Catalytic Addition of Olefinic C-H Bonds to Olefins

Fumitoshi Kakiuchi, Yasuo Tanaka, Taisuke Sato, Naoto Chatani, and Shinji Murai*
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565

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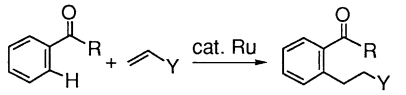
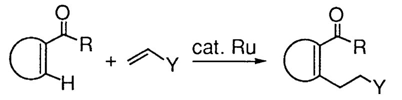
Addition of C-H bonds in α,β-enones to olefins were attained by $Ru(H)_2(CO)(PPh_3)_3$ catalyst. The reactions of acylated heterocyclic olefins with triethoxyvinylsilane in the presence of the ruthenium catalyst afforded the coupling product in good to excellent yields. The reactions of 3,4-dihydro-6-pivaloyl-2*H*-pyran with several olefins were also catalyzed by the ruthenium complex to give the corresponding coupling products.

Recently we have reported that the addition of aromatic C-H bonds in aromatic ketones to olefins can be attained by using ruthenium complexes as the catalyst (eq 1).[1-3] This catalytic reaction is so efficient that it should find practical uses in organic synthesis, representing a rare example of a catalytic reaction involving cleavage of unreactive C-H bonds.[4] We have examined whether aromatic ketones in eq 1 can be replaced by enones (eq 2) leading to a new method of olefin-olefin coupling.[9] This paper describes that the β C-H bonds in α,β-enones can be added to olefins in a catalytic manner according to eq 2.

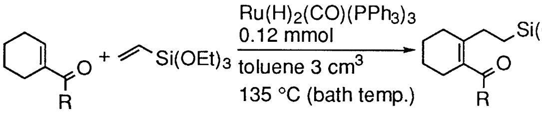


(1)



(2)

We first studied the reaction of 1-acetylcyclohexene (**1a**), which is structurally similar to acetyl benzene (eq 1), with triethoxyvinylsilane (**2**)[14] in the presence of $Ru(H)_2(CO)(PPh_3)_3$[1-3,15] as the catalyst (eq 3). The reaction gave the expected product **3a** but in only moderate yield.[16] Interestingly, however, the reaction of 1-pivaloylcyclohexene **1b** gave an almost quantitative yield of the coupling product **3b** in a short reaction period (eq 3).



(3)

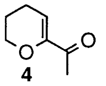
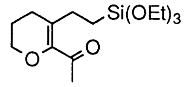
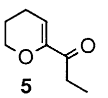
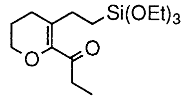
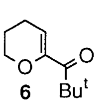
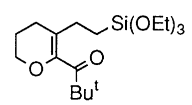
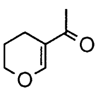
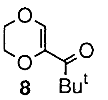
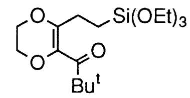
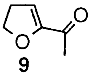
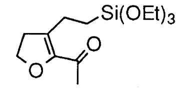
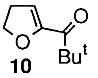
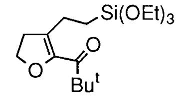
1 (2 mmol) **2** (4 mmol)

1a : R = CH_3 48 h **3a** ca. 50%
1b : R = ${}^tBu$ 0.5 h **3b** 96%

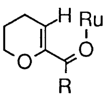
Next the catalytic reactions of some heterocyclic enones were examined. As shown in Table 1, 1:1 coupling products were obtained from heterocyclic enones and the olefin **2** in good to excellent yields.[17] The oxygen substitution can be either at α of the enone moiety (**4**-**6**, **9**, and **10**) or at β (**7**), or at both positions (**8**). As the catalyst, the use of $Ru(CO)_2(PPh_3)_3$[18] for the reaction of **6** gave the almost same result.

The observed order of the reactivity of **4**, **5**, and **6** is interesting. Supposing the catalytic reaction proceeds through an s-*cis* conformation for the enone and complexation of Ru syn to the ene group on the carbonyl double bond,[19] the larger R group would favor the s-*cis* conformation like **11** because larger allylic strain would disfavor the s-*trans* isomer **13**. This seems however not always to be true since decrease in the reactivity was observed neither in the case of **1b** (compared with **6**) nor in the case of **7** (even faster than **4**) where steric repulsion between the ketone alkyl group and the ring CH_2 group also exists in the s-*cis* conformation. The faster reaction rates observed with the larger R group may be attributed to an increase in the population of syn Ru configuration species (like **11**) rather than the sterically crowded anti form (not shown).[20]

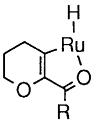
Table 1. Catalytic Addition of Heterocyclic Enones to Triethoxyvinylsilane (**2**)[a]

Enone	Time/h	Product	Yield[b]/%
 **4**	10		quant. (96)[c]
 **5**	4		quant.
 **6**	0.5		quant.
 **7**	1		quant.
 **8**	0.5		quant.
 **9**	36		20
 **10**	1		73

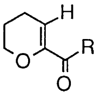
[a]Reaction conditions: enone (2 mmol), triethoxyvinylsilane (4 mmol), $Ru(H)_2(CO)(PPh_3)_3$ (0.12 mmol), toluene (3 cm^3), 135 °C (oil bath tempereature). [b]GC yield based on the enone. [c]Isolated by bulb-to-bulb distillation.



11 s-*cis, syn*



12

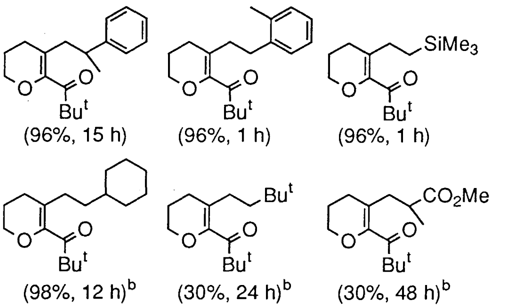


13 s-*trans*

Catalytic reactions of various acyclic enones have been examined. These proceeded only sluggishly in most cases. This may suggest the importance of conformational rigidity of enones.

The new enone/olefin coupling can be applied to various terminal olefins. Selected results of the catalytic reaction using **6** as the enone are given in Table 2. From α-methylstyrene, *o*-

Table 2. Products of the Catalytic Reaction of **6** with Olefins[a]



[a]Reaction conditions: **6** (2 mmol), olefin (4 mmol), $Ru(H)_2(CO)(PPh_3)_3$ (0.12 mmol), toluene (3 cm^3), 135 °C (oil bath tempereature). [b]Olefin: 10 mmol.

methylstyrene, trimethylvinylsilane, and vinylcyclohexane, the coupling products were obtained in excellent yields. The yields were moderate in the case of *t*-butylethylene and methyl methacrylate. It is interesting to note that α-methylstyrene and methyl methacrylate are the olefins that do not undergo coupling with aromatic ketones (eq 1). In contrast, *t*-butylethylene, which reacted very nicely with aromatic ketones, underwent coupling with enone **6** only in a low yield. These facts suggest that the catalytic reactions of eq 1 and eq 2 are not straightforwardly similar to each other.

We have also found that olefins in eq 1 can be replaced with acetylenes, which is the subject of the accompanying paper.

Supplementary Material (7 pages) including spectral data of new compounds are available on request to the author by telefax (+81-6-879-7396).

References and Notes

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3 F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, N. Chatani, and S. Murai, *Bull. Chem. Soc., Jpn.*, **68**, 62 (1995); S. Murai, *J. Synth. Org. Chem., Jpn.*, **56**, 992 (1994) (in English).

4 Efficient catalytic manipulation of α-C-H bonds in pyridine derivatives has been recently reported using a cationic zirconium complex[5] and $Ru_3(CO)_{12}$[6]. See also, intramolecular insertion of isonitrile to a C-H bond catalyzed by a ruthenium complex.[7] Very recently, Kim and co-workers reported rhodium-catalyzed alkylation of phenyl ring of 2-phenylpyridines with olefins.[8]

5 R. F. Jordan and D. F. Taylor, *J. Am. Chem. Soc.*, **111**, 778 (1989); S. Rodewald and R. F. Jordan, *J. Am. Chem. Soc.*, **116**, 4491 (1994).

6 E. J. Moore, W. R. Pretzer, J. T. O'Connell, J. Harris, L. Labounty, L. Chou, and S. S. Grimmer, *J. Am. Chem. Soc.*, **114**, 5888 (1992).

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8 Y.-G. Lim, Y. H. Kim, and J.-B. Kang, *J. Chem. Soc., Chem. Commun.*, **1994**, 2267.

9 Olefin-olefin coupling[10] may be classified into three types; dimerization,[11] cross coupling of two different olefins,[10,12] and cyclocoupling.[10] Among these direct cross coupling is most difficult to attain, except for those in intramolecular manner.[13]

10 For a representative review, see: W. Keim, A. Behr, and M. Röper, In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds., Pergamon: Oxford U.K., 1982; Vol. 8, Chapter 52, pp 371-462; S. Muthukumaru Pillai, M. Ravidranathan, and S. Sivaram, *Chem. Rev.*, **86**, 353 (1986); F. J. McQuillin, D. G. Parker, and G. R. Stephenson, *Transition Metal Organometallics for Organic Synthesis*; Cambridge University: New York, 1991; pp 334-359.

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12 Recently Wakatsuki, Yamazaki, and Mise reported cross coupling of vinylsilanes with 2,3-dihydrofuran using $Ru(H)(Cl)(CO)(PPh_3)_3$ as the catalyst. This catalyst was not effective for the reaction described in the present paper and in turn our catalyst, $Ru(H)_2(CO)(PPh_3)_3$, was not effective for their reaction. See, T. Mise, H. Yamazaki, and Y. Wakatsuki, *Abstracts of Papers*, 65th Annual Meeting of Chemical Society of Japan, Tokyo; Chemical Society of Japan: Tokyo, 1993; 4P50. Also see, ref. 10.

13 R. Grigg, T. R. B. Mitchell, and A. Ramasubbu, *J. Chem. Soc., Chem. Commun.*, **1979**, 669; R. Grigg, T. R. B. Mitchell, and A. Ramasubbu, *J. Chem. Soc., Chem. Commun.*, **1980**, 27.

14 The olefin **2** was shown to be one of the most reactive olefins in the reaction 1[1-3] and is easy to handle.

15 N. Ahmad, J. J. Levison, S. D. Robinson, and M. F. Uttley, *Inorg Synth.*, **15**, 48 (1974).

16 All new compounds have been adequately characterized, see supplementary material.

17 A typical procedure is as follows. A toluene (3 cm^3) solution of $Ru(H)_2(CO)(PPh_3)_3$ (110 mg, 0.12 mmol), enone (2 mmol), triethoxyvinylsilane (**2**) (760 mg, 4 mmol), and hexadecane (an internal standard for gas chromatography) was heated under vigorous reflux (at 135 °C, oil bath temperature) with stirring. After heating for several hours, the product was isolated by a bulb-to-bulb distillation. The product was obtained as an analytically pure sample.

18 T. R. Greffney and J. A. Ibers, *Inorg. Chem.*, **21**, 2851 (1982).

19 Importance of complexation of the carbonyl group to the ruthenium has been suggested (refs. 1-3).

20 Further experiments will be needed before drawing mechanistic conclusions. Even the rate step is not known at present.