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Synthesis of Isochromene and Related Derivatives by Rhodium-Catalyzed Oxidative Coupling of Benzyl and Allyl Alcohols with Alkynes

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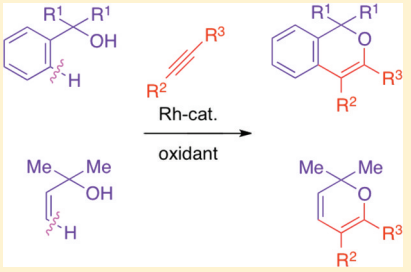
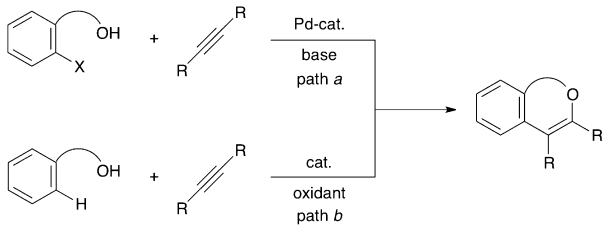
Supporting Information

ABSTRACT: The straightforward synthesis of isochromene derivatives and related cyclic ethers is achieved by the rhodium-catalyzed oxidative coupling of α,α-disubstituted benzyl and allyl alcohols with alkynes. The hydroxy groups effectively act as the key function for the regioselective C−H bond cleavage.



Isochromene and related cyclic ether structures can be widely seen in various biologically active compounds and natural products.[1] Therefore, the development of methods for their effective construction from simple, readily available building blocks has attracted considerable attention.[2] One of the most reliable and versatile methods for their syntheses is the palladium-catalyzed annulation by the coupling of aryl halides

Scheme 1. Catalytic Synthesis Pathways for Cyclic Ethers



bearing an oxygen nucleophile with alkynes (Scheme 1, path *a*).[3]

Obviously, a more atom- and step-economical version is the oxidative coupling using nonhalogenated aromatic substrates via C−H bond cleavage,[4] as depicted in Scheme 1, path *b*. Needless to say, compared to the disubstituted aromatic substrates in path *a*, the parent monosubstituted ones in path *b* are readily available.

In the course of our study of the rhodium-catalyzed oxidative coupling of monosubstituted arenes with alkynes to form benzannulated heterocyclic compounds,[5,6] we have undertaken the coupling of benzyl alcohols with alkynes under rhodium catalysis. As a result, the expected reaction has been found to proceed smoothly through hydroxy-directed C−H bond cleavage by employing a copper oxidant to produce isochromene derivatives. In addition, the reactions of related alcohols such as a naphthalenemethanol and an allyl alcohol have also been examined. The new findings are described herein.

In an initial attempt, α,α-dimethylbenzyl alcohol (**1a**) (1.5 mmol) was treated with diphenylacetylene (**2a**) (0.5 mmol) in the presence of $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.02 mmol, Cp* = pentamethylcyclopentadienyl) and $Cu(OAc)_2\cdot H_2O$ (1 mmol) as catalyst and oxidant, respectively, in refluxing dioxane (3 mL) under N_2 for 6 h. As a result, a heterocyclic product, 1,1-dimethyl-3,4-diphenyl-1*H*-isochromene (**3a**), was formed in 82% isolated yield (entry 1 in Table 1). Under similar conditions, the couplings of **1a** with 4-methyl- (**2b**), methoxy- (**2c**), and chloro-substituted (**2d**) diphenylacetylenes proceeded smoothly to form the corresponding 3,4-diarylisochromenes **3b−d** (entries 2−4). 1-Phenylpropyne (**2e**) also reacted with **1a** to give a 4-methyl-3-phenylisochromene derivative **3e** predominantly, along with a minor amount of regioisomer **3e′** (entry 5). The reaction of **1a** with 4-octyne (**2f**) gave 3,4-dipropylisochromene **3f** in a moderate yield (entry 6). We previously reported that treatment of triphenylmethanol (**1b**) with **2a** in the presence of $[RhCl(cod)]_2$, 1,2,3,4-tetraphenylcyclopenta-1,3-diene, and $Cu(OAc)_2\cdot H_2O$ as catalyst, ligand, and oxidant, respectively, in refluxing *o*-xylene resulted in quantitative formation of 1,2,3,4-tetraphenylnaphthalene, accompanied by C−H and C−C bond cleavages.[7] In contrast, under the present milder conditions using the cationic rhodium catalyst, isochromene formation exclusively took place in the coupling of **1b** and **2a** (entry 7). In this case, no naphthalene

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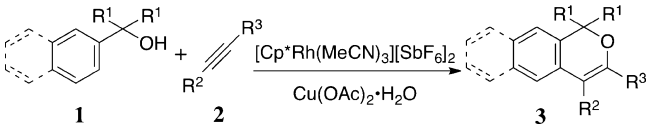
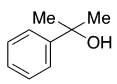
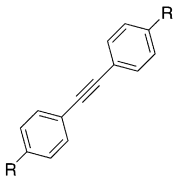
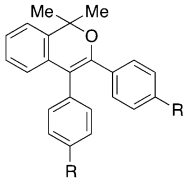
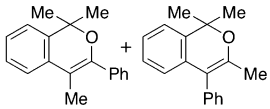
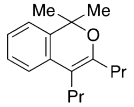
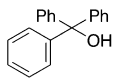
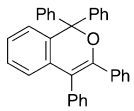
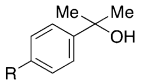
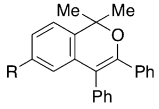
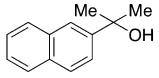
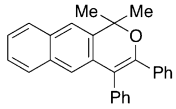
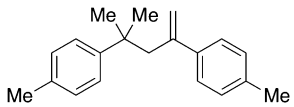
Table 1. Coupling of Alcohols 1 with Alkynes 2[a]



1 2 3

entry	1	2	product(s), % yield
1			
2	1a	**2b**: R = Me	**3b**: R = Me, 88
3		**2c**: R = OMe	**3c**: R = OMe, 89
4		**2d**: R = Cl	**3d**: R = Cl, 68
5	1a	 **2e**	 **3e+3e'**, 67 [82:18]
6	1a	 **2f**	 **3f**, 36
7	 **1b**	 **2a**	 **3g**, 53
8	 **1c**: R = Me	**2a**	 **3h**: R = Me, 45[b]
9	**1d**: R = Cl		**3i**: R = Cl, 83
10	 **1e**	**2a**	 **3j**, 43

[a]Reaction conditions: **1** (1.5 mmol), **2** (0.5 mmol), [Cp*Rh(MeCN)$_3$][SbF$_6$]$_2$ (0.02 mmol), Cu(OAc)$_2$·H$_2$O (1 mmol), in refluxing dioxane (3 mL) under N$_2$ for 6 h. [b]**4** (0.12 mmol) was also formed.



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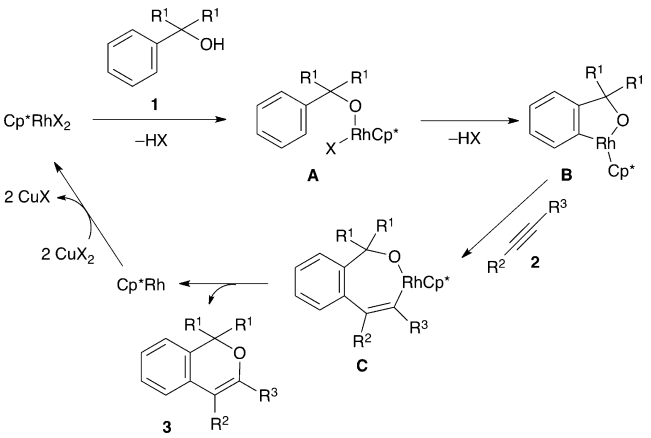
formation could be detected. *para*-Substituted benzyl alcohols **1c** and **1d** also underwent the coupling with **2a** to form **3h** and **3i**, respectively (entries 8 and 9). In the former case, homocoupling[8] of relatively electron-rich **1c** took place competitively to form a considerable amount (0.12 mmol) of **4** in addition to **3h**. The reaction using α,α-dimethyl-2-naphthalenemethanol (**1e**) in place of benzyl alcohols occurred in a similar manner to give a tricyclic product **3j** (entry 10). In contrast to these tertiary alcohols, α,α-unsubstituted benzyl alcohol showed low reactivity: only a small amount (~15%) of coupling product was detected by GC–MS.

A plausible mechanism for the coupling of **1** with **2** is illustrated in Scheme 2, in which neutral ligands are omitted.

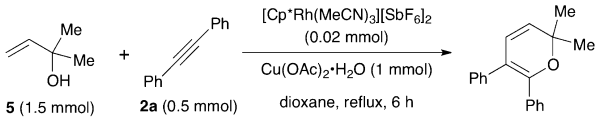
Scheme 2. Plausible Mechanism for the Reaction of 1 with 2



Coordination of the alcoholic oxygen of **1** to Cp*Rh(III)X$_2$ gives a rhodium(III) alcoholate **A**. Subsequent *ortho*-rhodation to form a rhodacycle intermediate **B**, alkyne insertion, and reductive elimination occur to produce an isochromene **3**. The resulting Cp*Rh(I) species may be oxidized by a copper(II) salt to regenerate Cp*Rh(III)X$_2$.

Besides aromatic alcohols, α,α-dimethylallyl alcohol (**5**) also underwent the oxidative coupling. Thus, the reaction of **5** (1.5 mmol) with **2a** (0.5 mmol) in the presence of [Cp*Rh(MeCN)$_3$][SbF$_6$]$_2$ (0.02 mmol) and Cu(OAc)$_2$·H$_2$O (1 mmol) in refluxing dioxane for 6 h proceeded smoothly, accompanied by vinylic C–H bond cleavage to produce the corresponding 2*H*-pyran derivative **6** in 60% yield (Scheme 3). However,

Scheme 3. Coupling of Alcohol 5 with 2a



treatment of γ-substituted allyl alcohols such as cinnamyl alcohol and (*E*)-2-methylpent-3-en-2-ol with **2a** under similar conditions gave no or trace amount of coupling products.

In summary, we have demonstrated that the oxidative coupling of α,α-disubstituted benzyl alcohols with alkynes can be performed in the presence of a rhodium catalyst and a copper salt oxidant to afford the corresponding isochromene derivatives. The reaction system has also been found to be applicable to the 2*H*-pyran synthesis from an allyl alcohol.

EXPERIMENTAL SECTION

General Procedures. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz for CDCl$_3$ solutions. MS data were obtained by EI. GC analysis was carried out using a silicon OV-17 column (i.d. 2.6 mm × 1.5 m). GC–MS analysis was carried out using a CBP-1 capillary column (i.d. 0.25 mm × 25 m). The structures of all products listed below were unambiguously determined by ^{1}H and ^{13}C NMR with the aid of NOE, COSY, HMQC, and HMBC experiments.

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Alcohols **1c–e**,[9] diarylacetylenes **2b–d**,[10] and $[Cp^*Rh(MeCN)_3][SbF_6]_2$[6e] were prepared according to published procedures. Other starting materials and reagents were commercially available.

General Procedure for Coupling of Alcohols with Alkynes. To a 20 mL two-necked flask with a reflux condenser, a balloon, and a rubber cup were added alcohol **1** or **5** (1.5 mmol), alkyne **2** (0.5 mmol), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.02 mmol, 17 mg), $Cu(OAc)_2·H_2O$ (1 mmol, 200 mg), 1-methylnaphthalene (ca. 50 mg) as internal standard, and dioxane (3 mL). Then, the resulting mixture was stirred under nitrogen at 110 °C (bath temperature) for 6 h. After cooling, the reaction mixture was extracted with ethyl acetate (100 mL) and ethylenediamine (2 mL). The organic layer was washed by water (100 mL, three times) and dried over Na_2SO_4. After evaporation of the solvents under vacuum, product **3** or **6** was isolated by column chromatography on silica gel using hexane/ethyl acetate (97:3, v/v) as eluant.

1,1-Dimethyl-3,4-diphenyl-1*H*-isochromene (3a). A solid: mp 90–91 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.78 (s, 6H), 6.89 (d, J = 8.0 Hz, 1H), 7.10–7.14 (m, 4H), 7.19 (d, J = 5.1 Hz, 2H), 7.22–7.35 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.1, 77.7, 115.7, 122.2, 123.6, 126.8, 126.9, 127.2, 127.4, 127.7, 128.5, 128.8, 131.7, 132.0, 136.0, 136.3, 137.0, 148.1; HRMS m/z calcd for $C_{23}H_{20}O$ (M^+) 312.1514, found 312.1523.

1,1-Dimethyl-3,4-bis(4-methylphenyl)-1*H*-isochromene (3b). An oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.79 (s, 6H), 2.28 (s, 3H), 2.40 (s, 3H), 6.91 (d, J = 7.6 Hz, 1H), 6.97 (d, J = 8.3 Hz, 2H), 7.12–7.21 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 21.3, 27.0, 77.5, 115.04, 122.1, 123.5, 126.6, 127.1, 128.2, 128.6, 129.3, 131.5, 132.3, 133.3, 134.1, 136.3, 136.4, 137.5, 148.0; HRMS m/z calcd for $C_{25}H_{24}O$ (M^+) 340.1827, found 340.1824.

3,4-Bis(4-methoxyphenyl)-1,1-dimethyl-1*H*-isochromene (3c). An oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.76 (s, 6H), 3.73 (s, 3H), 3.82 (s, 3H), 6.67 (d, J = 9.1 Hz, 2H), 6.90–6.91 (m, 3H), 7.10–7.23 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.0, 55.1, 55.2, 77.4, 112.9, 114.1 (overlapped), 122.1, 123.4, 126.5, 127.1, 128.6, 129.4, 130.1, 132.5, 132.7, 136.2, 147.8, 158.4, 158.9; HRMS m/z calcd for $C_{25}H_{24}O_3$ (M^+) 372.1725, found 372.1727.

3,4-Bis(4-chlorophenyl)-1,1-dimethyl-1*H*-isochromene (3d). A solid: mp 115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.78 (s, 6H), 6.84 (d, J = 7.6 Hz, 1H), 7.13–7.24 (m, 9H), 7.34 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.1, 78.0, 114.8, 122.3, 123.4, 127.3, 127.4, 127.9, 129.0, 130.0, 131.3, 132.9, 133.1, 133.8, 134.2, 135.3, 136.2, 147.4; HRMS m/z calcd for $C_{23}H_{18}Cl_2O$ (M^+) 380.0735, found 380.0732.

1,1,4-Trimethyl-3-phenyl-1*H*-isochromene (3e) and 1,1,3-Trimethyl-4-phenyl-1*H*-isochromene (3e′). An oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67 (s, 6H, **3e′**), 1.69 (s, 6H, **3e**), 1.79 (s, 3H, **3e′**), 2.13 (s, 3H, **3e**), 6.60 (d, J = 7.3 Hz, 1H, **3e′**), 7.03–7.08 (m, 1H, **3e′**), 7.11 (d, J = 3.6 Hz, 2H, **3e′**), 7.15 (d, J = 6.5 Hz, 1H, **3e**), 7.20–7.42 (m, 6H, **3e** and 5H, **3e′**), 7.50–7.53 (m, 2H, **3e**); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 18.5, 26.8, 27.1, 77.0, 106.8, 113.9, 121.8, 122.0, 122.1, 122.7, 126.0, 126.6, 126.8, 127.1, 127.3, 127.8, 128.2, 128.4, 129.4, 131.1, 131.9, 132.6, 135.6, 135.9, 137.1, 137.5, 147.6, 148.6; HRMS m/z calcd for $C_{18}H_{18}O$ (M^+) 250.1358, found 250.1353 and 250.1356.

1,1-Dimethyl-3,4-dipropyl-1*H*-isochromene (3f). An oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00 (t, J = 7.6 Hz, 6H), 1.52–1.64 (m, 10H), 2.24 (t, J = 7.1 Hz, 2H), 2.43 (t, J = 8.0 Hz, 2H), 7.09–7.15 (m, 3H), 7.20–7.24 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 14.3, 20.5, 22.6, 26.9, 28.5, 32.8, 76.1, 109.3, 120.8, 122.2, 125.6, 127.1, 131.1, 136.9, 150.8; HRMS m/z calcd for $C_{17}H_{24}O$ (M^+) 244.1827, found 244.1829.

1,1,3,4-Tetraphenyl-1*H*-isochromene (3g). A solid: mp 224–225 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.69 (d, J = 7.6 Hz, 1H), 6.92 (d, J = 7.6 Hz, 1H), 6.97–6.99 (m, 2H), 7.05–7.32 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 86.8, 117.9, 123.4, 126.3, 126.9, 127.0, 127.4, 127.5, 127.6, 127.7, 127.9, 128.4, 128.5, 128.8, 131.4 (overlapped), 133.7, 134.0, 135.7, 136.9, 143.9 (overlapped), 148.5; HRMS m/z calcd for $C_{33}H_{24}O$ (M^+) 436.1827, found 436.1823.

1,1,6-Trimethyl-3,4-diphenyl-1*H*-isochromene (3h). A solid: mp 81–82 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.77 (s, 6H), 2.21 (s, 3H), 6.70 (s, 1H), 7.01 (d, J = 8.0 Hz, 1H), 7.09–7.13 (m, 4H), 7.22–7.24 (m, 4H), 7.27–7.36 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 27.2, 77.6, 115.6, 122.2, 124.1, 126.8, 127.4, 127.5, 127.7, 128.5, 128.8, 131.7, 131.8, 133.6, 136.1, 136.8, 137.1, 148.2; HRMS m/z calcd for $C_{24}H_{22}O$ (M^+) 326.1671, found 326.1668.

6-Chloro-1,1-dimethyl-3,4-diphenyl-1*H*-isochromene (3i). A solid: mp 105–106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.77 (s, 6H), 6.85 (d, J = 2.3 Hz, 1H), 7.10–7.16 (m, 5H), 7.20–7.24 (m, 4H), 7.28–7.37 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0, 77.6, 114.8, 123.3, 123.7, 126.5, 127.2, 127.5, 128.0, 128.7, 128.8, 131.6, 133.3, 134.0, 134.5, 135.6, 136.3, 149.4; HRMS m/z calcd for $C_{23}H_{19}ClO$ (M^+) 346.1124, found 346.1128.

1,1-Dimethyl-3,4-diphenyl-1*H*-benzo[*g*]isochromene (3j). A solid: mp 153–154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.88 (s, 6H), 7.13–7.15 (m, 3H), 7.26–7.40 (m, 10H), 7.60 (d, J = 6.9 Hz, 1H), 7.63 (s, 1H), 7.76 (d, J = 6.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.5, 77.9, 115.8, 120.9, 121.9, 125.4, 125.9, 127.0, 127.4, 127.5, 127.8, 127.8, 128.6, 128.8, 130.5, 131.8, 132.6, 132.9, 136.1, 136.5, 137.2, 148.8; HRMS m/z calcd for $C_{27}H_{22}O$ (M^+) 362.1671, found 362.1661.

4-Menthyl-2,4-bis(4-methylphenyl)pent-1-ene (4).[8d] An oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (s, 6H), 2.30 (s, 3H), 2.32 (s, 3H), 2.78 (s, 2H), 4.73 (s, 1H), 5.12 (s, 1H), 7.05 (d, J = 6.4 Hz, 4H), 7.18 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.1, 28.7, 38.4, 49.5, 116.1, 125.8, 126.4, 128.5, 128.7, 134.8, 136.5, 140.6, 146.5, 146.7; HRMS m/z calcd for $C_{20}H_{24}$ (M^+) 264.1878, found 264.1879.

2,2-Dimethyl-5,6-diphenyl-2*H*-pyran (6). A solid: mp 77–78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74 (s, 3H), 1.89 (s, 3H), 5.88 (d, J = 11.9 Hz, 1H), 7.06 (d, J = 11.9 Hz, 1H), 7.19–7.30 (m, 3H), 7.34–7.42 (m, 4H), 7.51 (t, J = 7.3 Hz, 1H), 7.95 (d, J = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.4, 26.5, 121.6, 126.0, 126.8, 127.5, 128.6, 128.7, 129.8, 133.4, 136.9, 137.7, 137.8, 141.4, 198.9; HRMS m/z calcd for $C_{19}H_{18}O$ (M^+) 262.1358, found 262.1347.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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