C-H Bond Cleavage of 8-Quinolinecarboxaldehyde by Rh(I) and A Hydride Addition Into Vinylcyclohexenes

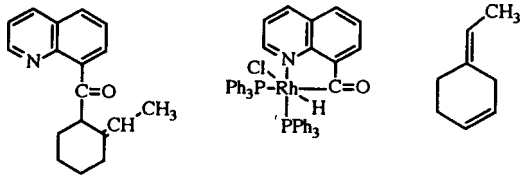
Chul-Ho Jun*, Yeong-Gweon Lim†, and Jung-Bu Kang†

Department of Chemistry, Yonsei Univeristy, Seoul 120-749, Korea
†Agency for Defense Development, Yuseong 305-600, Korea

Received September 10, 1996

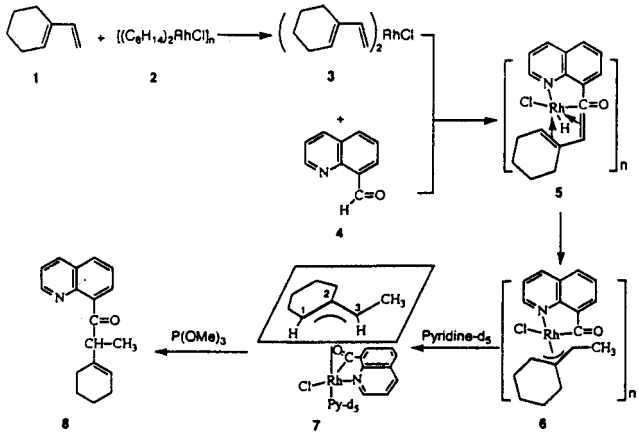
The C-H bond of aldehyde can be readily cleaved by transition metals through cyclometallation.[1] 8-Quinolinecarboxaldehyde is known to be one of the best models for the C-H bond cleavage with transition metals.[2] The C-H bond cleavage of 8-quinolinecarboxaldehyde by Wilkinson's complex gives a stable acylrhodium(III) hydride.[3] When the olefin- or diene-coordinated rhodium(I) complexes were used in the place of Wilkinson's complex, the acylrhodium(III) hydride generated as a transient intermediate, hydrometallates coordinate olefins or diene, to give acylrhodium(III) alkyls[4] or η^3-allyl complexes.[5] Treatment of these acylrhodium(III) alkyls or η^3-allyl complexes with phosphine or phosphite induces ligand-promoted reductive-elimination to give the corresponding ketones under very mild conditions.[6] Here we describe the reaction of the conjugated and nonconjugated vinylcycloalkene rhodium(I) complexes with 8-quinolinecarboxaldehyde, and the olefin-isomerization mechanism in the rhodium alkenyl intermediate.

The 1-vinylcyclohexene rhodium complex[7] (**3**) was generated *in situ* by the reaction of 1-vinylcyclohexene (**1**) and bis(cyclooctene)rhodium(I) chloride (**2**)[8] (Scheme 1). Compound **3** reacted with a solution of **4** in $CHCl_3$ at room temperature to give an insoluble yellow precipitate, which supposed to be the chlorine-bridged complex **6**. Addition of two equivalents of pyridine-d_5 to a suspension of **6** in $CDCl_3$ gave *syn*-η^3-2-ethylidenecyclohexyl rhodium(III) complex **7**.[9] The ^{13}C NMR chemical shifts for the allyl group in **7** appear at 63.2 (d, *J*(Rh-C) 9.4 Hz, C-1 of the allyl group), 58.6 ppm (d, *J*(Rh-C) 10.3 Hz, C-3 of the allyl group adjacent to the *syn*-methyl group) as doublets indicating that terminal two carbons in the allyl group are coupled with the Rh while that of the meso-carbon (C-2) in the allyl group hardly appears probably due to little nOe (nuclear overhauser effect) since this carbon does not contain any proton. Treatment of **7** with trimethylphosphite caused facile ligand-promoted reductive-elimination to give a β,γ-unsaturated ketone **8**[10] in 82% yield. Complex **5** is regarded as an intermediate in the reaction of **3** and **4** *via* C-H bond cleavage of **4**. The hydride addition to 1-vinylcyclohexene takes place at the terminal carbon in the vinyl group in **5**. Any hydride addition to the C-2 carbon in the cyclohexenyl group does not take place, maybe due to the steric congestion of the cyclohexenyl group compared with the vinyl group. Another interesting thing is the selectivity of the reductive elimination of **7** to afford **8**. Since two terminal carbons bonded to the methyl group and the methylene group in the allyl group of **7** are available, ligand-promoted reductive elimination should have given two mixtures of **8** and **9**. However, **8** is the only product isolated.

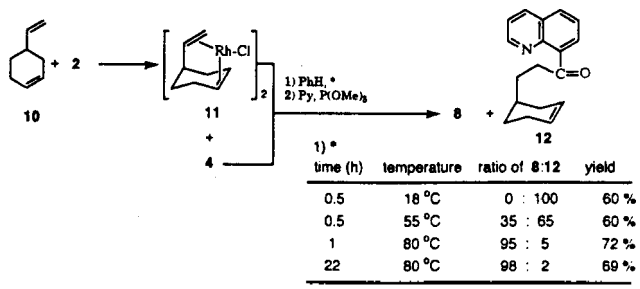


9 **23** **24**

(4-Vinylcyclohexene)rhodium(I) chloride (**11**) can be also generated *in situ* from the reaction of **2** and nonconjugated diene, 4-vinylcyclohexene (**10**) at room temperature for 1 h (Scheme 2).[11] Compound **4** was allowed to react with a solution of **11** in benzene at 55 ℃ for 30 min to give a yellow precipitate. Reductive-elimination of this yellow solid precipitate by trimethylphosphite gave **8** and 8-quinolinyl cyclohex-3'-enylethyl ketone (**12**)[12] in 60% yield in a 35 : 65 ratio. The structure of the acylrhodium(III) cyclohex-3'-enylethyl complex **14** was inferred from the reductive-elimination product **12** (Scheme 3). The hydride in **13**, formed from the C-H bond activation of **4** by **11**, inserted into the C-1 in the vinyl group to form complex **14** according to the Markovnikoff's rule. When the reaction of **4** and **11** was carried out at 18 ℃ for 30 min, only **12** was isolated in 60% yield after reductive elimination. For longer reaction times and higher temperature, 80 ℃ for 1h and 80 ℃ for 22 h, the reaction yielded a mixture of **8** and **12** in a 95 : 5 ratio and a 98 : 2 ratio, respectively. These results explain that initially hydrometallated complex **14** must be isomerized into the complex **6**

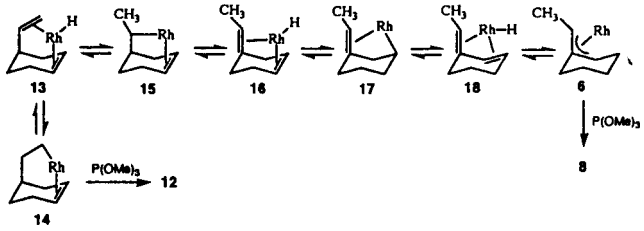


Scheme 1.

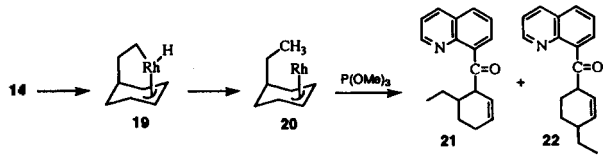


time (h)	temperature	ratio of 8:12	yield
0.5	18 °C	0 : 100	60 %
0.5	55 °C	35 : 65	60 %
1	80 °C	95 : 5	72 %
22	80 °C	98 : 2	69 %

Scheme 2.



Scheme 3.



Scheme 4.

on high temperature and long reaction time. Two possible mechanisms can be considered for the isomerization of **14** to **6**; a hydride addition-elimination mechanism[13] and a π-allyl hydrido mechanism.[14] Already we proposed π-allyl hydrido mechanism for the 4-pentenylrhodium(III) complex to the 1-ethyl-η^3-allylrhodium(III) complex. However, in this case, we can not explain the isomerization of **14** to **6** in terms of π-allyl hydrido mechanism since complex **14** should have given **21** and (or) **22** through **19** and **20** (Scheme 4). According to the π-allyl hydrido mechanism, an allylic proton should have been abstracted in **14** to give **19**, and complex **20** was obtained by reductive elimination of hydridoalkylrhodium(III) complex **19**. Therefore, we conclude that a hydride addition-elimination mechansim might be operated for the isomerization of **14** to **6** as shown in Scheme 3. When **10** was heated at 100 ℃ for 16 h with catalytic amount (10 mol%) of acylrhodium(III) hydride complex **23**, prepared from the reaction of **4** and tris(triphenylphosphine)rhodium chloride, 38% of **10** was isomerized to **24**, which must be liberated from the complex **16**. This can be one of the evidences in a hydride addition-elimination mechanism of **14** to **6**.

In conclusion, we have tried to find a hydride-insertion reaction to vinylcycloalkene, conjugate diene and nonconjugate diene, and isomerization mechanism of cyclohex-3'-enylethyl group in **14** into η^3-2-ethylidenecyclohexyl group in **6**. A hydride addition-elimination mechanism is the most plausible since π-allyl hydrido mechanism cannot explain the formation of **6** and **24** which were produced by catalytic isomerization of **10** with complex **23**.

Acknowledgment. This work was supported by the Basic Science Research Institute Program, Project No. BSRI-96-3422 from Ministry of Education. Author (C.-H. Jun) also thanks IBRD for purchasing a 250 MHz NMR spectrophotometer.

References

1. (a) Motschi, H.; Pregosin, P. S. *J. Organomet. Chem.* **1979**, *171*, C37. (b) Suggs, J. W.; Pearson, G. D. N. *Tetrahedron Lett.* **1980**, *106*, 3054. (c) Landvatter, E. F.; Rauchfuss, T. B. *Organometallics* **1982**, *1*, 506. (d) Lee, H.; Jun, C.-H. *Bull. Korean Chem. Soc.* **1995**, *16*, 66.
2. (a) Albinati, A.; Anklin, C. G.; Pregosin, P. S. *Inorg. Chim. Acta* **1984**, *90*, L37. (b) Anklin, C. G.; Pregosin, P. S. *J. Organomet. Chem.* **1983**, *243*, 101.
3. Suggs, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 640.
4. (a) Jun, C.-H. *Bull. Korean Chem. Soc.* **1989**, *10*, 404. (b) Jun, C.-H.; Kang, J.-B.; Lim, Y.-G. *Bull. Korean Chem. Soc.* **1991**, *12*, 251. (c) Jun, C.-H.; Han, J.-S.; Kang, J.-B.; Kim, S.-I. *Bull. Korean Chem. Soc.* **1994**, *15*, 204.
5. (a) Jun, C.-H. *J. Organomet. Chem.* **1990**, *390*, 361. (b) Jun, C.-H.; Kang, J.-B. *Bull. Korean Chem. Soc.* **1989**, *10*, 114. (c) Jun, C.-H.; Kang, J.-B. *Bull. Korean Chem. Soc.* **1993**, *14*, 153. (d) Jun, C.-H. *Organometallics* **1996**, *15*, 895.
6. (a) Suggs, J. W.; Wovkulich, M.; Cox, S. D. *Organometallics* **1985**, *4*, 1101. (b) Suggs, J. W.; Jun, C.-H. *J. Am. Chem. Soc.* **1986**, *108*, 4679.
7. (a) Johnson, B. F. G.; Lewis, J.; Yarrow, D. J. *J. Chem. Soc., Danton Trans*, **1974**, 1054. (b) Porri, L.; Lionetti, A.; Allegra, G.; Immirzi, A. *J. Chem. Soc., Chem. Comm.* **1965**, 336. (c) Nelson, S. M.; Sloan, M. S.; Drew, M. G. B. *J. Chem. Soc., Dalton, Trans.* **1973**, 2195.
8. Van der Ent, A.; Onerdelinden, A. L. *Inorg. Syn.* **1973**, *14*, 92.
9. *syn*-η^3-2-ethylidenecyclohexyl rhodium(III) complex (**7**): ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 10.8 (d, 1H, J=8.7 Hz, H of C-2 in quinoline), 8.5-7.4 (m, 5H, Hs of quinoline ring), 4.8 (d, J=5.1 Hz, 1H, *anti*-H1 of η^3-allyl group), 4.1 (q, J=6.3 Hz, 1H, *anti*-H3 of η^3-allyl group), 2.8-1.0 (m, 6H, saturated Hs of cyclohexyl group), 1.5 (d, J=6.3 Hz, 3H, *syn*-CH_3); ^{13}C NMR (50.5 MHz, $CDCl_3$) δ (ppm) 153-122 (Cs of quinoline & pyridine), 63.2 (d, J=9.4 Hz, C1 in η^3-allyl group), 58.6 (d, J=10.3 Hz, C3 in η^3-allyl group), 25.2, 22.5, 21.0, 20.1 (four methylene carbons of cyclohexyl group), 12.0 (carbon in *syn*-CH_3 group).
10. **8**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.9 (dd, J=1.8 Hz, 4.2 Hz, 1H, H2 in quinoline group), 8.2-7.3 (m, 5H, quinoline), 5.4 (s, 1H, vinylic H), 4.4 (q, J=6.8 Hz, 1H, α-CH to CO), 1.9 (m, 4H, 4,5-Hs in cyclohexenyl group), 1.4 (m, 4H, allylic Hs in cyclohexenyl group), 1.4 (d, J=6.9 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 208 (CO), 150-121 (Cs of quinoline & vinylic carbons), 54.9 (α-carbon to CO), 26.4, 25.4 (allylic carbons in cyclohexenyl group), 22.9, 22.2 (C4, C5-carbons in hexenyl group), 14.6 (CH_3); IR spectrum (neat) 3020, 2920, 1685 (CO), 1594, 1570, 1496, 1451, 1363, 1320, 1269, 1168, 1051, 923, 832, 794, 655 cm^{-1}; mass spectrum. m/e (assignment, relative intensity) 266 (M^++1, 1.7), 265 (M^+, 8.4), 264 (M^+-1, 19.4), 250 (M^+-CH_3, 2.2), 237 (15.1), 222 (10), 208 (8.0), 157 (11.5), 156 (100, quinolinylCO^+), 129 (7.3), 128 (35, quinolinyl$^+$); HRMS calcd for $C_{18}H_{19}NO$ 265.1467, found 265.1460.
11. (a) Young, J. F.; Gillard, R. D.; Wilkinson, G. *J. Chem. Soc.* **1964**, 5176. (b) Winkhaus, G.; Singer, H. *Chem. Ber.* **1966**, *99*, 3602.
12. **12**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.9 (dd, J=1.8 Hz, 4.2 Hz, 1H, H2 in quinoline group), 8.2-7.4 (m, 5H, quinoline), 5.6 (s, 2H, vinylic Hs), 3.4 (t, J=7.0 Hz, 2H, α-CH_2 to CO), 2.1 (m, 4H, allylic Hs in cyclohexenyl group), 1.76 (m, 2H, β-CH_2 to CO), 1.60 (m, 1H, H in C-1 in hexenyl group), 1.26 (m, 2H, Hs in C-6 in hexenyl

group); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 207.2 (CO), 150.4-121.4 (Cs of quinoline & vinylic carbons), 42.5 (α-carbon to CO), 33.3, 31.7, 31.0, 28.7, 25.2 (β-carbon & saturated carbons in cyclohexenyl group); IR spectrum (neat) 3040, 2929, 2856, 2835, 1691 (CO), 1595, 1571, 1496, 1447, 1369, 1331, 1256, 1170, 1135, 1117, 1046, 960, 935, 917, 829, 795, 763, 633 cm^{-1}; mass spectrum. m/e (assignment, relative intensity) 265 (M^+, 5.1), 264 (M^+-1, 9.2), 185 (M^+-C_6H_9+1, 17.7), 184 (M^+-C_6H_9, 67.4), 171 (M^+-C_7H_{11}+1, 13.6), 170 (M^+-C_7H_{11}, 8.8), 156 (50, quinolinylCO$^+$), 129 (29.4), 128 (31.4, quinolinyl$^+$); HRMS calcd for $C_{18}H_{19}NO$ 265.1467, found 265.1464.

13. (a) Bingham, D.; Webster, D. E.; Wells, P. B. *J. Chem. Soc., Dalton Trans.* **1974**, 1514. (b) *ibid*, **1974**, 1519.
14. (a) Arthurs, M.; Regan, C. M.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1980**, 2053. (b) Arthurs, M.; Sloan, M.; Drew, M. G. B.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1975**, 1974. (c) Bingham, D.; Hudson, B.; Webster, D.; Wells, P. B. *J. Chem. Soc., Dalton Trans.* **1974**, 1521.

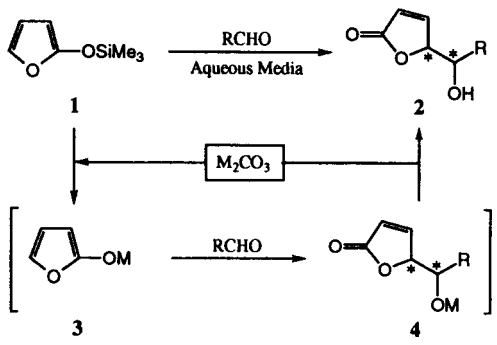
Diastereoselective Coupling Reaction of Moisture Sensitive 2-(Trimethylsilyloxy)furan with Aldehydes in Aqueous Media

Chan-Mo Yu*, Jongho Lee, Sung-Soo Lee, Ha-Soon Choi, and Seung-Ki Park†

Department of Chemistry, Sung Kyun Kwan University, Suwon 440-746, Korea
†Department of Chemsistry, The University of Suwon, P.O.Box 77, Suwon 445-743, Korea

Received September 23, 1996

The availability of efficient synthetic methodology for achieving diastereoselectivity in the construction of stereochemically rich compounds is of considerable current interest because allowed structures are featured in many useful substances.[1] In this regard, the aldol reaction and its numerous variants provide an excellent stereoselective route to β-hydroxy carbonyl compounds.[2] Even though the aldol reaction represents one of successful stereochemical courses in organic reaction, there are still limited scopes of reagents and reaction conditions for the stereoselection mainly due to equilibrium between aldolates through retroaldol and realdol.[3] In order to obtain useful levels of diastereoselectivity, specific enolates such as boron and titanium must be employed with particular substrates whereas more readily available alkali metal enolates often revealed their significant problems. We considered that the equilbrium could be controlled by the reaction in aqueous media through the protonation of aldolate from water. Recently, aqueous media or phase organic reactions have gained much attention from the organic chemist because of chemical and environmental issues.[4] According to recent report, aldol condensation of silyl enol ether with aldehyde, so called Mukaiyama aldol,[5] in aqueous solution was realized with marginal diastereoselectivity (2~1 : 1) by the use of Lewis acid catalyst.[6] In this communication we describe that the coupling reaction of moisture sensitive 2-(trimethylsilyloxy)furan with aldehydes in the presence of cataltyic amount of M_2CO_3 (M=K, Cs) in aqueous media (THF/H_2O) afforded *erythro*-selective δ-hydroxy-γ-lactones in high yield with reasonable levels of diastereoselectivity. The choice of 2-(trimethylsilyloxy)furan is based on widely applicabilities of its coupling product.[7]



Scheme 1. Plausible. Reaction Pathway.

The rationale for the aqueous media carbonyl addition is outlined in Scheme 1. The alkali metal enolate can be generated from **1** as a consequence of the Si-O bond breaking mediated by alkali carbonate. The central step in this reaction can be formulated as an addition of enolate **3** to aldehyde with competition of direct protonation, involving the formation of aldolate **4** which is readily protonated to product **2** along with regeneration of catalyst. The basic solution would offer more possibility of C-C bond formation instead of protonation.

Our initial studies began with commercially available 2-(trimethylsilyloxy)furan and hydrocinnamaldehyde under the various reaction conditions. Preliminary investigations for the coupling indicated that the conversion to the corresponding lactone **2** could be realized with alkai metal carbonates, but would be unpromising with Lewis acid. Interesting observation was made that the reaction with K_2CO_3 and Cs_2CO_3 showed much better catalytic ability than the reaction with Li_2CO_3 and Na_2CO_3; these bases were generally superior and were chosen for systematic studies. Upon optimal, the reaction was conducted by the addition of 2-(trimethylsilyloxy)furan (**1**) to the homogeneous solution of hydrocinnamaldehyde in the presence of K_2CO_3 (0.1 eq) at −20 ℃ in THF/H_2O (4 : 1). After being proceeded for 10 min at −20 ℃, the reaction mixture was quenched by the addition of 10% aqueous HCl. After usual work up procedure, final purification was effected by silica gel chromatography to afford lactone in 68% isolated yield.

Diastereoselectivities were determined unambiguously by the direct comparison of ^1H NMR spectral data of product with authentic samples prepared from the reaction of **1** with hydrocinnaldehyde in the presence of catalytic amount (0.5 eq) of BF_3OEt_2 at −78 ℃ for 4h in anhydrous CH_2Cl_2.[8] Major component of aqueous media coupling turned out to be *ery-*