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

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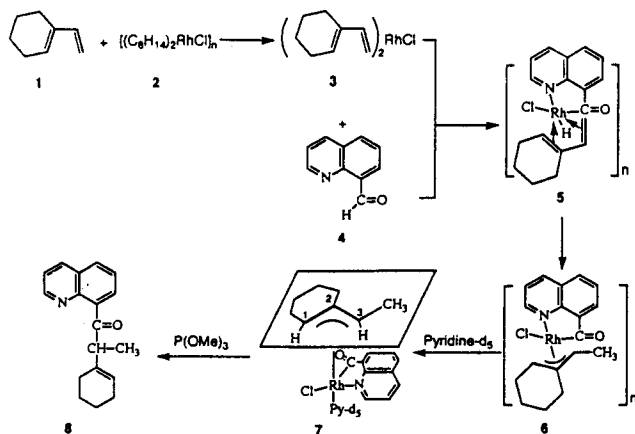*†Agency for Defense Development,*
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The C-H bond of aldehyde can be readily cleaved by transition metals through cyclometallation.[1] 8-Quinolinecarboxaldehyde is known to be one of the best models for the C-H bond cleavage with transition metals.[2] 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 η³-allyl complexes.[5] Treatment of these acylrhodium(III) alkyls or η³-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 CHCl₃ 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 CDCl₃ gave *syn*-η³-2-ethylidenecyclohexyl rhodium(III) complex 7.[9] The ¹³C 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
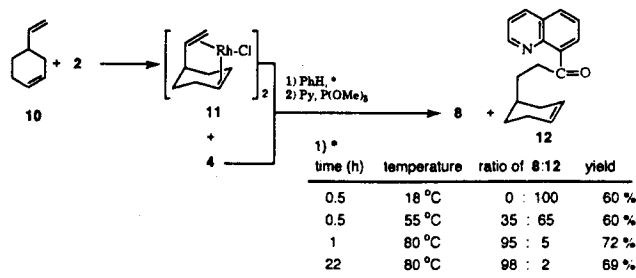
syn-methyl group) as doublets indicating that terminal two carbons in the allyl group are coupled with the Rh while that of the meso-carbon (C-2) in the allyl group hardly appears probably due to little nOe (nuclear overhauser effect) since this carbon does not contain any proton. Treatment of 7 with 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**
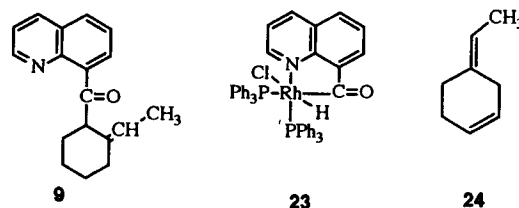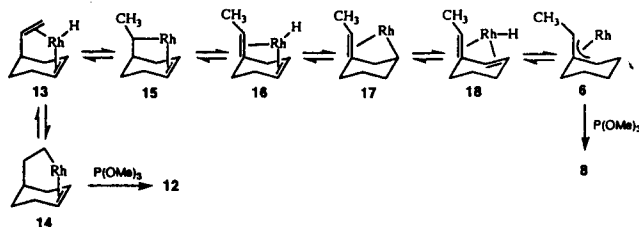
(4-Vinylcyclohexene)rhodium(I) chloride (11) can be also generated *in situ* from the reaction of 2 and nonconjugated diene, 4-vinylcyclohexene (10) at room temperature for 1 h (Scheme 2).[11] Compound 4 was allowed to react with a solution of 11 in benzene at 55 ℃ for 30 min to give a yellow precipitate. 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

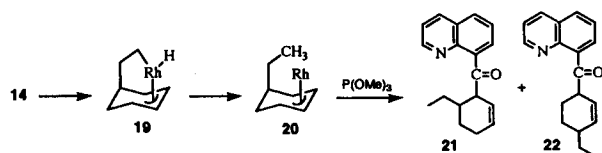| time (h)	temperature	ratio of 8:12	yield
0.5	18 ℃	0 : 100	60 %
0.5	55 ℃	35 : 65	60 %
1	80 ℃	95 : 5	72 %
22	80 ℃	98 : 2	69 %

Scheme 1.

Scheme 2.

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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-η³-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 η³-2-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**.

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9. syn-η³-2-ethylidenecyclohexyl rhodium(III) complex (7): ¹H NMR (200 MHz, CDCl₃) 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 η³-allyl group), 4.1 (q, *J*=6.3 Hz, 1H, *anti*-H3 of η³-allyl group), 2.8-1.0 (m, 6H, saturated Hs of cyclohexyl group), 1.5 (d, *J*=6.3 Hz, 3H, *syn*-CH₃); ¹³C NMR (50.5 MHz, CDCl₃) δ (ppm) 153-122 (Cs of quinoline & pyridine), 63.2 (d, *J*=9.4 Hz, C1 in η³-allyl group), 58.6 (d, *J*=10.3 Hz, C3 in η³-allyl group), 25.2, 22.5, 21.0, 20.1 (four methylene carbons of cyclohexyl group), 12.0 (carbon in *syn*-CH₃ group).

10. 8: ¹H NMR (300 MHz, CDCl₃) 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, CH₃); ¹³C NMR (75 MHz, CDCl₃) 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 (CH₃); 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⁺-CH₃, 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 C₁₈H₁₉NO 265.1467, found 265.1460.

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12. 12: ¹H NMR (300 MHz, CDCl₃) 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-CH₂ to CO), 2.1 (m, 4H, allylic Hs in cyclohexenyl group), 1.76 (m, 2H, β-CH₂ to CO), 1.60 (m, 1H, H in C-1 in hexenyl group), 1.26 (m, 2H, Hs in C-6 in hexenyl

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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$_6$H$_9$+1, 17.7), 184 (M$^+$-C$_6$H$_9$, 67.4), 171 (M$^+$-C$_7$H$_{11}$+1, 13.6), 170 (M$^+$-C$_7$H$_{11}$, 8.8), 156 (50, quinoliny-lCO$^+$), 129 (29.4), 128 (31.4, quinolinyl$^+$); HRMS calcd for C$_{18}$H$_{19}$NO 265.1467, found 265.1464.

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

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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
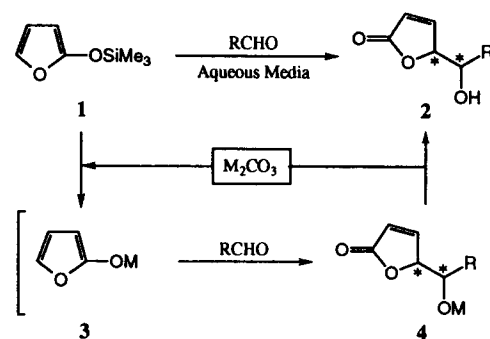
Scheme 1. Plausible. Reaction Pathway.

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$_2$CO$_3$ (M=K, Cs) in aqueous media (THF/H$_2$O) 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]

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$_2$CO$_3$ and Cs$_2$CO$_3$ showed much better catalytic ability than the reaction with Li$_2$CO$_3$ and Na$_2$CO$_3$; 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$_2$CO$_3$ (0.1 eq) at -20 ℃ in THF/H$_2$O (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 ^{1}H 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$_3$OEt$_2$ at -78 ℃ for 4h in anhydrous CH$_2$Cl$_2$.[8] Major component of aqueous media coupling turned out to be *ery-*