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2. (a) J. T. Park, Ph. D. Thesis, University of Illinois at Urbana (1983); (b) M. R. Churchill and Y. -J. Li, *J. Organomet. Chem.*, **291**, 61 (1985).
3. Compound **1**: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.2-7.14 (m, 4H), 5.30 (s, 5H), 3.54-3.44 (m, 2H), 2.36 (s, 3H); IR (CCl_4) ν (CO) 2095 (m) 2064 (s), 2032 (sh), 2022 (s), 2011 (s), 1978 (m) cm^{-1}; MS (70eV, ^{98}Mo, ^{192}Os) *m/z* 1180 (M^+).
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5. Compound **2**: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.19-7.12 (m, 4H), 5.33 (s, 5H), 3.74-3.56 (m, 2H), 2.35 (s, 3H), −12.2 (s, 1H), −17.6 (s, 1H); ^{13}C-NMR (75 MHz, CD_2Cl_2, −10 ℃) δ 224.7, 187.2, 185.1, 180.2, 177.4, 176.1, 175.9 (d, $^2J_{CH}$=11.8 Hz), 174.5, 173.4 (acyl), 168.9 (d, $^2J_{CH}$=7.3 Hz), 168.0; IR (CCl_4) ν (CO) 2119 (m), 2076 (s), 2059 (vw), 2045 (s), 2033 (sh), 2024 (m), 2012 (vs), 2000 (sh), 1981 (m), 1946 (m) cm^{-1}.
6. Compound **3a**: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.17-7.27 (m, 4H), 6.67 (dd, 1H, J=8.6 Hz, J=6.4 Hz), 5.90 (s, 5H), 4.01 (dd, 1H, J=14.4 Hz, J=6.4 Hz), 3.52 (dd, 1H, J=14.4 Hz, J=8.6 Hz), 2.39 (s, 3H), −16.6 (s, 1H); MS (70eV, ^{98}Mo, ^{192}Os) *m/z* 1126 (M^+). Compound **3b**: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.14-7.27 (m, 4H), 5.89 (s, 5H), 5.70 (dd, 1H, J=8.7 Hz, J=6.4 Hz), 3.71 (dd, 1H, J=14.5 Hz, J=6.4 Hz), 3.37 (dd, 1H, J=14.5 Hz, J=8.7 Hz), 2.38 (s, 3H), −19.2 (s, 1H). Compound **3c**: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.14-7.23 (m, 4H), 6.59 (dd, 1H, J=11.4 Hz, J=5.9 Hz), 5.38 (s, 5H), 4.74 (dd, 1H, J=12.2 Hz, J=5.9 Hz), 2.52 (dd, 1H, J=12.2 Hz, J=11.4 Hz), 2.40 (s, 3H), −18.6 (s, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$, −10℃) δ 189.0, 185.2, 185.1, 182.4, 176.1, 175.2, 170.2, 169.7 (d, $^2J_{CH}$=13.1 Hz), 168.3 (d, $^2J_{CH}$=9.8 Hz), 140.5 (d, $^1J_{CH}$=140.6 Hz, alkylidene carbon); IR (C_6H_{12}) ν (CO) 2086 (s), 2060 (vs), 2028 (vs), 2012 (s), 2000 (m), 1990 (w), 1955 (w), 1941 (m) cm^{-1}; MS (70 eV, ^{98}Mo, ^{192}Os) *m/z* 1126 (M^+). Satisfactory microanalyses (C, H) have been obtained for all new compounds.
7. Crystal data for **2**: $C_{24}H_{16}O_{11}Os_3Mo$; M=1146.9; orthorhombic; space group $Pna2_1$; a=12.966(9) Å, b=11.256(3) Å, c=38.505(10) Å; V=5620(7) Å^3; ρ (calcd)=2.71g cm^{-3}; Z=8; μ=(Mo Kα)=140 cm^{-1}. Diffraction data were collected with a CAD4 diffractometer. The structure was solved by a combination of direct method and difference Fourier technique. Two crystallographically independent molecules (**2-A** and **2-B**) were refined in alternating full matrix least-squares cycles (anisotropic thermal parameters for metal atoms and hydrogen atoms not included in the structure factor calculations). As the poor diffraction quality did not permit a well-tempered refinement, a restrained refinement procedure was employed as follows: Os-C (carbonyl)=(1.94± 0.01) Å, C-O (carbonyl)=(1.15± 0.01) Å. Furthermore, the phenyl and cyclopentadienyl rings were approximated to regular polygons with C-C= 1.39 and 1.42 Å, respectively. This refinement scheme led to convergence with R_F=9.7% and R_{wF}=9.9% for 2530 data ($F \geqq 3\sigma_F$).
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11. Crystal data for **3c**: $C_{23}H_{16}O_{10}Mo$; M=1118.9; orthorhombic; space group $Pmn2_1$; a=12.438(7), b=8.797(2), c= 11.846(4); V=1296(1) Å^3; ρ (calcd)=2.87 g cm^{-3}; Z=2; μ(Mo Kα)=152 cm^{-1}. Diffraction data were collected and treated as described for **2**. Full matrix least-squares refinement with the disordered model (anisotropic thermal parameters for the metal atoms) led to convergence with R_F=5.6% and R_{wF}=5.5% for 999 data ($I \geqq \sigma_I$).
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The Hydrometallation of Vinylcyclopropane by the Rh-H Gernerated from C-H Bond Activation

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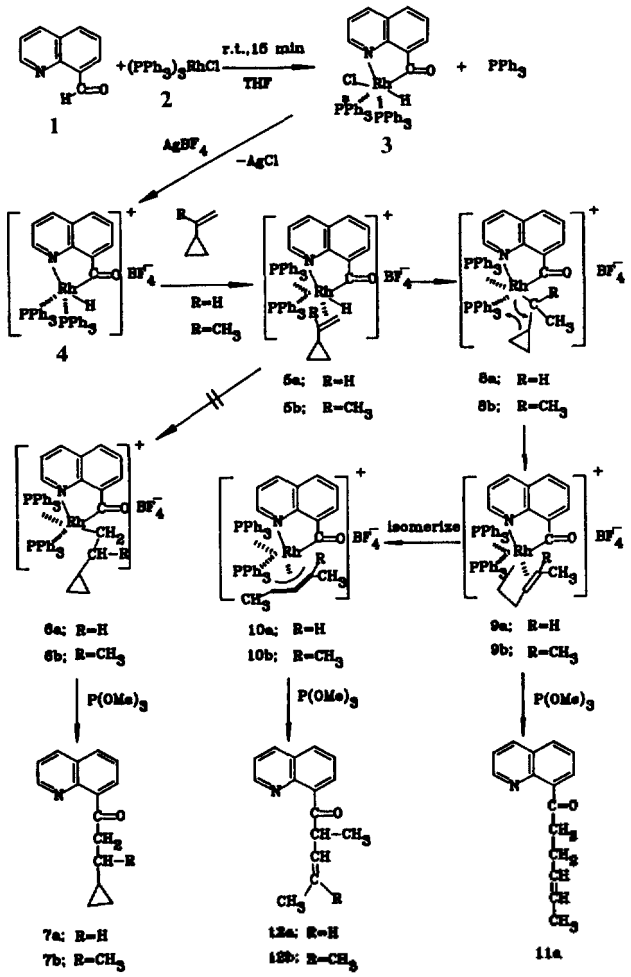
C-H bond activation is one of the recent interests in organometallic chemistry[1]. Although the C-H bond of aldehyde can be easily cleaved by transition metals, subsequent decarbonylation of the acylmetal hydride and reductive-elimination of the resulting alkylmetal hydride gives alkane[2]. This decarbonylation can be prevented by cyclometallation, since a five-membered ring is the right size for a stable metallacycle complex[3]. The C-H bond activation of 8-quinolinecarboxaldehyde (**1**), a good cyclometallation substrate, by Wilkinson's complex (**2**) gives a stable acylrhodium(III) hydride (**3**) (Scheme 1)[4]. This report describes the hydrometallation of the acylrhodium(III) hydride **3** into vinylcyclopropanes and subsequent ring-cleavage of the cyclopropyl group of the hydrometallated intermediate complexes.

Compound **1** was allowed to react with a solution of **2** in THF at room temperature for 15 min. The white precipitate was isolated in 95% yield with addition of pentane to the resulting reaction mixture and characterized as a stable acyl rhodium(III) hydride **3**, the coordinatively saturated complex[4]. Addition of one equivalent of $AgBF_4$ into the complex **3** in THF generated a vacant coordination site like **4**,



Schem 1.

a coordinatively unsaturated 16-electron species, since Ag^+ abstracted a chloride from **3** to afford precipitation of AgCl. Vinylcyclopropane[5] was added to the solution of **4** and the reaction mixture was stirred for 30 min at room temperature to give a brown solution. Without further isolation of the complexes, the ligand promoted reductive-elimination[6] of this resulting mixtures by trimethyl phosphite gave 8-quinolinyl pent-3'-enyl ketone (**11a**) and 8-quinolinyl pent-3'-en-2'-yl ketone (**12a**) in a 4:6 ratio in 92% overall yield, after chromatographic isolation; **11a**: ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 8.9 (dd, J=4.2 Hz, J=1.8 Hz, 1H, H of C-2 in quinoline) 8.2-7.3 (m, 5H, Hs of quinoline) 5.5 (m, 2H, -CH=CH-) 3.3 (t, J=7.5Hz, 2H, $COCH_2$) 2.4 (m, 2H, $-CH_2$-CH=) 1.6 (d, 3H, =C-CH_3); ^{13}C-NMR (50.5 MHz, $CDCl_3$) δ (ppm) 150-121 (Cs of quinoline & -CH=CH-) 44.6 (s, C of α-CH_2 to CO) 22.0 (s, C of β-CH_2 to CO) 16.6 (s, C of CH_3); **12a**: ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 8.9 (dd, J=4.2 Hz, J=1.8 Hz, 1H, H of C-2 in quinoline) 8.2-7.4 (m, 5H, Hs of quinoline) 5.5 (m, 2H, -CH=CH-) 4.5 (q, J=6.2 Hz, 1H, CO-CH) 1.6 (dd, J=4.8 Hz, J=0.8 Hz, 3H, =C-CH_3) 1.35 (d, J=6.8 Hz, 3H, CO-C-CH_3); ^{13}C-NMR (50.5 MHz, $CDCl_3$) 150-121 (m, Cs of quinoline & -CH=CH-) 50.3 (s, α-C to CO) 17.9 (C of CH_3 in =CH-CH_3) 16.4 (C of CH_3 in CO-CH-CH_3); IR (neat) 2960, 2940, 1680, 1565, 1490, 1250, 963, 830 cm^{-1}; mass spectrum, m/e: 225 (M^+), 224 (M^+-1), 210, 196, 156; TLC R_f=0.50, hexane: ethylacetate=5:2, SiO_2. Although the metal complexes were not completely characterized because of complication of the ^{1}H-NMR spectra for two complex mixtures, the structures of the acylrhodium(III) pent-3'-enyl complex (**9a**) and the acylrhodium(III)-η^3-1,3-dimethylallyl complex (**10a**)[7] were inferred from the reductive-elimination products, **11a** and **12a**. Under prolonged reaction times (24 hrs) to allow complete isomerization of **9a**, only **12a** was isolated in 90% yield. Already the allyl-hydrido mechanism has been proposed for the isomerization of the acylrhodium(III) alkenyl complexes to the acylrhodium(III) η^3-allyl complexes with some evidences[7,8]. One of the interesting features was the hydride addition into vinylcyclopropane in 5a. When vinylcyclopropane was hydrometallated in **5a**, two possible positional isomers such as **6a** and **8a** might be formed. Even though **6a** has a higher stability owing to primary C-Rh bond compared with that of **8a** which has a secondary C-Rh bond which causes more steric congestion, any evidence for generating **6a** or **7a** has not been observed. Instead, the hydride inserted into the terminal olefinic carbon of vinylcyclopropane in **5a** to give the cyclopropylcarbinyl rhodium(III) complex (**8a**) as a transient intermediate, and the consecutive C-C bond cleavage of the cyclopropyl group afforded **9a**. The reason for generating **8a**, not **6a**, is not clear, but the formation of the cyclopropylcarbinyl group of **8a** and a subsequent ring-opening of the cyclopropyl group to generate the strain-free alkenyl group of **9a** may give a driving force for this reaction. The ring-cleavages of the cyclopropyl-or cyclobutyl carbinyl rhodium(III) complexes generated from hydride insertion into methylenecyclopropane and methylenecyclobutane, have been reported[8,9]. The rapid isomerization of the cyclopropylcarbinyl radical to the allyl carbinyl radical is well known in free radical chemistry[10]. Since there are many evidences that both the 'insertion' and the hydrogenation reaction of the transition metal hydrides proceed *via* the radical pair mechanism rather than *via* conventional migratory insertion processes[11], it is possible to explain the formation of the stable secondary alkyl radical in **8a** rather than that of the less stable primary alkyl radical in **6a** with hydrogen atom transfer. The evidence for the radical formation by Rh-C bond homolysis[12] due to the relatively weak Rh-C bond in the quinolinyl acylrhodium(III) alkyl complex may give a clue for the Rh-H bond homolysis to generate a hydrogen atom which can be transferred into olefin forming alkyl radical. This kind of hydrogen atom transfer mechanism from the metal hydride complex to vinylcyclopropane has been proposed recently[13].

Very interesting result was obtained from the reaction of **4** and α-methyl vinylcyclopropane, more sterically hindered olefin than vinylcyclopropane. α-methyl vinylcyclopropane was added to the solution of **4** and the resulting solution was stirred overnight at room temperature to allow complete isomerization of **9b**. Ligand-promoted reductive-elimination of the resulting dark brown solution of **10b** by a mixture of pyridine and trimethylphosphite gave only 8-quinolinyl 4'-methyl-3'-en-2'-yl ketone (**12b**) in 97% yield after chromatographic isolation; **12b**: ^{1}H-MNR (200 MHz, C_6D_6) δ (ppm) 8.6 (dd, J=4.2 Hz, J=1.8 Hz, 1H, H of C-2 in quinoline) 7.7-6.7 (m, 5H, Hs of quinoline) 5.3 (d, J=9.8 Hz, 1H, -CH=) 4.9 (q, J=6.7 Hz, 1H, CO-CH) 1.5 (d, J=6.7 Hz, 3H, CO-C-CH_3) 1.48 (s, 3H, C=C-CH_3) 1.26 (s, 3H, C=C-CH_3); ^{13}C-NMR (50.5 MHz, C_6D_6) δ (ppm) 150-121 (Cs of quinoline

& -CH=) 47.1 (s, C of α-CH to CO) 25.6 (s, C of CH_3 in =C-CH_3) 18 (s, C of CH_3 in =C-CH_3) 16.8 (s, C of CH_3 in CO-CH-CH_3); IR (neat) 3040, 2970, 2930, 2870, 1690, 1570, 1492, 1450, 1375, 1260, 1170, 1065, 955, 825, 795 cm^{-1}; mass spectra, m/e; 239 (M^+), 224 (M^+-CH_3), 211 (M^+-CO), 156, 128; TLC R_f=0.55, hexane; ethylacetate=2;5, SiO_2. The reaction mechanism is similar to that of vinylcyclopropane. Hydrogen addition to the terminal olefinic methylene group of α-methyl vinylcyclopropane in **5b** gave **8b**, a sterically much more congested cyclopropylcarbinyl complex than **6b**. Ring-opening of cyclopropyl group of 8b and subsequent isomerization of the resulting **9b** gave **10b**. Above hydride insertion reaction, **5** to **8**, follows the Markovnikov's rule which is the unusual cases for the hydrometallation due to the steric hindrance. All these results confirm the radical involvement in hydrogen atom insertion in **5** to generate secondary or tertiary alkyl complexes of **8**. More detailed mechanistic investigation is under study.

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Characteristic Oxidative Aromatization Pattern of Isophorone, 4-Hydroxyisophorone, and Rearrangement of 4-Oxoisophorone Under a Strong Acidic Condition

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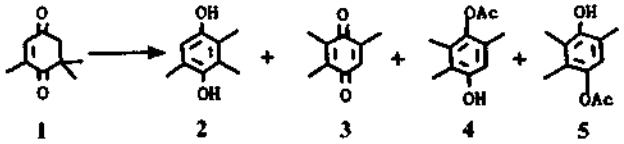
2,3,5-Trimethyl-1,4-hydroquinone (**2**), an intermediate for the production of vitamin E[1], is being prepared by rearrangement of 4-oxoisophorone[4], or by oxidation of trimethylphenols[2], isophorone[3a], or 2,5,6-trimethyl-2-cyclohexen-1-one[3b]. Thus, much attention has been paid to the preparation of 4-oxoisophorone[4], or trimethylphenols[5a]. During our investigation on the method for the production of 2,3,5-trimethyl-1,4-hydroquinone (**2**)[6], we found that 4-oxoisophorone (**1**) was converted to the 2,3,5-trimethyl-1,4-hydroquinone under an acidic condition[1b]. Thus, we examined the products formed from isophorone and 4-hydroxyisophorone when treated similarly with sulfuric acid, and isolated many products which seemed to be formed by multiple oxidations and rearrangements. The results are summarized in Table 1.

Table 1. Products (yields, %) Formed on Treatment of Isophorone (**6**), 4-hydroxyisophorone (**7**) and 4-oxoisophorone (**1**) with Sulfuric Acid

Starting material	Products, yields (%)						
	3	**4**	**5**	**11**	**12**	**13**	**14**
isophorone (**6**)	–	–	–	46	1	9	1
4-hydroxyisophorone(**7**)	–	–	–	11	36	23	2
4-oxoisophorone (**1**)	37	24	7	–	–	–	–



1 **2** **3** **4** **5**

Scheme 1.

As shown in Table 1, when 4-oxoisophorone (**1**) was dissolved in acetic anhydrde to give a 5% solution and added with concentrated sulfuric acid (5 eq) portion by portion at room temperature, 2,3,5-trimethyl-1,4-benzoquinone (**3**), 2,3,5-trimethyl-4-acetoxyphenol (**4**), and 2,3,6-trimethyl-4-acetoxyphenol (**5**) were isolated in 37%, 24% and 7% yields, respectively[7]. However, 4-hydroxyisophorone (**7**) was converted to completely unexpected products under a similar treatment of sulfuric acid; 3,4,5-trimethylphenol (**13**)[5b], 2,3,5-trimethylphenol (**14**), 3,4,5-trimethyl-1,2-hydroquinone (**12**)[7], and 4,5-dimethyl-3-hydroxymethylphenol (**11**)[7] were isolated in 23%, 2%, 36%, and 11% yields, respectively. Treatment of isophorone (**6**) with sulfuric acid gave similar products as in the case of 4-hydroxyisophorone (**7**); 3,4,5-trimethylphenol (**13**), 2,3,5-trimethylphenol (**14**), 4,5-dimethyl-3-hydroxymethylphenol (**11**) and 3,4,5-trimethyl-1,2-hydroquinone (**12**) were isolated in 9%, 1%, 46%, and 1% yields, respectively. The reaction proceeded at room temperature in 3-4 hrs.

Clearly, the products obtained from 4-oxoisophorone (**1**) should occur by an acid catalyzed rearrangement to give 2,3,6-trimethyl-1,4-hydroquinone (**2**), which was further oxidized or acetylated to the final products. However, formation of the prducts obtained from 4-hydroxyisophorone (**7**) and from isophorone (**6**) was not mechanistically quite clear. The phenols (**11-14**) obtained from isophorone (**6**) seemed to be produced by multiple oxidations of the carbonium ions formed by protonation on the oxygen atom of the carbonyl group followed by rearrangements (Scheme 2).

To prove the multiple oxidative rearrangement mecha-