JOC The Journal of Organic Chemistry

NOTE

pubs.acs.org/joc

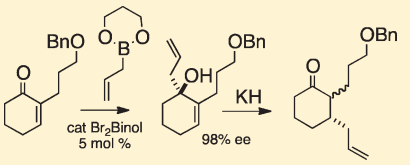
Enantioselective Conjugate Allylation of Cyclic Enones

Douglass F. Taber,* David A. Gerstenhaber, and James F. Berry

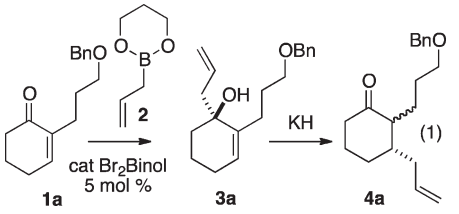
Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716, United States

Supporting Information

ABSTRACT: Enantioselective organocatalytic 1,2-allylation of a cyclic enone followed by anionic oxy-Cope rearrangement delivered the ketone as a mixture of diastereomers. This appears to be a general method for the net enantioselective conjugate allylation of cyclic enones.



Several procedures have been put forward in recent years[1] for enantioselective conjugate addition to prochiral cyclic enones. To date, however, there has been only one report[1b] of enantioselective conjugate addition to an α-substituted cyclic enone such as **1a**. It occurred to us that catalytic enantioselective 1,2-allylation[2] followed by oxy-Cope rearrangement[3] could offer a solution[4,5] to this long-standing problem (eq 1).



α-Iodo and α-alkyl[6] cyclic enones (Table 1) are easily prepared.[7] Of the several methods[2] that have been put forward for the catalytic enantioselective allylation of ketones, we were attracted to that of Schaus,[2g,8] which employed the easily prepared allylboronate **2** as the allyl donor and the commercially available 3,3′-dibromo-BINOL as the enantioselective catalyst.

We initiated our studies with the enone **1a**[6a,f] (Table 1). Following the updated Schaus protocol,[8] stirring the enone with **2** in concentrated *t*-BuOH solution with a catalytic amount of (*S*)-3,3′-dibromo-1,1′-bi-2-naphthol at room temperature for 24 h, we found that the 1,2-addition proceeded smoothly. It was gratifying that 5 mol % of the organocatalyst was sufficient and that >90% of the catalyst could be recovered by extraction.

We found that this protocol worked equally well for 5-, 6-, and 7-membered rings and with 2-alkyl and 2-iodo substitution. The enantiomeric excess for each of the 1,2-allylations was established by chiral HPLC, except for **3b**, the ee of which was secured by comparison of the optical rotation of the chromatographed and distilled product with that of the same substance prepared by methyl coupling of **3d**.

For the oxy-Cope rearrangements (Table 2), we found it convenient to use KH in paraffin.[9] With the alkyl enones, it was also necessary to include an equivalent of 18-crown-6.[10] The oxy-Cope rearrangement of the aryl-substituted allylated alcohols (**3dAr**, **3cAr**) proceeded efficiently without 18-crown-6, but the yields were slightly higher when it was included.

Of the substances reported here, only **4b** had previously been reported, in racemic form and without characterization.[11] We expect that the net catalytic enantioselective conjugate allylation of cyclic enones introduced here will have many applications in target-directed synthesis. The practicality of the Schaus organocatalytic allylation (room temperature in *t*-BuOH, 5 mol % catalyst, commercial, and easily recoverable) is particularly noteworthy.

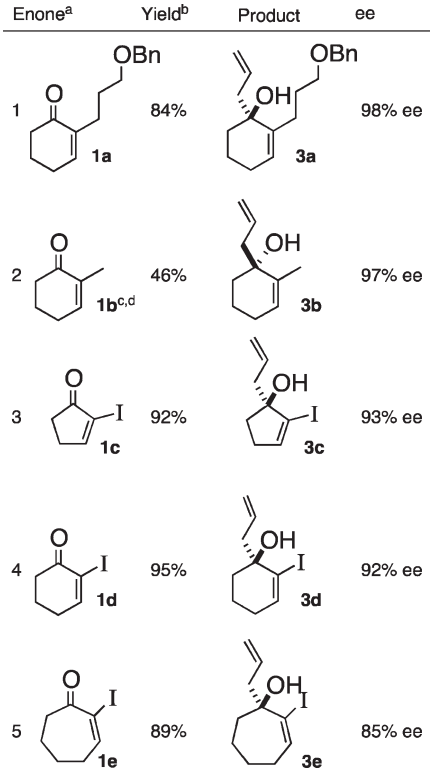
EXPERIMENTAL SECTION

General Procedures. ^{1}H NMR and ^{13}C NMR spectra were recorded, as solutions in deuteriochloroform ($CDCl_3$) unless otherwise indicated, at 400 and 100 MHz, respectively. ^{13}C multiplicities were determined with the aid of a JVERT pulse sequence, differentiating the signals for methyl and methine carbons as "d" from methylene and quaternary carbons as "u". The infrared (IR) spectra were determined as neat oils. R_f values indicated refer to thin-layer chromatography (TLC) on 2.5 × 10 cm, 250 μm analytical plates coated with silica gel GF and developed in the solvent system indicated. All glassware was oven-dried and rinsed with dry solvent before use. THF was distilled from sodium metal/benzophenone ketyl under dry nitrogen. Toluene, dichloromethane, and acetonitrile were distilled from calcium hydride under dry nitrogen. CH_2Cl_2 is dichloromethane, MTBE is methyl *tert*-butyl ether, and PE is petroleum ether. All reactions were conducted under N_2 and stirred magnetically. We prepared KH in paraffin, but it is now commercially available.

(*R*)-1-(2-Propenyl)-2-(3-phenoxymethoxypropyl)-2-cyclohexenol (3a). To a dry 10 mL round-bottom flask was charged (*S*)-(−)-3,3′-dibromo-1,1′-bi-2-naphthol (73 mg, 0.165 mmol), followed by *tert*-butyl alcohol (362 mg, 8.23 mmol) and allylborane **2** (778 mg, 6.17 mmol). This suspension was stirred until all of the BINOL was dissolved. To this clear solution was charged enone **1a** (1.00 g, 4.12 mmol), and the reaction was stirred at room temperature overnight.

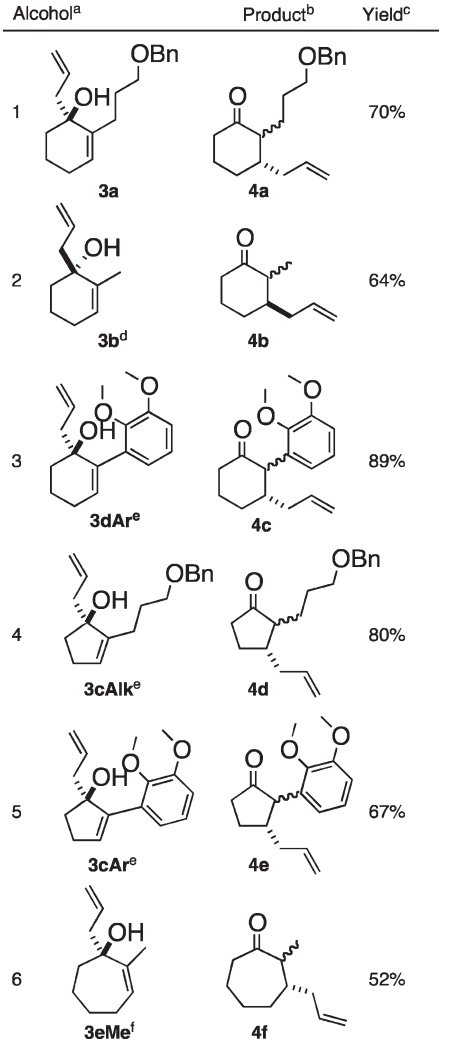
Received: July 6, 2011
Published: August 10, 2011

Table 1. Enantioselective Allylation of Cyclic Enones



[a] Additions were carried out using 5 mol % of (*S*)-3,3′-dibromo-BINOL. [b] Yields are for pure isolated substances. [c] Addition was effected using 5 mol % of (*R*)-3,3′-dibromo-BINOL. [d] Both the starting material and the product were volatile.

Table 2. KH-Mediated Oxy-Cope Rearrangement



[a] Oxy-Cope rearrangement was carried out with dicyclohexyl-18-crown-6 and KH in THF. [b] Products were a mixture of α-epimers. [c] Yields are for pure isolated substances. [d] *t*-BuOK was used for the rearrangement. [e] Prepared by Stille coupling of the corresponding iodoalkene. [f] Prepared by Kumada coupling of the corresponding alkene.

The reaction was concentrated directly to silica and chromatographed to give **3a** (938 mg, 84% yield, 98% ee) as a yellow oil: enantioselective HPLC (3% *i*-PrOH/hexanes, Chiralpak IA 4.6 mm × 250 mm, UV detection at 254 nm, 0.08 mL/min) t_R = 6.74 (major) t_R = 4.68 (minor); TLC R_f = 0.24 (MTBE/PE, 20:80); $[\alpha]_D$ +23.3 (DCM, 20 °C); IR (neat, cm^{-1}) 3439 (s), 2928 (s), 2850 (m), 1668 (m), 1633.8 (s), 1442.1 (s), 1363.5 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.5−2.5 (m, 13H), 3.5 (m, 2H), 4.5 (s, 2H), 5.1 (m, 1H), 5.2 (m, 1H), 5.8 (m, 1H), 7.3−7.4 (m, 5H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm u: 139.9, 138.0, 117.6, 77.0, 76.7, 76.3, 72.5, 71.4, 69.9, 43.5, 35.7, 28.4, 27.0, 25.3, 18.5; d: 133.9, 127.9, 127.3, 127.1, 124.9; HRMS calcd for $C_{19}H_{25}O$ (M^+ −OH) 269.1905, found 269.1909.

(*S*)-1-(2-Propenyl)-2-methyl-2-cyclohexenol (3b): light yellow oil; $[\alpha]^{20}_D$ = −34.9 (*c* = 1.00, CH_2Cl_2); TLC R_f (MTBE/PE, 1:4) = 0.46; ^{1}H NMR δ 5.78 (m, 1H), 5.64 (m, 1H), 5.2 (m, 2H), 2.40 (dt, J = 7.2, 1.2 Hz, 2H), 1.98 (m, 2H), 1.77 (m, 1H), 1.76 (s, 3H), 1.64 (m, 4H); ^{13}C NMR δ u: 137.0, 118.2, 71.6, 43.6, 35.7, 25.6, 19.1; d: 134.1, 126.6, 17.8; IR 1639, 1440, 1174, 973, 912 cm^{-1}; HRMS calcd for $C_{10}H_{15}$ (M − OH) 135.1174, obsd 135.1173.

(*R*)-1-(2-Propenyl)-2-iodo-2-cyclopentenol (3c): yellow solid (mp 32−35 °C, 92% yield, 93% ee); TLC R_f = 0.29 (DCM/MTBE/PE 10:20:70); chiral HPLC (3% *i*-PrOH/hexanes, Chirapak IA 4.6 mm × 250 mm, UV detection at 254 nm, 0.08 mL/min) t_R = 8.420 (major), t_R = 9.205 (minor); $[\alpha]_D$ +52.4 (DCM, 20 °C); IR (neat, cm^{-1}) 3400 (s), 3066 (m), 2918 (s), 2840 (m), 1638 (m), 1599 (m), 1427 (m), 1373 (m), 1309 (m) ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.9 (m, 2H), 2.2−2.6 (m, 5H), 5.1−5.2 (dd, 2H), 5.6−5.9 (m, 1H), 6.3 (s, 1H) ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm u: 119, 134.0, 106.5, 86.0, 123.5, 44.5, 33.0, 32.8 d: 142.1, 132.7; HRMS calcd for $C_8H_{10}I$ (M^+ − OH) 232.9827, found 232.9826.

(*R*)-1-(2-Propenyl)-2-iodo-2-cyclohexenol (3d): clear oil (95% yield, 92% ee); TLC R_f = 0.29 (MTBE/PE 20:80); $[\alpha]_D$ −34.9 (DCM, 20 °C); chiral HPLC (2% *i*-PrOH/hexanes, Chirapak IA 4.6 mm × 250 mm; UV detection at 254 nm, 0.08 mL/min) t_R = 17.34 (major), t_R = 16.80 (minor); IR (neat, cm^{-1}) 3436 (s), 3074 (m), 2937 (m), 1638 (m), 1435 (s); ^{1}H NMR (400 MHz, $CDCl_3$) d ppm 1.6−1.8 (m, 2H), 1.8−2.2 (m, 5H), 2.4−2.5 (d, 2H), 5.1−5.2 (m, 2H), 5.7−5.9 (m, 1H), 6.6 (m, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) d ppm u: 118.9, 111.7, 73.0, 47.1, 34.1, 29.6, 18.9; d: 141.9, 132.9; HRMS calcd for $C_9H_{12}I$ (M^+ −OH) 246.9992, found 246.9984

(*R*)-1-(2-Propenyl)-2-iodo-2-cycloheptenol (3e): yellow oil (89% yield, 85% ee); TLC R_f = 0.50 (MTBE/PE, 20:80); $[\alpha]_D$ −46 (DCM, 20 °C); chiral HPLC (0.1% *i*-PrOH/hexanes, Chiracel OJH 4.6 mm × 250 mm, UV detection at 254 nm, 0.08 mL/min) t_R = 10.721 (major), t_R = 12.399 (minor); IR (neat, cm^{-1}) 3459 (b), 3076 (m), 2918 (s), 2859 (m), 1682 (m), 1643 (m), 1609 (m), 1442 (m), 1343 (m) ^{1}H

dx.doi.org/10.1021/jo2013753 |*J. Org. Chem.* 2011, 76, 7614–7617

NMR (400 MHz, $CDCl_3$) δ ppm 1.6−1.9,(m, 5H), 2.0−2.2 (m, 4H), 2.5 (m, 2H), 5.2 (ds, 2H), 5.8−5.9 (m, 1H), 6.7 (t, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 141.5, 132.5, 118.6, 118.0, 77.7, 44.3, 33.0, 28.5, 24.7, 20.7; HRMS calcd for $C_{10}H_{14}I$ (M^+ − OH) 261.0141, found 261.0198.

(1*S*,2*S*)- 2-(3-Phenoxymethoxypropyl)- 3-(2-propenyl)cyclohexanone (4a): To a 100 mL round-bottom flask was charged **3a** (1.07 g, 3.77 mmol), followed by 18-crown-6 (996 mg, 3.77 mmol) and 50 mL of THF. The reaction was sparged with N_2 for 10 min, and KH(P) (452 mg 5.65 mmol) was added portionwise. The reaction was heated to reflux for 1 h and then quenched with saturated aqueous ammonium chloride. The organic layer was partitioned between Et_2O and water. The organic layer was dried (anhydrous Na_2SO_4) and concentrated. The residue was chromatographed giving **4a** (749 mg, 70% yield) as a yellow oil: TLC R_f = 0.20 (DCM/MTBE/PE, 10:20:70); $[\alpha]_D$ +18 (c = 0.02, CH_2Cl_2, 20 °C) IR (neat, cm^{-1}) 3029 (m), 2931 (s), 1709 (m), 1639 (m), 1495 (s), 1453 (s), 1360 (s); major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.49 - 2.45 (m, 14H) 3.5 (t, 2 H) 4.5 (s, 2 H) 5.1 (m, 2 H) 5.8 (m, 1 H) 7.21 - 7.4 (m, 5H); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm u: 213.3, 138.6, 117.0, 72.7, 70.3, 37.8, 28.7, 27.3, 26.2, 24.7, 24.1, 22.0 d: 135.7, 128.3, 127.5, 54.6, 41.9; HRMS calcd for $C_{19}H_{27}O_2$ (M + H) 287.2011, found 287.2002.

(1*R*,2*R*)-2-Methyl-3-(2-propenyl)cyclohexanone (4b). To a 500 mL round-bottom flask were charged toluene (140 mL), 18-crown-6 (6.48 g, 24.5 mmol), and potassium *tert*-butoxide (5.49 g, 49 mmol). Ketone **3b** (5.33 g, 35 mmol) was charged in 30 mL of toluene. The reaction was heated to 84 °C for 1 h and was then quenched with saturated aqueous NH_4Cl. The toluene/PE solution was then diluted with more PE and placed directly on a column for purification by silica gel chromatography to afford ketone **4b** (2.162 g, 64% yield, mixture of trans/cis diastereomers) as a light yellow oil: $[\alpha]^{20}_D$ = +10.0 (c = 1.00, CH_2Cl_2, 2:1 mixture of trans:cis diastereomers); TLC R_f (MTBE/PE, 1:4) = 0.67; ^{1}H NMR δ 5.85−5.73 (m, 1H, trans diastereomer), 5.75−5.63 (m, 1H, cis diastereomer), 5.11−5.03 (m, 2H, trans diastereomer), 5.03−4.98 (m, 2H, cis diastereomer), 2.66−2.00 (m, 6H), 1.93−1.41 (m, 4H), 1.05 (d, J = 12.8 Hz, 3H, trans diastereomer), 1.02 (d, J = 12.8 Hz, 3H, cis diastereomer); ^{13}C NMR (trans diastereomer) δ u: 213.4, 117.1, 41.5, 38.2, 30.3, 25.7; d: 135.5, 49.4, 45.2, 11.9; (cis diastereomer) δ u: 214.5, 116.3, 39.8, 33.7, 26.7, 23.7; d: 136.5, 48.7, 41.9, 11.5; IR: 1711, 1640, 1447, 1221, 999, 914 cm^{-1}; HRMS calcd for $C_{10}H_{17}O$ (M + H) 153.1279, obsd 153.1283.

(1*R*,2*S*)-2-(2,3-Dimethoxyphenyl)-3-(2-propenyl)cyclohexanone (4c): white solid (89% yield, mp = 70−75 °C); TLC R_f = 0.5 (MTBE/PE 20:80); $[\alpha]^{20}_D$ −64 (c = 0.2 CH_2Cl_2, 20 °C); IR (neat, cm^{-1}) 2934 (s), 2931 (s), 1710 (s), 1584 (m), 1475 (s), 1267 (s), ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.5 (m, 2H) 1.8 (m, 2 H) 2.0−2.2 (m, 4 H) 2.4 (m, 1H) 2.6 (m, 1 H), 3.6 (d, 1H, J = 9.2 Hz), 3.7 (s, 3H), 3.9 (s, 3H), 4.9 (m, 2H), 5.6−5.8 (m, 1H), 6.6 (d, 1H, J = 8.2 Hz) 6.8 (d, 1H, J = 8.2 Hz) 7.1 (t, 1H, J = 8.2 Hz) ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm u: 210.0, 152.6, 147.4, 131.6, 116.8, 41.8, 39.0, 30.6, 25.1 d: 135.8, 123.7, 121.7, 111.0, 60.4, 56.8, 55.6, 43.5; HRMS calcd for $C_{17}H_{23}O_3$ (M + H) 275.1647, found 275.1659.

(1*S*,2*S*)-2-(3-Phenoxymethoxypropyl)-3-(2-propenyl)cyclopentanone (4d): yellow oil (52% yield); TLC R_f = 0.35 (MTBE/PE, 20:80); $[\alpha]^{20}_D$ −72 (c = 0.1 CH_2Cl_2, 20 °C); IR (neat, cm^{-1}) 2909 (m), 2857 (s), 1735 (s), 1700 (s), 1638 (m), 1450 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.3−2.5 (m, 13H) 3.4−3.5 (m, 2H) 4.5 (m, 2H), 2.1 (m, 1H) 5.0−5.1 (m, 2H), 5.7−5.9 (m, 1H), 7.2−7.4 (m, 5H), ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm u: 220.2, 138.1, 116.2, 72.4, 69.9, 38.1, 37.2, 27.3, 26.5, 21.6 d: 137.5, 127.9, 126.5, 126.0, 52.1, 41.9; HRMS calcd for $C_{18}H_{25}O_2$ (M + H) 273.1854, found 273.1850.

(1*R*,2*S*)-2-(2,3-Dimethoxyphenyl)-3-(2-propenyl)cyclopentanone (4e): yellow oil (67% yield); TLC R_f = 0.67 (MTBE/PE, 20:80);); $[\alpha]^{20}_D$ +38 (c = 0.1 CH_2Cl_2, 20 °C); IR (neat, cm^{-1}) 3073 (m), 2939 (s), 2836 (s), 1740 (s), 1640 (m), 1584 (m), 1478 (s), 1268 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.4−1.6 (m, 1H) 2.0 (m, 1H) 2.2−2.4 (m, 2H) 2.4−2.5 (m, 2H) 3.0 (d, 1H, J = 10.8 Hz), 3.7 (s, 3H), 3.9 (s, 3H), 5.0 (m, 2H), 5.7 (m, 1H), 6.6 (d, 1H, J = 8.2 Hz), 6.8−6.9 (d, 1H, J = 8.2 Hz), 7.0 (t, 1H, J = 8.2 Hz); ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm u: 218.4, 152.7, 146.9, 132.7, 116.6, 38.2, 38.0, 27.3 d: 135.7, 123.7, 122.8, 111.8, 59.8, 58.4, 55.7, 44.0; HRMS calcd for $C_{16}H_{20}O_3$ (M^+) 260.1412, found 260.1401.

(1*S*,2*S*)-2-Methyl-3-(2-propenyl)cycloheptanone (4f): yellow oil (52% yield) as a mixture of diastereomers; TLC R_f = 0.30 (MTBE/PE, 5:95); $[\alpha]^{20}_D$ −45.0 (c = 0.03; CH_2Cl_2, 20 °C); IR (neat, cm^{-1}) 3074 (m), 2927 (s), 2862 (s), 1700 (s), 1640 (m), 1451 (m), 1374 (m), ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.0−1.1 (d, 2H, J=8.2 Hz) 1.1−1.2 (d, 1H, J=8.2 Hz) 1.5−2.0 (m, 8H) 2.1 (m, 1H) 2.3−2.4 (m, 2H), 2.6 (m, 1H), 2.8−2.9 (m, 1H), 5.0 (m, 2H), 5.0−5.1 (m, 2H), 5.6−5.8 (m, 1H); major ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm u: 215.7, 116.2, 43.3, 34.5, 32.3, 25.9, 24.2 d: 137.2, 49.3, 40.1, 12.9; HRMS calcd for $C_{11}H_{19}O$ (M + H) 167.1436, found 167.1435.

■ ASSOCIATED CONTENT

Supporting Information. ^{1}H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: taberdf@udel.edu.

■ ACKNOWLEDGMENT

We thank Dr. John Dykins for mass spectrometric measurements, supported by the NSF (0541775), Dr. Shi Bai for NMR assistance (NSF CRIF:MU, CHE 0840401), and the NIH (GM42056) for financial support. We thank the Schaus group for sharing their results prior to publication.

■ REFERENCES

(1) (a) Catalytic enantioselective conjugate allylation is effective with doubly activated cycloalkenones: Shizuka, M.; Snapper, M. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 5049. (b) Despite excellent progress with catalytic enantioselective conjugate addition, there has been only one report of addition to an α-alkyl or α-aryl cyclic enone: Vuagnoux-d'Augustin, M.; Alexakis, A. *Chem.—Eur. J.* **2007**, *13*, 9647. For other leading references, see: (c) Alexakis, A.; Li, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 7600. (d) Wencel, J.; Rix, D.; Jennequin, T.; Labat, S.; Crévisy, C.; Mauduit, M. *Tetrahedron: Asymmetry* **2008**, *19*, 1804. (e) Malmgren, M.; Granander, J.; Amedjkouh, M. *Tetrahedron: Asymmetry* **2008**, *19*, 1934. (f) Feringa, B. L.; Harutyunyan, S. R.; den Hartog, T.; Geurts, K.; Minnaard, A. J. *Chem. Rev.* **2008**, *108*, 2824. (g) Riguet, E. *Tetrahedron Lett.* **2009**, *50*, 4283. (h) Alexakis, A.; Palais, L. *Tetrahedron: Asymm.* **2009**, *20*, 2866.

(2) Several methods have been developed for the enantioselective 1,2-allylation of ketones: (a) Tietze, L. F.; Schiemann, K.; Wegner, C. *J. Am. Chem. Soc.* **1995**, *117*, 5851. (b) Tagliavini, E.; Casolari, S.; D'Addario, D. *Org. Lett.* **1999**, *1*, 1061. (c) Wada, R.; Oisaki, K.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2004**, *126*, 8910. (d) Walsh, P. J.; Kim, J. G.; Waltz, K. M.; Garcia, I. F.; Kwiatkowski, D. *J. Am. Chem. Soc.* **2004**, *126*, 12580. (e) Chong, J. M.; Wu, T. R.; Shen, L. *Org. Lett.* **2004**, *6*, 2701. (f) Yamamoto, H.; Wadamoto, M. *J. Am. Chem. Soc.* **2005**, *127*, 14556. (g) Schaus, S. E.; Lou, S.; Moquist, P. N. *J. Am. Chem. Soc.* **2006**, *128*, 12660. (h) Yamamoto, H.; Wadamoto., M. *Chem. Asian J.* **2007**, *2*, 692. (i) Feng, X.; Zheng, K.; Qin, B.; Liu, X. *J. Org. Chem.* **2007**, *72*, 8478. (j) Ishihara, K.; Hatano, M. *Synthesis* **2008**, 1647.

(3) For reviews of the oxy-Cope rearrangement, see: (a) Durairaj, K. *Curr. Sci.* **1994**, *66*, 917. (b) Paquette, L. A. *Tetrahedron* **1997**, *53*, 13971.

(4) For stoichiometric 1,2-allylation followed by oxy-Cope rearrangement, see: (a) Castle, S. L.; Nielsen, D. K.; Nielsen, L. L.; Jones, S. B.; Toll, L.; Asplund, M. C. *J. Org. Chem.* **2009**, *74*, 1187. (b) Li, F.; Tartakoff, S. S.; Castle, S. L. *J. Am. Chem. Soc.* **2009**, *131*, 6674.

(5) Conjugate addition/enolate trapping offers an alternative solution to this problem but is limited to α-substituents that can be introduced by alkylation. For an overview, see: (a) Stork, G.; Rosen, P.; Goldman, N.; Coombs, R. V.; Tsuji, J. *J. Am. Chem. Soc.* **1965**, *87*, 275. (b) Taylor, R. J. K. *Synthesis* **1985**, 364. (c) Coates, R. M.; Jin, A. Q. *J. Org. Chem.* **1997**, *62*, 7475. (d) Feringa, B. L.; Pineschi, M.; Arnold, L. A; Imbos, R.; de Vries, A. H. M. *Angew. Chem., Int. Ed.* **1997**, *36*, 2620. (e) Alexakis, A.; Vuagnoux-d'Augustin, M. *Chem.—Eur. J.* **2007**, *13*, 9647. (f) Alexakis, A; Henon, H.; Mauduit, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 9122. (g) Jarugumilli, G. K.; Cook, S. P. *Org. Lett.* **2011**, *13*, 1904.

(6) For the preparation of α-alkyl cyclic enones, see: (a) Taber, D. F. *J. Org. Chem.* **1976**, *41*, 2649. (b) Johnson, C. R.; Braun, M. P. *J. Am. Chem. Soc.* **1993**, *115*, 11014. (c) Armitage, M. A.; Lathbury, D. C.; Mitchell, M. B. *J. Chem. Soc., Perkin Trans. 1* **1994**, *12*, 1551. (d) Abbas, A. A.; Kobayashi, Y. *Tetrahedron Lett.* **2003**, *44*, 119. (e) Takeishi, K.; Sugishima, K.; Sasaki, K.; Tanaka, K. *Chem.—Eur. J.* **2005**, *10*, 5681. (f) Taber, D. F.; Sheth, R. *J. Org. Chem.* **2008**, *73*, 8030.

(7) For the preparation of α-aryl cyclic enones, see: (a) Bosse, F.; Tunoori, A. R.; Niestro, A. J.; Gronwald, O.; Maier, M. E. *Tetrahedron* **1996**, *52*, 9485. (b) Prasad, A. S. B.; Knochel, P. *Tetrahedron* **1997**, *53*, 16711. (c) Kim, J.; Kulawiec, R. *Tetrahedron Lett.* **1998**, *39*, 3107. (d) Felpin, F. *J. Org. Chem.* **2005**, *70*, 8575. To date, we have not been able to achieve high ee's in the addition to such α-aryl cyclic enones.

(8) For the preparation and use of the allyl boronate **2**, see: Schaus, S. E.; Barnett, D. S.; Moquist, P. N. *Angew. Chem., Int. Ed.* **2009**, *48*, 8679.

(9) For the preparation of KH in paraffin, see: (a) Taber, D. F.; Nelson, C. G. *J. Org. Chem.* **2006**, *71*, 8973. (b) Huang, H.; Nelson, C. G.; Taber, D. F. *Tetrahedron Lett.* **2010**, *51*, 3545.

(10) For rate acceleration of the oxy-Cope rearrangement using 18-crown-6, see: Evans, D.; Golob, A. M. *J. Am. Chem. Soc.* **1975**, *97*, 4765.

(11) Hayashi, M.; Mukaiyama, T. *Chem. Lett.* **1987**, 289.