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Synthesis of Functionalized α-Pyrone and Butenolide Derivatives by Rhodium-Catalyzed Oxidative Coupling of Substituted Acrylic Acids with Alkynes and Alkenes

Satoshi Mochida, Koji Hirano, Tetsuya Satoh,* and Masahiro Miura*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

satoh@chem.eng.osaka-u.ac.jp; miura@chem.eng.osaka-u.ac.jp

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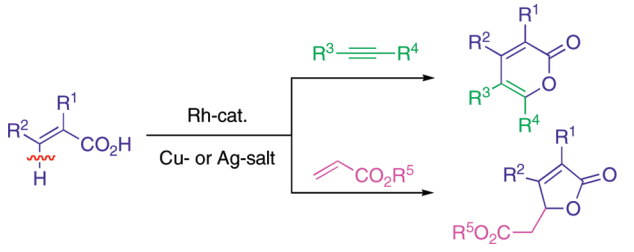
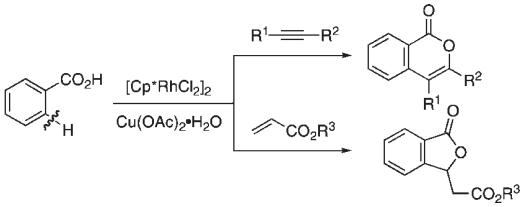


The straightforward and efficient synthesis of α-pyrone and butenolide derivatives has been achieved by the rhodium-catalyzed oxidative coupling reactions of substituted acrylic acids with alkynes and alkenes, respectively. Some α-pyrones obtained exhibit solid-state fluorescence.

α-Pyrone and butenolide structures are found in various natural products that exhibit a broad range of interesting biological properties.[1] They are also of interest for their fluorescence properties.[2] One of the useful procedures for their construction is the palladium-catalyzed annulation by the coupling of (*Z*)-*β*-iodopropenoates with internal alkynes.[3] The iodides are, however, prepared in more than four steps.

On the other hand, transition-metal-catalyzed organic reactions via C−H bond cleavage have been significantly developed in recent years[4] and, in some cases, successfully substituted for those of the corresponding organic halides. As one such example, we recently reported the direct oxidative coupling of benzoic acids with alkynes and alkenes, such as acrylates, under rhodium catalysis involving the cleavage of their ortho C−H bond (Scheme 1).[5] These reactions provide straightforward pathways to isocoumarin and phthalide derivatives from widely available benzoic acids.

SCHEME 1. Coupling of Benzoic Acids with Alkynes and Alkenes



Variously substituted acrylic acids are also readily available. During our further studies of rhodium-catalyzed oxidative coupling,[6,7] it has been found that our catalyst system is applicable to functionalization of acrylic acids through vinylic C−H bond cleavage.[8] Thus, the corresponding α-pyrone and butenolide derivatives can be synthesized efficiently by the oxidative coupling of such acids with alkynes and alkenes, respectively. Expectedly, some α-pyrones obtained have been found to show solid-state fluorescence. The results obtained for the coupling reactions are described herein.

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(8) For recent examples, see: (a) Shibata, Y.; Otake, Y.; Hirano, M.; Tanaka, K. *Org. Lett.* **2009**, *11*, 689. (b) Giri, R.; Yu, J.-Q. *J. Am. Chem. Soc.* **2008**, *130*, 14082. (c) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2008**, *130*, 3645. (d) Oi, S.; Sakai, K.; Inoue, Y. *Org. Lett.* **2005**, *7*, 4009.

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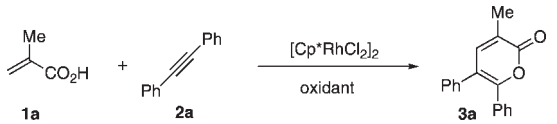
TABLE 1. Reaction of Methacrylic Acid (1a) with Diphenylacetylene (2a)[a]



entry	oxidant (mmol)	solvent	temp (°C)	time (h)	yield of **3a**[b]
1	$Cu(OAc)_2 \cdot H_2O$ (1)	*o*-xylene	120	2	4
2	$Cu(OAc)_2 \cdot H_2O$ (1)	DMF	120	4	25
3	Ag_2CO_3 (0.5)	DMF	120	2	91 (87)
4	Ag_2CO_3 (0.5)	*o*-xylene	120	4	10
5	Ag_2CO_3 (0.5)	DMF	100	6	77
6	AgOAc (1)	DMF	120	2	92

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), [$(Cp^*RhCl_2)_2$] (0.005 mmol), and solvent (2.5 mL) under N_2. [b]GC yield based on the amount of **1a** used. Value in parentheses indicates yield after purification.

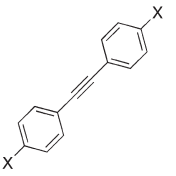
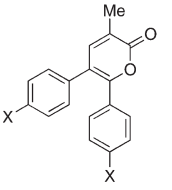
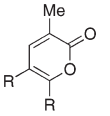
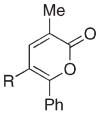
In an initial attempt, methacrylic acid (**1a**) (0.5 mmol) was treated with diphenylacetylene (**2a**) (0.5 mmol) under conditions similar to those employed for the coupling of benzoic acids with **2a**. Under conditions with [$Cp^*RhCl_2]_2$ (0.005 mmol) and $Cu(OAc)_2 \cdot H_2O$ (1 mmol) in *o*-xylene (2.5 mL) at 120 °C under N_2, 3-methyl-5,6-diphenyl-2*H*-pyran-2-one (**3a**) was formed in only 4% yield after 2 h (entry 1 in Table 1, Cp* = pentamethylcyclopentadienyl). In DMF, the product yield increased to 25% (entry 2). The use of Ag salts in place of $Cu(OAc)_2$ as oxidant gave superior results. Thus, in the presence of Ag_2CO_3 (0.5 mmol), **3a** was obtained in 91% yield within 2 h (entry 3). Even with the Ag salt, the reaction was sluggish in *o*-xylene (entry 4). At 100 °C, the reaction efficiency somewhat decreased (entry 5). AgOAc could also be employed as well as Ag_2CO_3 (entry 6).

The reactions of **1a** using various internal alkynes **2b**−**i** in place of **2a** were next examined. Under optimized conditions in Table 1 (entry 3), methyl- (**2b**), methoxy- (**2c**), and chloro- (**2d**) substituted diphenylacetylenes underwent the coupling with **1a** to afford the corresponding 5,6-diaryl-3-methylpyran-2-ones **3b**−**d** in good yields (entries 1−3 in Table 2). Bis(2-thienyl)acetylene (**2e**) and dialkylacetylenes such as 4-octyne (**2f**) and 8-octadecyne (**2g**) could also be employed to produce α-pyrones **3e**−**g** in 84−92% yields (entries 4−6). 1-Phenyl-1-propyne (**2h**) also reacted with **1a** to give 3,5-dimethyl-6-phenyl-2*H*-pyran-2-one (**3h**) selectively (entry 7), and only a trace amount of a regioisomer was detected by GC−MS. From the reaction of 1-phenyl-1-hexyne (**2i**) with **1a**, 5-butyl-3-methyl-6-phenyl-2*H*-pyran-2-one (**3i**) was obtained in 87% yield, along with a minor amount (8%) of a separable regioisomer, 6-butyl-3-methyl-5-phenyl-2*H*-pyran-2-one (**3i′**) (entry 8). 1-Phenyl-2-(trimethylsilyl)acetylene and phenylacetylene did not couple with **1a** at all, and only an alkyne dimer, diphenylbutadiyne, was detected by GC−MS as a single major product.

Table 3 summarizes the results for the coupling of a series of substituted and unsubstituted acrylic acids **1b**−**j** with **2a**. 2-Arylacrylic acids **1b**−**d** reacted with **2a** smoothly to form 3-aryl-5,6-diphenylpyranones **3j**−**l** (entries 1−3). Commercially available itaconic acid and its derivative, **1e** and **1f**, also underwent the reaction with **2a** to produce 2-oxo-5,6-diphenyl-2*H*-pyran-3-carboxylic acid derivatives **3m** and **3n**, respectively (entries 4 and 5). In the reactions of unsubstituted acrylic acid (**1g**) as well as 2,3-dimethyl- (**1h**) and 2,3-diphenylacrylic acids (**1i**), increasing the amount of [$Cp^*RhCl_2]_2$ to 2 mol % improved the reaction efficiency (entries 6−8). In contrast, the reaction of 1-cyclohexene-1-carboxylic acid (**1j**) proceeded efficiently under standard conditions with [$Cp^*RhCl_2]_2$ (1 mol %) to afford a bicyclic product **3r** in 76% yield (entry 9).

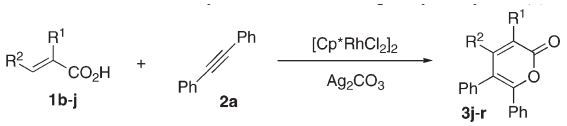
Some α-pyrones obtained above showed solid-state fluorescence in a range of 460−490 nm (see the Supporting Information). Notably, **3j** exhibited a relatively strong

TABLE 2. Reaction of Methacrylic Acid (1a) with Alkynes 2[a]

entry	**2**	product, % yield[b]
		
1	**2b**: X = Me	**3b**: X = Me, 96 (93)
2	**2c**: X = OMe	**3c**: X = OMe, 88 (73)
3	**2d**: X = Cl	**3d**: X = Cl, 86 (78)
		
4	**2e**: R = 2-thienyl	**3e**: R = 2-thienyl, 92 (86)
5	**2f**: R = Pr	**3f**: R = Pr, 84 (69)
6	**2g**: R = C_7H_{15}	**3g**: R = C_7H_{15}, 91 (85)
		
7	**2h**: R = Me	**3h**: R = Me, 81 (77)
8	**2i**: R = Bu	**3i**: R = Bu, 87 (78)[c]

[a]Reaction conditions: **1a** (0.5 mmol), **2** (0.5 mmol), [$(Cp^*RhCl_2)_2$] (0.005 mmol), Ag_2CO_3 (0.5 mmol), and DMF (2.5 mL) at 120 °C under N_2 for 4 h. [b]GC yield based on the amount of **1a** used. Value in parentheses indicates yield after purification. [c]A separable regioisomer was also isolated in 8% yield (see text).

TABLE 3. Reaction of Acrylic Acids 1 with Diphenylacetylene 2[a]



entry	**1**	R^1	R^2	time (h)	product, % yield[b]
1	**1b**	Ph	H	4	**3j**, 84 (77)
2	**1c**	4-$MeOC_6H_4$	H	10	**3k**, 61 (58)
3	**1d**	4-ClC_6H_4	H	10	**3l**, 60 (50)
4	**1e**	$(HO_2C)CH_2$	H	6	**3m**, 44 (40)
5[c]	**1f**	$(BuO_2C)CH_2$	H	4	**3n**, 81 (77)
6[d]	**1g**	H	H	4	**3o**, 60 (52)
7[d]	**1h**	Me	Me	8	**3p**, 82 (77)
8[d]	**1i**	Ph	Ph	6	**3q**, 22 (22)
9	**1j**	$-(CH_2)_4-$		6	**3r**, 76 (74)

[a]Reaction conditions: **1** (0.5 mmol), **2a** (0.5 mmol), [$(Cp^*RhCl_2)_2$] (0.005 mmol), Ag_2CO_3 (0.5 mmol), and DMF (2.5 mL) at 120 °C under N_2. [b]GC yield based on the amount of **2a** used. Value in parentheses indicates yield after purification. [c]**1** (1 mmol) was used. [d][$(Cp^*RhCl_2)_2$] (0.01 mmol) was used.

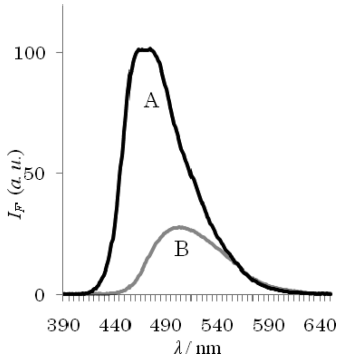


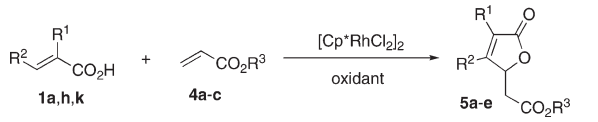
FIGURE 1. Fluorescence spectra of **3j** (A) and Alq_3 (B) in the solid state upon excitation at 380 nm.

emission compared to a typical emitter, tris(8-hydroxyquinolino)aluminum (Alq_3), by a factor of 3.2 (λ_{emis} = 474 nm, A versus B in Figure 1).

We also examined the oxidative cross-dimerization[9] using acrylic acids with acrylates. When methacrylic acid (**1a**) (0.5 mmol) was treated with butyl acrylate (**4a**) (1 mmol) in the presence of $[Cp^*RhCl_2]_2$ (0.005 mmol) and Ag_2CO_3 (0.5 mmol) in DMF (2.5 mL) at 120 °C under N_2 (conditions A) for 6 h, butyl 2,5-dihydro-4-methyl-5-oxo-2-furanacetate (**5a**) was formed in 50% yield (entry 1 in Table 4). Under the conditions using $Cu(OAc)_2 \cdot H_2O$ (1 mmol) in place of Ag_2CO_3 as oxidant at 100 °C (conditions B), the product yield was improved up to 65% (entry 3). Cyclohexyl- (**4b**) and *t*-butyl acrylates (**4c**) also underwent the cross-dimerization with **1a** to afford the corresponding butenolides **5b** and **5c**, respectively (entries 4 and 5). In contrast, in the reaction of 2,3-dimethylacrylic acid (**1h**) with **4a**, a better result was obtained by using Ag_2CO_3 as oxidant in DMAc compared with that under conditions B (entry 7 versus entry 6). Under similar conditions, the reaction of 2-methyl-3-phenylacrylic acids (**1k**) with **4a** proceeded effectively to produce a butenolide **5e** (entry 8).

The reaction of **1a** with **2** or **4** seems to proceed via fundamentally similar steps to those proposed for the oxidative coupling of benzoic acid with **2** or **4** using the $[Cp^*RhCl_2]_2/Cu(OAc)_2 \cdot H_2O$ system.[5] Thus, as depicted in Scheme 2, coordination of the carboxyl oxygen to Cp*Rh(III) X_2 gives a rhodium(III) carboxylate **A**, and directed cyclorhodation at the 3-position affords a key rhodacycle intermediate **B**.[10] Subsequent alkyne or alkene insertion occurs to produce the corresponding seven-membered rhodacycle **C** or **D**, which may undergo reductive elimination or β-hydrogen elimination and nucleophilic cyclization to form **3** or **5**, respectively. In both cases, the resulting Rh(I)X species seem to be oxidized in the presence of the copper(II) or silver(I) salt to regenerate a rhodium(III) species.[11] The direction of the insertion of **2h** and **2i** into the Rh−C bond of **B** is consistent with that in our previous work.[5,6] This regioselectivity may be attributed to the interaction of the Rh center with the phenyl group of alkynes, although the details are not definitive.

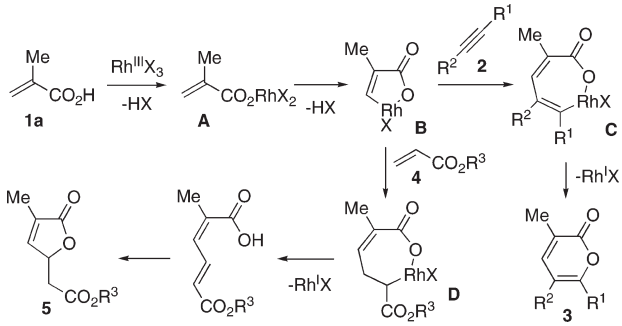
TABLE 4. Reaction of Acrylic Acids 1 with Acrylates 4[a]



entry	1	R^1	R^2	4	R^3	conditions	time (h)	product, % yield[b]
1	**1a**	Me	H	**4a**	Bu	A	6	**5a**, 50
2	**1a**	Me	H	**4a**	Bu	B[c]	6	**5a**, 54
3	**1a**	Me	H	**4a**	Bu	B	8	**5a**, 65 (63)
4	**1a**	Me	H	**4b**	Cy[d]	B	8	**5b**, 68 (61)
5	**1a**	Me	H	**4c**	*t*-Bu	B	8	**5c**, 60 (58)
6	**1h**	Me	Me	**4a**	Bu	B	8	**5d**, 11
7	**1h**	Me	Me	**4a**	Bu	A[e]	6	**5d**, 75 (72)
8	**1k**	Me	Ph	**4a**	Bu	A[e]	10	**5e**, 68 (62)

[a]Reaction conditions A: **1** (0.5 mmol), **4** (1 mmol), $[(Cp^*RhCl_2)_2]$ (0.005 mmol), Ag_2CO_3 (0.5 mmol), and DMF (2.5 mL) at 120 °C under N_2. Conditions B: **1** (0.5 mmol), **4** (1 mmol), $[(Cp^*RhCl_2)_2]$ (0.005 mmol), $Cu(OAc)_2 \cdot H_2O$ (1 mmol), and DMF (2.5 mL) at 100 °C under N_2. [b]GC yield based on the amount of **1** used. Value in parentheses indicates yield after purification. [c]At 120 °C. [d]Cy = cyclohexyl. [e]In DMAc (2.5 mL).

SCHEME 2. Plausible Mechanism for the Coupling of Methacrylic Acid (1a) with Alkynes 2 and Alkenes 4



In summary, we have demonstrated that the rhodium-catalyzed oxidative coupling of substituted acrylic acids with alkynes proceeds efficiently via vinylic C−H bond cleavage to give the corresponding α-pyrone derivatives. Cross-dimerization of acrylic acids with acrylate esters can also be conducted effectively under similar rhodium catalysis to form butenolides. Acrylic acids are apparently useful building blocks because of their wide and ready availability.

Experimental Section

General Procedure for Reactions of Acrylic Acid 1 with Alkynes 2. To a 20 mL two-necked flask were added acrylic acid **1** (0.5 mmol), alkyne **2** (0.5 mmol), $[(Cp^*RhCl_2)_2]$ (0.005 mmol, 3 mg), Ag_2CO_3 (0.5 mmol, 138 mg), 1-methylnaphthalene (ca. 40 mg) as internal standard, and DMF (2.5 mL). The resulting mixture was stirred under N_2 at 120 °C. GC and GC−MS analyses of the mixtures confirmed formation of **3**. Then, the reaction mixture was cooled to room temperature and extracted with Et_2O (100 mL). The organic layer was washed by water (100 mL, three times) and dried over Na_2SO_4. Product **3** was isolated by column chromatography on silica gel using hexane/ethyl acetate as eluant.

(9) For recent examples of cross-dimerization of alkenes without directing groups, see: (a) Xu, Y.-H.; Lu, J.; Loh, T.-P. *J. Am. Chem. Soc.* **2009**, *131*, 1372. (b) Lindhardt, A. T.; Mantel, M. L. H.; Skrydstrup, T. *Angew. Chem., Int. Ed* **2008**, *47*, 2668. (c) Hatamoto, Y.; Sakaguchi, S.; Ishii, Y. *Org. Lett.* **2004**, *6*, 4623.

(10) Similar ruthenacycles have been prepared: Kanaya, S.; Komine, N.; Hirano, M.; Komiya, S. *Chem. Lett.* **2001**, 1284.

(11) The participation of a silver acrylate before the formation of **A** as well as some cationic rhodium species under conditions with a Ag salt oxidant cannot be excluded.

3-Methyl-5,6-diphenyl-2*H*-pyran-2-one (3a) (entry 3 in Table 1):[3a] mp 124−126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.19 (d, J = 1.1 Hz, 3H), 7.16−7.35 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.4, 117.9, 123.7, 127.7, 128.0, 128.9, 129.1, 129.2, 129.5, 132.2, 136.6, 144.0, 155.4, 163.1; HRMS m/z calcd for $C_{18}H_{14}O_2$ (M^+) 262.0994, found 262.0996.

General Procedure for the Reaction of Acrylic Acids 1 with Acrylates 4 under Conditions B. To a 20 mL two-necked flask were added acrylic acid **1** (0.5 mmol), acrylate **4** (1 mmol), [(Cp*$RhCl_2$)$_2$] (0.005 mmol, 3 mg), $Cu(OAc)_2 \cdot H_2O$ (1 mmol, 199 mg), 1-methylnaphthalene (ca. 40 mg) as internal standard, and DMF (2.5 mL). The resulting mixture was stirred under N_2 at 100 °C. GC and GC−MS analyses of the mixtures confirmed formation of **5**. Then, the reaction mixture was cooled to room temperature and extracted with Et_2O (100 mL) and ethylenediamine (2 mL). The organic layer was washed by water (100 mL, three times) and dried over Na_2SO_4. Product **5** was isolated by column chromatography on silica gel using hexane/ethyl acetate as eluant.

Butyl 2,5-Dihydro-4-methyl-5-oxo-2-furanacetate (5a) (entry 3 in Table 4): oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, J = 7.3 Hz, 3H), 1.35−1.41 (m, 2H), 1.59−1.66 (m, 2H), 1.92−1.93 (t, J = 1.5 Hz, 3H), 2.59 (dd, J = 16.1, 7.0 Hz, 1H), 2.79 (dd, J = 16.1, 7.0 Hz, 1H), 4.13 (t, J = 7.0 Hz, 2H), 5.24−5.28 (m, 1H), 7.16−7.28 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.5, 13.5, 19.0, 30.5, 38.2, 65.0, 76.7, 130.6, 147.6, 169.1, 173.4; HRMS m/z calcd for $C_{11}H_{16}O_4$ (M^+) 212.1049, found 212.1046.

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Supporting Information Available: Characterization data of products. This material is available free of charge via the Internet at http://pubs.acs.org.