = 14.4, 3.7 Hz, 1 H), 2.94 (dd, J = 14.4, 7.1 Hz, 1 H), 2.56 (dd, J = 17.8, 10.7 Hz, 1 H), 1.90 (dd, J = 17.8, 10.7 Hz, 1 H), 1.43 (d, J = 6.1 Hz, 3 H); ^{13}C NMR (75 MHz; $CDCl_3$) diastereomer A δ 216.3, 137.1, 129.5, 128.4, 126.6, 80.2, 71.7, 44.0, 37.1, 21.4; diastereomer B 215.9, 137.1, 129.6, 128.1, 126.5, 82.4, 72.0, 44.8, 37.2, 21.0; HRMS calcd for $C_{12}H_{14}O_2$ m/e 190.099 38, found m/e 190.09995] along with 10 mg 1,2-diphenylethane **5** (11%).

Preparation of Tetrahydro-2-(2-phenyl-2-oxoethyl)-4,4-dimethylfuran-3-one (2e). A 0.04 M solution of **1e** (108 mg, 0.41 mmol) in CH_2Cl_2 (10 mL) was treated with rhodium acetate (11 mg, 0.025 mmol) in CH_2Cl_2 (30 mL) in the usual manner to produce a yellow oil which was purified using flash chromatography (13 g of silica gel; 15-mm i.d. column; 85:15 EtOAc/hexanes) to yield 17 mg (17%) of **2e** as a colorless oil [R_f 0.32 (15:85 EtOAc/hexanes); IR (neat) 1775, 1700 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 7.95–7.92 (m, 2 H), 7.62–7.26 (m, 3 H), 4.79 (d, J = 16.9 Hz, 1 H), 4.77 (d, J = 16.9 Hz, 1 H), 4.04 (t, J = 6.2 Hz, 1 H), 3.26 (dd, J = 18.0, 6.8 Hz, 1 H), 3.18 (dd, J = 18.0, 5.6 Hz, 1 H), 1.26 (s, 3 H), 1.21 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 212.0, 195.5, 134.7, 133.7, 128.7, 127.9, 74.9, 72.9, 63.3, 50.1, 21.6, 16.6; HRMS calcd for $C_{14}H_{16}O_3$ m/e 232.109 94, found m/e 232.11008] accompanied by a large quantity of polar, uncharacterizable material.

Preparation of 2-Benzyl-3-coumaranone (2f). A 0.04 M solution of **1f** (215 mg, 0.85 mmol) in CH_2Cl_2 (21 mL) was treated with rhodium acetate (11 mg, 0.025 mmol) in CH_2Cl_2 (64 mL) in the usual manner to produce a yellow oil which was purified using flash chromatography (13 g of silica gel; 15-mm i.d. column; 5:95 EtOAc/hexanes) to yield 152 mg (78%) of **2f** as a colorless oil: R_f 0.38 (15:85 EtOAc/hexanes); IR (neat) 1715 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 7.63–7.53 (m, 2 H), 7.32–7.21 (m, 5 H), 7.09–7.00 (m, 2 H), 4.77 (dd, J = 8.6, 3.6 Hz, 1 H), 3.34 (dd, J = 14.7, 3.6 Hz, 1 H), 2.98 (dd, J = 14.7, 8.6 Hz, 1 H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 200.9, 172.5, 137.9, 136.0, 129.3, 128.4, 126.8, 124.2, 121.8, 120.9, 113.4, 85.7, 37.3; HRMS calcd for $C_{15}H_{12}O_2$ m/e 224.083 73, found m/e 224.084 06.

Preparation of 2-Benzyl-3-chromanone (2g). A solution of **1g** (123 mg, 0.46 mmol) in CH_2Cl_2 (15 mL) was treated with rhodium acetate (6 mg, 1.3×10^{-2} mmol) in CH_2Cl_2 (30 mL) in the usual manner to produce a yellow oil which was purified using flash chromatography (27 g of silica gel; 22-mm i.d. column; 5:95 EtOAc/hexanes) to yield 73 mg (67%) of **2g** as a colorless oil: R_f 0.34 (10:90 EtOAc/hexanes); IR (neat) 1730 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 7.28–7.16 (m, 7 H), 7.04–6.96 (m, 2 H), 4.46 (ddd, J = 8.4, 3.7, 2.7 Hz, 1 H), 3.55 (d, J_{AB} = 19.5 Hz, 1 H), 3.39 (d, J_{AB} = 19.4 Hz, 1 H), 3.21 (dd, J = 14.5, 3.7 Hz, 1 H), 3.01 (dd, J = 14.5, 8.4 Hz, 1 H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 208.0, 153.6, 136.7, 132.9, 131.7, 129.5, 128.3, 126.7, 123.1, 121.7, 118.1, 82.8, 41.0, 37.1. Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.70; H, 5.96.

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Supplementary Material Available: ^1H and ^{13}C NMR spectra of **1a–g**, **2a–g**, and **3** (31 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Mild and Stereoselective Hydroborations of Functionalized Alkynes and Alkenes Using Pinacolborane

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Alkane and alkeneboronic esters are useful intermediates in organic synthesis.[2] They can be prepared by several methods,[2] notably by hydroboration using catecholborane.[3] This direct preparation often requires harsh reaction conditions (100 °C for alkenes and 70 °C for alkynes). Furthermore, it leads to water-sensitive[3a-c] *B*-alkyl- and alkenylcatecholboranes of variable thermal stability.[4] Their transesterification to more stable boronic esters via intermediate boronic acids is often necessary if further transformations have to be performed with conservation of the boronic ester functionality.[2g] We report herein a new hydroboration reagent, pinacolborane (1), which is easy to prepare and adds with excellent regio- and stereoselectivity to alkynes under very mild conditions (25 °C, several hours). The reagent displays a good chemoselectivity and can also be used to add to olefins.

Thus, the addition of borane–dimethyl sulfide (10.0 M solution in Me_2S, 1 equiv) to a solution of pinacol (1 equiv)

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