Published in final edited form as:
J Org Chem. 2011 September 16; 76(18): 7614–7617. doi:10.1021/jo2013753.

Enantioselective Conjugate Allylation of Cyclic Enones

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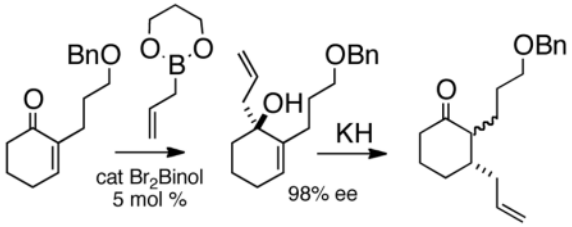
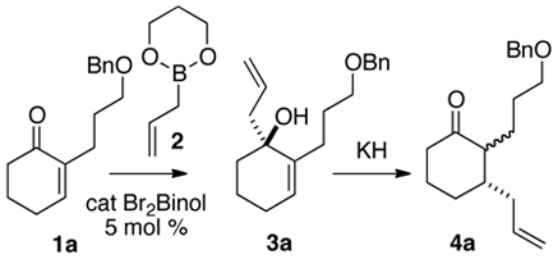
Abstract



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).



(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] that employed the easily-prepared allylboronate **2** as the allyl donor and the commercially-available 3, 3′-dibromobinol 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-

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Supporting Information Available: ^{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.

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 MHz 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 *t*-butyl alcohol (362 mg, 8.23 mmol) and allyl borane **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. 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 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 minutes and KH(P) (452 mg 5.65 mmol) was added portion wise. The reaction was heated to reflux for 1 hour 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 was 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 hour 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.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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.

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[PubMed: 16209612] To date, we have not been able to achieve high ee's in the addition to such α-aryl cyclic enones.

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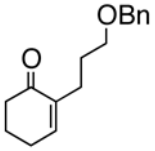
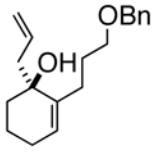
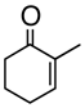
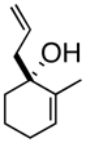
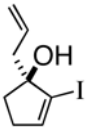
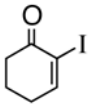
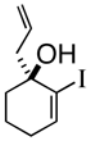
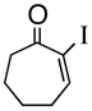
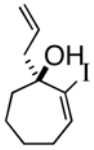
Table 1

Enantioselective Allylation of Cyclic Enones.

Enone[a]	Yield[b]	Product	ee
1  **1a**	84%	 **3a**	98% ee
2  **1b**[c,d]	46%	 **3b**	97% ee
3  **1c**	92%	 **3c**	93% ee
4  **1d**	95%	 **3d**	92% ee
5  **1e**	89%	 **3e**	85% ee

[a] Additions were carried out using 5 mol % (*S*)-3,3′-dibromobinol.

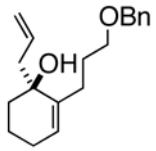
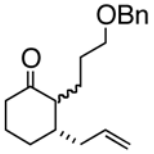
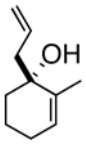
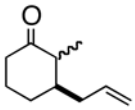
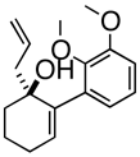
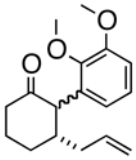
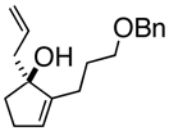
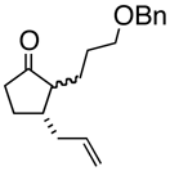
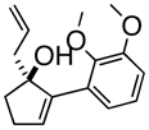
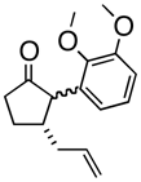
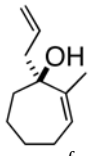
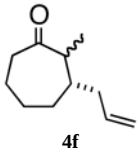
[b] Yields are for pure isolated substances.

[c] Addition was effected using 5 mol % (*R*)-3,3′-dibromobinol.

[d] Both the starting material and the product were volatile.

Table 2

KH-Mediated oxy-Cope Rearrangement.

Alcohol[a]	Product[b]	Yield[c]
1  **3a**	 **4a**	70%
2  **3b**[d]	 **4b**	64%
3  **3dAr**[e]	 **4c**	89%
4  **3cAlk**[e]	 **4d**	80%
5  **3cAr**[e]	 **4e**	67%
6  **3eMe**[f]	 **4f**	52%

[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.