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Diastereoselective Synthesis of γ-Substituted 2-Butenolides via (CDC)-Rh-Catalyzed Intermolecular Hydroalkylation of Dienes with Silyloxyfurans

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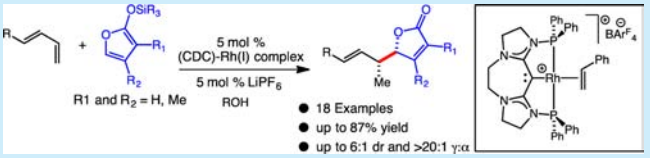
Supporting Information

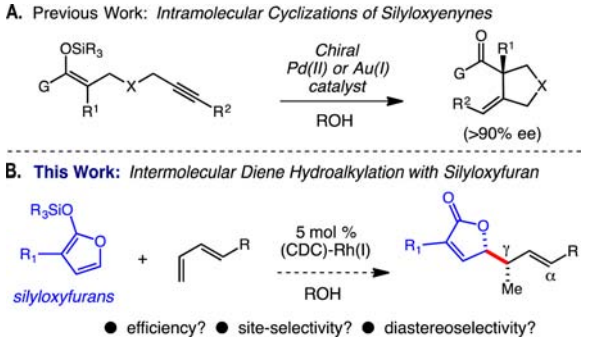
ABSTRACT: Catalytic intermolecular hydroalkylation of dienes with silyloxyfuran nucleophiles is reported. Reactions are catalyzed by 5 mol % of a (CDC)-Rh complex and proceed in up to 87% yield and 6:1 dr (*syn*/*anti*) to provide allylic butenolides bearing vicinal stereocenters. Reactions proceed with terminal aryl and alkyl dienes and with modified silyl enol ether nucleophiles including a thiophenone variant. Utility of the products is demonstrated in the synthesis of a polypropionate *anti*,*syn*-stereotriad.



Direct functionalization of olefins is one of the most enabling classes of chemical transformations in organic synthesis[1] and benefits from the commercial availability of many olefin substrates. A subgroup of these reaction types is catalytic hydroalkylation involving the net C−H addition across the unsaturated C−C double bond to form a $C(sp^3)-C(sp^3)$ bond. Hydroalkylation of C−C multiple bonds with enolate-type nucleophiles provides a direct strategy to generate a C−C bond at the same time as diastereoselectively establishing vicinal stereogenic centers.[2] Many thermally enolizable carbon nucleophiles have been employed in catalytic olefin hydroalkylation methods to generate C−C bonds promoted by Cu,[3] Ag,[4] Au,[5] Pd,[6] Pt,[6e,6,7] Rh,[8] Ru,[9] and Brønsted acid[10] catalysts, but comparatively few examples of hydroalkylation with enolate[11] nucleophiles exist. This is a significant limitation in current methods for hydroalkylation as only a relatively small subset of carbonyl nucleophiles are thermally enolizable. Enol silanes provide useful synthetic enolate equivalents that are minimally constrained by the acidity of the position α to the carbonyl;[12] however, their translation to olefin hydroalkylation remains challenging. A number of examples of the catalytic intramolecular addition of silyl enol ethers to alkynes have been reported (Scheme 1A);[13] to our knowledge, no examples of catalytic intermolecular additions of silyl enol ethers to olefins have been reported.

We disclosed the intermolecular carbodicarbene (CDC)-Rh(I)-catalyzed diastereoselective hydroalkylation of dienes with thermally enolizable oxazolone nucleophiles[14] and were interested in expanding this new class of catalyst to other useful C−C bond-forming reactions. We envisioned that development of a catalytic diene hydroalkylation process with silyloxyfuran nucleophiles would form butenolides (Scheme 1B), common structural motifs present in a number natural products.[15] The proposed diastereoselective synthesis of allylic butenolide products would provide a useful synthetic method and expand the applications of underexplored carbodicarbene supported complexes in catalysis.

Scheme 1. Olefin Hydroalkylation with Silyl Enol Ethers



We describe our efforts toward the development of a catalytic diastereo- and site-selective synthesis of 2-allylbutanones through the first intermolecular hydroalkylation of dienes with silyloxyfurans (Scheme 1B). The reaction proceeds through electrophilic activation of a C−C π-bond and represents the first intermolecular hydroalkylation of olefins with vinylogous silyl enol ether nucleophiles. Reactions generate allylic butenolides in up to 87% yield, 6:1 dr, and >20:1 γ/α regioselectivity using 5 mol % of a (CDC)-Rh(I) complex and 5 mol % of $LiPF_6$ as a cocatalyst.

We initiated our studies toward developing a (CDC)-Rh-catalyzed intermolecular hydroalkylation involving the addition of silyl enol ether nucleophiles to dienes by exploring the effect of various silyl protecting groups in reactions catalyzed by (CDC)-Rh complex **1**.[16] It should be noted that in situ generated cationic Rh complexes formed from **2a**,**b** by chloride abstraction with $AgBF_4$ results in <5% conversion. Reactions were run with

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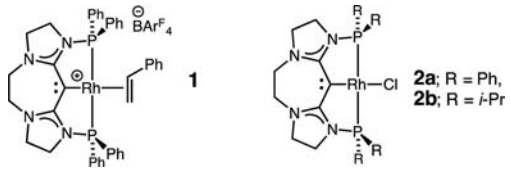
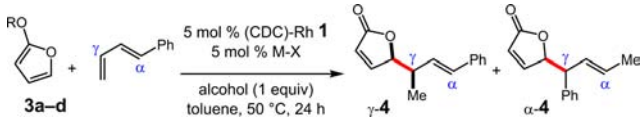


silyloxyfurans bearing trimethyl- (**3a**), *tert*-butyldimethyl- (**3b**), tris(trimethylsilyl)- (**3c**), and triisopropylsilyl (**3d**) groups at 50 °C with 1 equiv of H_2O as a proton source and silyl scavenger, and using 5 mol % of **1** and 5 mol % of $LiPF_6$ as a Lewis acid for catalyst activation (Table 1).[16b] **3a** hydrolyzed readily (>98% conv) under

Table 1. Rh(I)-Catalyzed Hydroalkylation Optimization[a]



Entry	R	alcohol	M-X	Yield (%)	γ-4:α-4[b]	dr[b]
1	**3a**; $SiMe_3$	H_2O	$LiPF_6$	0	-	-:-
2	**3b**; Si(*t*-Bu)Me_2	H_2O	$LiPF_6$	29	5:1	5:1
3	**3c**; $Si(SiMe)_3$	H_2O	$LiPF_6$	16	2:1	3:1
4	**3d**; Si(*i*-Pr)$_3$	H_2O	$LiPF_6$	29	5:1	4:1
5	**3d**; Si(*i*-Pr)$_3$	H_2O	AgCl	21	3:1	3:1
6	**3d**; Si(*i*-Pr)$_3$	H_2O	$LiBAr^F{}_4$	20	5:1	4:1
7	**3d**; Si(*i*-Pr)$_3$	MeOH	$LiPF_6$	36	5:1	4:1
8	**3d**; Si(*i*-Pr)$_3$	*i*-PrOH	$LiPF_6$	41	6:1	4:1
9[c]	**3d**; Si(*i*-Pr)$_3$	*i*-PrOH	$LiPF_6$	68	>20:1	4:1
10[c,d]	**3d**; Si(*i*-Pr)$_3$	*i*-PrOH	-	0	-	-
11	**3d**; Si(*i*-Pr)$_3$	*i*-PrOH	-	0	-	-

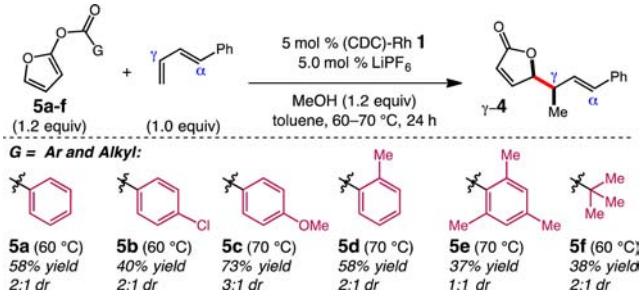
[a]See Supporting Information for experimental details. All reactions performed under N_2 atm. Yields of purified products are an average of two runs. [b]Values determined by analysis of 400 or 600 MHz ^{1}H NMR spectra of unpurified mixtures with hexamethyldisiloxane as an internal standard. [c]Reactions run with 4 equiv of *i*-PrOH and **3d**, added portion wise over 3 h. [d]Control reaction run with $[Rh(cod)Cl]_2$ as catalyst with 5 mol % of $AgBF_4$.

the reaction conditions to generate furanone and failed to afford **4** (entry 1). The more stable silyl protecting groups in **3b**, **3c**, and **3d** provided **4** in 29% yield, 5:1 dr; 16% yield, 3:1 dr; and 29% yield, 4:1 dr, respectively (entries 2–4, dr refers to the γ regioisomer). **4** was generated as a 5:1 mixture of the γ and α regioisomers when TBS- and TIPS-silyloxyfuran are used but in a 2:1 ratio with **3c**.

$LiPF_6$ was identified as the optimal cocatalyst for the reaction; hydroalkylation with 5 mol % of AgCl generated **4** in 21% yield as a 3:1 mixture of the γ/α regioisomers with 3:1 dr for the major product (entry 5), whereas 5 mol % of $LiBAr^F{}_4$ afforded **4** in 20% yield as a 5:1 mixture of the γ/α regioisomers in 4:1 dr (entry 6). We observed that the majority of **3d** was hydrolyzed under the reaction conditions to form furanone. To avoid this undesired side reaction, a series of larger alcohols were screened, and *i*-PrOH proved optimal; reaction with MeOH provided **4** in 36% yield as a 5:1 mixture of the γ/α regioisomers with 4:1 dr of the major product (entry 7), while *i*-PrOH gave 41% yield, 6:1 regioselectivity, and 4:1 dr (entry 8).[17] Conversion to product was improved using excess **3d** (4 equiv) added over the course of 4 h to increase the relative concentration of diene to furan and further limit hydrolysis; increasing the substrate loading to 4 equiv of **3d** generates **4** in 68% yield, 20:1 regioselectivity, and 4:1 dr (entry 9). These conditions proved to be optimal for hydroalkylation to form allylic butenolide products. A control reaction was performed with 2.5 mol % of $[Rh(cod)Cl]_2$ instead of (CDC)-Rh **1** and failed to furnish **4** (<2% conv, entry 10).

To decrease the equivalents of **3d** used in the reaction, we sought a possible alternative oxygen protecting group. Scheme 2

Scheme 2. (CDC)-Rh-Catalyzed Hydroalkylation with Acyloxyfurans[a]

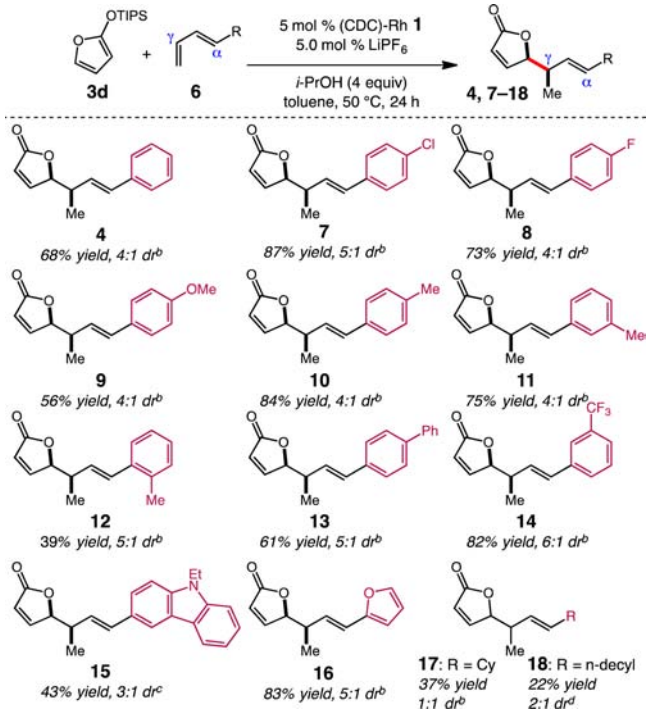


[a]See Supporting Information for experimental details.

illustrates our brief studies with furans bearing various acyloxy substituents (**5a–f**). (1) Only 1.2 equiv of the nucleophile is required to obtain useful conversions. (2) Acyloxyfurans are less reactive and require 60–70 °C. (3) Diastereoselectivities are lower than those of **3d** (cf., 4:1 vs 3:1 dr) but favor the *syn* stereoisomer; the lower dr is likely due to reduced sterics of the acyl group compared to the alkylsilane. (4) Reactions proceed to ~20% conversion with larger alcohols (e.g., *i*-PrOH). Therefore, **3d** was used for the rest of our studies.

With **3d** (vs acyloxyfuran) as the optimal nucleophile for efficient hydroalkylation of 1,3-phenylbutadiene under the reaction conditions (Table 1), we explored the diene scope of the transformation (Scheme 3). The reaction was tolerant of electronic modifications to the aryl diene, and electron-poor and

Scheme 3. (CDC)-Rh-Catalyzed Hydroalkylation Diene Scope[a]



[a]See Table 1. [b]Isolated with >10:1 γ/α regioselectivity. [c]Isolated with 4:1 γ/α regioselectivity. [d]Isolated with 2:1 γ/α regioselectivity.

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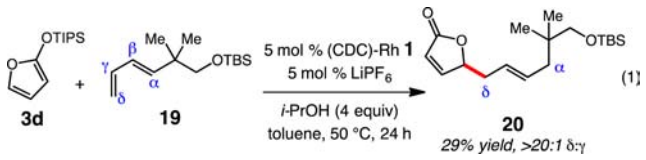
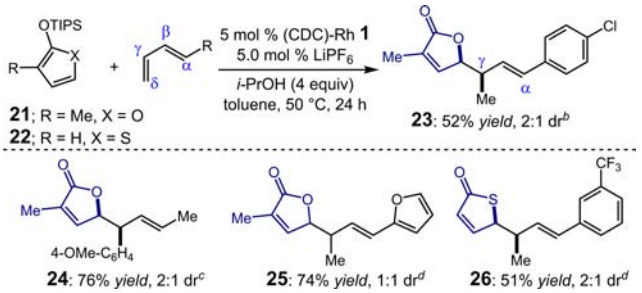
electron-rich aryl dienes react with increased conversion compared to 1,3-phenylbutadiene. Electron-poor *p*-chloro-1,3-phenylbutadiene reacts to yield **7** in 87% yield and 5:1 dr as a single regioisomer, and reaction with *p*-fluoro-1,3-phenylbutadiene was similarly successful, resulting in **8** in 73% yield, as a 17:1 mixture of the γ/α regioisomers with 4:1 dr for the major product. Dienes with electron-donating groups proceed to >98% conversion but are less regio- and diastereoselective; for example, **9** is formed in 56% yield and 4:1 dr. Reduction in yield is caused by partial conversion to the 1,4-addition product (e.g., α-**9**), which can be efficiently separated by silica gel column chromatography. Substitution on the aryl ring in the *ortho*-, *meta*-, and *para*-positions is also well-tolerated and equally diastereoselective; substituted butenolides **10**–**12** are isolated in 39–84% yield and up to 5:1 dr (*syn*/*anti*). The catalytic protocol was also effective for the generation of **13** (61% yield, 5:1 dr) and **14** (82% yield, and 6:1 dr) bearing *p*-phenyl and *m*-trifluoromethyl groups. Heteroaryl-containing dienes are also competent reaction partners as both **15** and **16** are formed in 43 and 83% yield (3:1 and 5:1 dr), respectively. Note that **15** is formed as a 4:1 mixture of γ/α regioisomers.

In contrast to aryl dienes, less reactive alkyl dienes undergo site-selective Rh-catalyzed hydroalkylation to furnish allylic butenolides in only modest yield and dr. Under optimal reaction conditions (5 mol % of **1** at 50 °C), α-branched cyclohexyl-substituted butadiene reacts to form **17** in 37% yield in 1:1 dr. Low diastereoselectivity was also observed for *n*-alkyl diene substrates; 1,3-dodecadiene derived **18**, formed in 22% yield and 2:1 dr, is representative. Lower yields of *n*-alkyl-substituted 1,3-dienes are also due to competitive isomerization to the corresponding unreactive internal diene. We hypothesized that substrates that cannot isomerize should participate more effectively. In the catalytic hydroalkylation of α-*gem*-dimethyl-substituted diene **19**, under standard reaction conditions, we were surprised to observe δ-addition product **20**, resulting from addition of the silyloxyfuran to the terminus of the diene, formed in 29% yield as a single regioisomer (eq 1). The increased sterics of the α-*gem*-dimethyl direct the nucleophile toward the anti-Markovnikov addition product.



Our studies of the diene scope were followed by brief investigations to determine the tolerance of the reaction protocol to variations in the enol ether nucleophile. As illustrated in Scheme 4, the rhodium-catalyzed hydroalkylation translates effectively to deliver α-Me-substituted butenolide products **23**–**25** in good yield; treatment of 2-methyl silyloxyfuran **21** with 5 mol % of **1** and $LiPF_6$ in toluene at 50 °C, in the presence of an aryl diene, affords **23** and **24** in 52–76% yield but in markedly decreased diastereo- (2:1 dr) and regioselectivity. *p*-$MeOC_6H_4$ butenolide **24** is formed in 76% yield (2:1 dr) as a 1:2 mixture of γ/α regioisomers. Furanyl-substituted 1,3-dienes also work well with **21** to afford **25** in 74% yield, 1:1 dr, and >20:1 γ-isomer. To expand the scope of the silyl enol nucleophile to see if other 5-membered heterocycles other than furan could be employed as nucleophiles, we synthesized triisopropylsilyloxy thiophene **22**. Slow addition of **22** (4 equiv vs diene) in the presence of 5 mol % of **1** and $LiPF_6$ results in hydroalkylation efficiency similar to that

Scheme 4. Silyloxyfuran Variation[a]

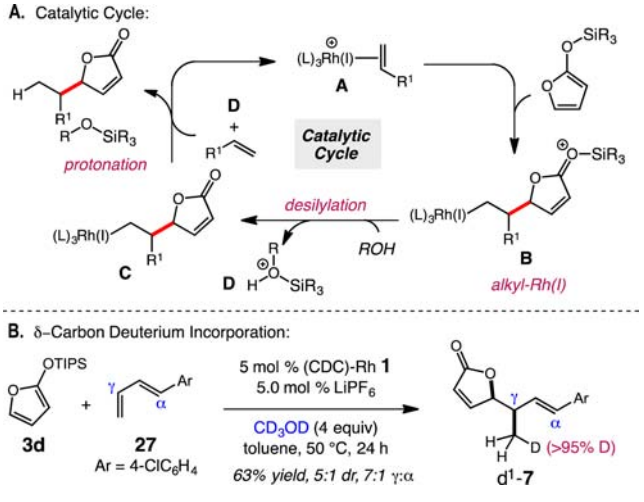


[a]See Table 1. [b]Isolated as a 2:1 mixture of γ/α regioisomers. [c]Isolated as a 1:2 mixture of γ/α regioisomers. [d]Isolated in >20:1 regioselectivity.

of the corresponding oxygen analogue to deliver **26** in 51% yield, 2:1 dr, and >20:1 γ/α regioselectivity. It is not currently clear why the regio- and stereoselectivity decrease when **21** and **22** are employed as nucleophiles, but we were encouraged by the minimal decrease in yield compared to the unsubstituted silyloxyfuran nucleophile. Additional variations to the enol ether nucleophile are currently under study.

To obtain mechanistic insight into our proposed catalytic cycle for the intermolecular hydroalkylation process (Scheme 5A), we

Scheme 5. Proposed Hydroalkylation Mechanism



conducted a reaction in the presence of MeOH-d_4. Reaction of **3d** and diene **27** with MeOH-d_4 (4 equiv) affords 7-d_1 in 63% yield and 5:1 dr with >95% D incorporation at the methyl group (Scheme 5B), thus supporting site-selective protonation of alkylrhodium **C**. The absence of deuterium incorporation at γ-carbon suggests that β-hydride elimination and reinsertion is not operative.

To demonstrate utility of the *syn*-allylic butenolide products generated through the intermolecular (CDC)-Rh-catalyzed hydroalkylation process, we explored further stereoselective functionalization (Scheme 6). *anti*,*syn*-Allylic butenolides are important intermediates for the synthesis of polypropionate motifs[18] (e.g., protomycinolide IV)[19] and can be generated in a single operation. Diastereoselective methyl conjugate addition to **7** with Me_2CuLi in Et_2O at −78 °C affords *anti*,*syn*-lactone **28** in 98% yield, >20:1 dr. Subsequent ozonolysis and reductive workup with $NaBH_4$ (85% yield) generates lactone **29**[20,21] bearing an

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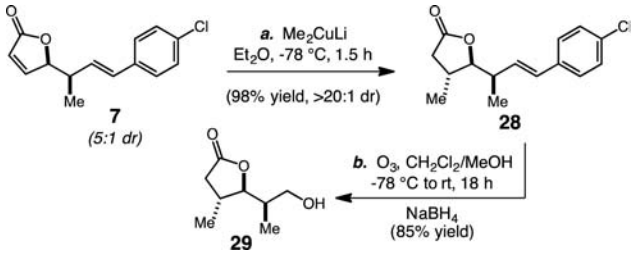
Scheme 6. Diastereoselective Synthesisof *anti,syn*-Stereotriad



anti,syn-stereotriad that can be mapped onto intermediates in the synthesis of several natural products.[22]

Studies to further nucleophile and olefin scope, as well as render hydroalkylation processes enantioselective, are in progress.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b03369.

Experimental procedures, spectral and analytical data (PDF)

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Notes

The authors declare no competing financial interest.

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