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Catalytic and Stoichiometric Hydroacylation of Olefin Derivatives with 8-Quinolinecarboxaldehyde by Rh(I)

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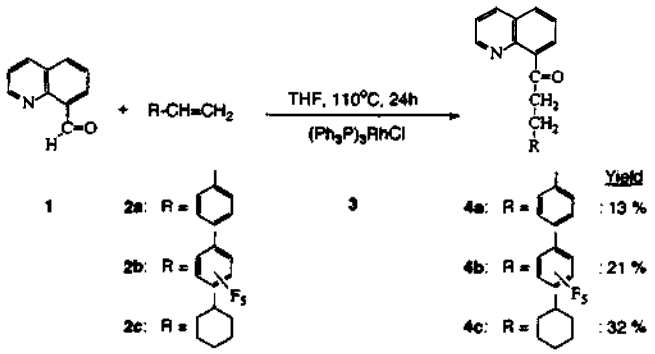
Catalytic hydroacylation has been achieved by the reaction of 8-quinolinecarboxaldehyde (**1**) and various vinyl derivatives such as **2a**, **2b** and **2c** with Wilkinson's complex (**3**) to give linear alkyl ketones, **4a**, **4b** and **4c**, respectively. However, stoichiometric ligand-promoted hydroacylation of **2a** and **2b** with $[(C_8H_{14})_2RhCl]_2$ (**5**) resulted in a mixture of the branched alkyl ketones and the linear alkyl ketones in different ratios. Stoichiometric hydroacylation of some other olefin derivatives such as **6**, **11**, **12** and **26**, produced functionalized alkyl ketone compounds.

Introduction

The activation of C-H bond by transition metals is one of current interests in organometallic chemistry.[1] Especially, aldehydic C-H bond cleavage and its application to organic synthesis of ketone through hydroacylation have received much interest.[2] One major limitation for this process is decarbonylation.[3] There are some ways to overcome this limitation; for example, pressurizing the reaction with carbon monoxide or using special aldehyde such as 8-quinolinecarboxaldehyde and 2-iminopicoline systems which can cyclometallate the catalyst. Although carbon monoxide pressure retards decarbonylation of the acylmetal hydride intermediate formed from the aldehydic C-H bond cleavage by metal complexes, the reaction still requires vigorous conditions.[4] 8-Quinolinecarboxaldehyde is a good cyclometallation substrate, since it does not show any decarbonylation due to its formation of the stable 5-membered metallacyclic complex.[5]

As a model study for hydrometallation through C-H bond activation, hydroacylation has been applied to many different reactions such as C-C bond cleavage of the strained ring molecule,[6] synthesis of β, γ-unsaturated ketones,[7] and the elucidation of olefin isomerization mechanism.[8] Recently, catalytic hydroacylation of α, ω-diene has been repored.[9] In this paper, we report the results of the catalytic hydroacylation and the stoichiometric ligand-promoted hydroacylation



Scheme 1. Catalytic hydroacylation of vinyl derivatives with 8-quinoline-carboxaldehyde (**1**) under 10 mol% Wilkinson's complex (**3**).

of various vinyl derivatives.

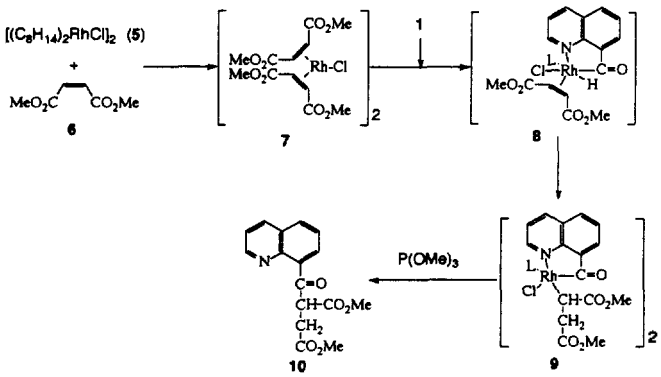
Results and Discussion

Compound **1** reacted with styrene (**2a**) at 110℃ for 24 h in the presence of 10 mol% Wilkinson's complex (**3**) to give 8-quinolinyl 2-phenylethyl ketone (**4a**) in 13% yield after chromatographic isolation (Scheme 1). Under the identical reaction conditions, hydroacylation of 2,3,4,5,6-pentafluorostyrene (**2b**) and vinylcyclohexane (**2c**) with **1** gave 8-quinolinyl 2-pentafluorophenylethyl ketone (**4b**) and 8-quinolinyl 2-cyclohexylethyl ketone (**4c**) in 21% and 32% yields, respectively.

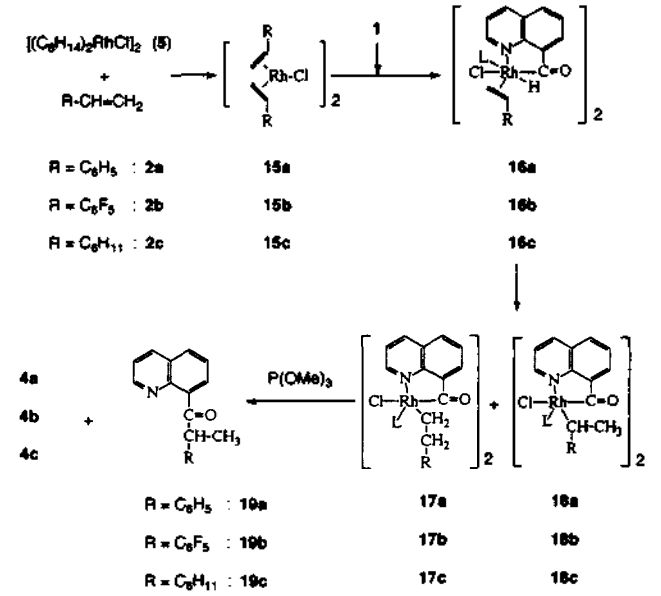
Hydroacylation has close similarity to hydroformylation in terms of hydrometallation of olefins by the metal hydride intermediate. In the case of hydroformylation, the branched alkyl aldehydes were usually produced as side products in addition to the linear ones.[10] However, in the above metioned catalytic hydroacylation, any branched alkyl ketone was not obtained. The reason must be that the hydride, formed from C-H bond cleavage of **1** by Rh(I) in **3**, might migrate into the vinyl group according to anti-Markownikoff's rule due to the steric hindrance.

As olefins to be hydroacylated, the functionalized olefins such as dimethyl maleate (**6**), triethoxylvinylsilane (**11**) or methyl vinyl ketone (**12**) are quite interesting, because hydroacylated products of these olefins might have various functional groups like carboxylic ester, triethoxysilyl, and δ-diketone groups, respectively. However, catalytic hydroacylation of these olefins, **6**, **11**, and **12**, with **1** did not take place with Wilkinson's complex (**3**) as a catalyst. Therefore, stoichiometric ligand-promoted hydroacylation by $[C_8H_{14})_2RhCl]_2$ (**5**) was applied to **6**, **11**, and **12**. It has been reported that dimethyl maleate can be coordinated to Rh(I) by olefin-exchange reaction of **5** with **6** to generate **7** *in situ*, which will be used for C-H bond activation in **1** (Scheme 2).[11]

Without isolation of **7**, addition of **1** gave an yellow precipitate, which was supposed to be **9**, and ligand-promoted reductive-elimination[12] of this precipitate with a mixture of pyridine and trimethylphosphite produced **10** exclusively in 75 % yield after chromatographic isolation. The mechanism can be inferred that Rh(I) in **7** might oxidatively add the aldehydic C-H bond in **1** to give **8** as a transient intermediate, and the subsequent hydride-migration into the coordinate



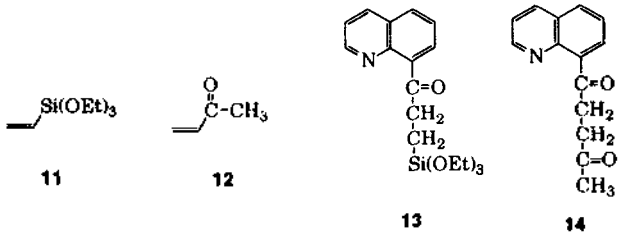
Scheme 2. Stoichiometric ligand-promoted hydroacylation of dimethylmaleate with **1** by **5** through olefin-exchange reaction (L : methyl maleate).



Scheme 3. Stoichiometric hydroacylation reaction of vinyl derivatives with 8-quinoline-carboxadehyde (**1**) by **5** through hydrometallation and reductive elimination (L : CH_2=CH-R).

maleate in **8** gave **9**.

When triethoxyvinylsilane (**11**) and methyl vinyl ketone (**12**) were used as hydroacylation substrates, 8-quinolinyl 2-triethoxysilylethyl ketone (**13**) and 8-quinolinyl 3-oxobutyl ketone (**14**) were obtained in 54% and 37% yields, respectively. Any branched alkyl ketone has not been isolated in the final product.

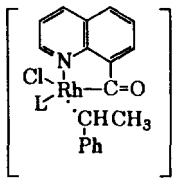


On the contrary, the stoichiometric hydroacylation of styrene (**2a**) with **1** by **5** gave quite different results. As shown in Scheme 3, the stoichiometric ligand-promoted hydroacyla-

Table 1. Stoichilmetric Hydroacylation of R-CH=CH_2 with **1** by **5** through C-H Bond Cleavage by Rh(I), Hydride-insertion, and Reductive-elimination of the Resulting Acylrhodium(III)alkyl Complexes

Entry	Starting olefin	Hydroacylated products ratio (product, **19/4**)	Isolated yield
1	**2a**	64/36 (**19a/4a**)	62%
2	**2b**	35/65 (**19b/4b**)	52%
3	**2c**	0/100 (**19c/4c**)	78%

tion of styrene (**2a**) with **1** gave a mixture of the branched alkyl ketone **19a** and the linear alkyl ketone **4a** in a 64 : 36 ratio in 62% yield (Table 1, entry 1). This result is very unusual since only linear alkyl ketone has been observed in the catalytic hydroacylation by **3**. From the ratio of **19a** and **4a**, that of pre-reductive elimination products, **18a** and **17a**, was inferred as 64 : 36. Higher yield of **18a** than that of **17a** is unreasonable on the base of the steric consideration. In some cases of a hydrogen transfer into styrene, the similar result has been reported and explained by the radical pair mechanism.[13]



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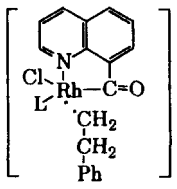

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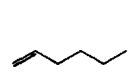
In the intermediate **16a**, a hydride insertion into the coordinated styrene might generate the complex **20** in perference to the complex **21**, since the benzyl radical **20** is much more stable than the primary alkyl radical **21**, although sterically the complex **21** is more stable than the complex **20**. Moreover, contrary to catalytic reaction with **3**, $(Ph_3P)_3RhCl$, the stoichiometric reaction with **5** does not experience the severe steric hindrance due to the absence of the sterically demanding triphenylphosphine in intermediate **18a**. In case of **2b**, the ratio of **19b** and **4b** was dropped to 35 : 65 (Table 1, entry 2). It is not clear whether the pentafluorophenyl group less stablizes the benzylic carbon radical than the phenyl group or the former experiences a little bigger steric hindrance than the latter in **20**. The use of vinylcyclohexane (**2c**) for the stoichiometric hydroacylation supports the plausibility of the radical pathway for styrene derivatives, because it gave the linear alkyl ketone **19c**, exclusively. This can be explained by that the cyclohexyl group would make much smaller contribution to the stability of the radical intermediate analogous to **20**, even though the size of the cyclohexyl group in **18c** is comparable to that of the pentafluorophenyl group in **18b**.

The results of the stoichiometric hydroacylation of **2a**, **2b**, and **2c** also can be explained by the steric effect of R group in olefin. However, when 1-hexene (**22**), in which the alkyl substituent is less sterically hindered *n*-butyl group compared with those of **2a**, **2b**, and **2c**, was used in the stoichiometric hydroacylation, 8-quinolinyl 1-hexyl ketone (**23**) was obtained in 80% yield. Trace amount (about 1.6%) of presumed 8-quinolinyl hex-2-yl ketone (**24**) was detected by GC-MSD. This result supports the formation of the benzyl radical intermediate for styrene derivatives. Predominant formation of the linear alkyl ketone from 1-hexene is hard to be explained on the base of the steric effect in connection with the results of the other vinyl derivatives, **2a**, **2b**, and **2c**. In case of methyl vinyl ketone (**12**), even though the ketone group can stabilize the α-carbon radical which should have given the secondary alkyl radical, the stable 5-membered ring metallacycle intermediate **25** might play an important role in this reaction to give the linear product, exclusively.



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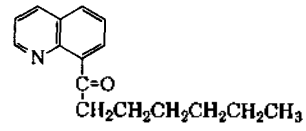

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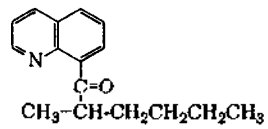

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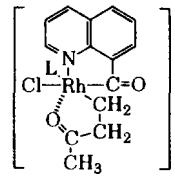

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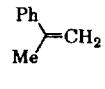
Another interesting olefin substrate is α-methylstyrene (**26**). The hydrogen transfer to this olefin was expected to give **29** as an intermdiate because it might generate very stable tertiary α-dimethylbenzyl radical. However, stoichiometic ligand-promoted hydroacylation of **26** produced only **27**. Compound **28** has not been detected in this reaction, maybe due to the strong contribution of the steric bulkiness of α-dimethylbenzyl group.



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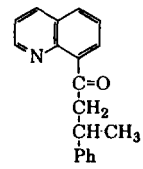

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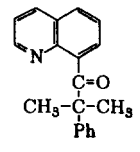

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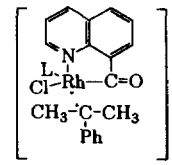

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Up to now, the hydroacylation of the olefin drivatives were examined catalytically and stoichiometrically. Major factor which determines the regioselectivity of hydrometallation of the coordinated olefin in the metal hydride intermediate might be steric. But in case of styrene, the formation of the stable alkyl radical intermediate seems to play another major role in regioselectivity of the hydrometallation step.

Experimental

Compound **1**[14] and complex **5**[15] were prepared by the published procedures. Wilkinson's complex (**3**), styrene (**2a**), 2,3,4,5,6-pentafluorostyrene (**2b**), vinylcyclohexane (**2c**), dimethyl maleate (**6**), triethoxyvinylsilane (**11**), methyl vinyl ketone (**12**), 1-hexene (**22**) and α-methylstyrene (**26**) were purchased from Aldrich Chemical Co. and used without further purification. All solvents were distilled and stored over molecular sieves (4 Å). NMR spectra were recorded with a Bruker

AC-300F (300 MHz) or a Buker AC-200 (200 MHz) spectrometer. The chemical shifts (δ) of the ^{1}H-NMR and ^{13}C-NMR resonances are in ppm relative to internal Me_4Si. Infrared spectra were recorded with a Bruker IFS 88 FT-IR or a Perkin-Elmer 683 spectrophotometer. Microanalyses were conducted by ADD Analytical Laboratory. Mass spectra were obtained on Hewlett-Packard HP 5971A mass spectrometer equipped with a HP 5890 series II Gas Chromatograph. Column chromatography was performed on Merck Silica Gel 60.

Catalytic Hydroacylation of Styrene (2a) with 1 Using 3. A screwcapped pressure vial was charged with 0.0588 g (0.0637 mmol) of Wilkinson's complex (**3**) dissolved in 3 m*l* of THF, the solution was flushed with nitrogen, and 0.1 g (0.637 mmol) of **1** was added. To the mixture was added 0.133 g (1.28 mmol) of **2a** and allowed to be heated at 110℃ for 24 h. After cooling to room temperature, the products were extracted with 20 m*l* of ether and purified by column chromatography to give 32.6 mg (13% yield) of 8-quinolinyl 2-phenylethyl ketone (**4a**). **4a**: ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.95 (dd, J=1.81 Hz & 4.1 Hz, 1H, H-2 in quinoline group), 8.2-7.4 (m, 5H, quinoline group), 7.24 (br, 5H, C_6H_5), 3.69 (t, J=7.8 Hz, 2H, α-CH_2 to CO), 3.13 (t, J=7.8 Hz, 2H, β-CH_2 to CO); ^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 205.5 (C=O), 150.4-121.4 (C's of quinoline & phenyl group), 46.4 (α-$\underline{C}H_2$ to CO), 30.5 (β-$\underline{C}H_2$ to CO); IR (neat) 3060, 3026, 2925, 1949, 1683 (s, CO), 1594, 1569, 1496, 1453, 1359, 1287, 1255, 1167, 1099, 1059, 1030, 969, 827, 793, 750, 699 cm^{-1}; mass spectrum m/e (assignment, relative intensity) 261 (M^+, 22.8), 233 (M^+-CO, 3.7), 170 (M^+-C_7H_7, 47.5), 156 (QCO^+, 30.2), 129 (QH^+, 100). Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 81.90; H, 5.71; N, 5.29. TLC R_f=0.65, hexane : ethylacetate=5 : 2, SiO_2.

Catalytic Hydroacylation of 2,3,4,5,6-Pentafluorostyrene (2b) with 1 Using 3. Under the identical reaction conditions with catalytic experimental section using 0.248 g (1.27 mmol) of **2b** instead of **2a**, the reaction proceeded. The final extract was purified by column chromatography to give 0.473 mg (21% yield) of 8-quinolinyl 2-pentafluorophenylethyl ketone (**4b**). **4b**: ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.93 (dd, J=1.77 Hz & 4.2 Hz, 1H, H-2 in quinoline group), 8.2-7.4 (m, 5H, quinoline group), 3.72 (t, J=7.7 Hz, 2H, α-CH_2 to CO), 3.23 (t, J=7.7 Hz, 2H, β-CH_2 to CO); ^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 203.6 (C=O), 150.5-121.5 (C's of quinoline & pertafluorophenyl group), 43.4 (α-$\underline{C}H_2$ to CO), 17.6 (β-$\underline{C}H_2$ to CO); IR (neat) 3067, 3009, 2916, 1956, 1694 (s, CO), 1593, 1572, 1495, 1451, 1366, 1285, 1265, 1171, 1114, 1066, 1032, 966, 944, 832, 800, 773, 656, 604 cm^{-1}; mass spectrum m/e (assignment, relative intensity) 351 (M^+, 16.7), 331 (M^+-F-1, 6.2), 194 ($C_6F_5CH=CH_2$, 9.3), 170 (M^+-$C_6F_5CH_2$, 100), 156 (QCO^+62.7), 129 (QH^+, 75.3). Anal. Calcd for $C_{18}H_{10}F_5NO$: C, 61.55; H, 2.87; N, N, 3.99. Found: C, 62.1; H, 2.78; N, 3.91. TLC R_f=0.74, hexane : ethylacetate=5 : 2, SiO_2.

Catalytic Hydroacylation of Vinylcyclohexane (2c) with 1 Using 3. Under the identical reaction conditions with catalytic experimental section using 0.163 g (1.48 mmol) of **2c** instead of **2a**, the reaction proceeded. The final extract was purified by column chromatography to give 0.0542 g (32 % yield) of 8-quinolinyl 2-cyclohexylethyl ketone (**4c**). **4c**: ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.95 (dd, J=1.76 Hz & 4.2 Hz, 1H, H-2 in quinoline group), 8.2-7.4 (m, 5H, quinoline group), 3.33 (t, J=7.8 Hz, 2H, α-CH_2 to CO), 1.8-0.88 (m, 13H, cyclohexylmethylene group); ^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 207.4 (C=O), 150.4-121.3 (C's of quinoline), 42.5 ($\underline{C}$H in cyclohexyl group) 37.4-26.2 (C's of cyclohexyl group & β-$\underline{C}H_2$ to CO); IR (neat) 3048, 2921 (s), 2849, 1950, 1685 (s, CO), 1594, 1569, 1496, 1449, 1364, 1322, 1274, 1170, 1134, 1103, 1049, 1030, 961, 832, 793, 761, 719 cm^{-1}; mass spectrum m/e (assignment, relative intensity) 267 (M^+, 6.2), 239 (M^+-CO, 4.8), 184 (M^+-cyclohexyl, 97.8), 171 ($QC(=CH_2)OH^+$, 79.0), 156 (QCO^+, 100.0), 128 (Q^+, 50.2). Anal. Calcd for $C_{18}H_{21}NO$: C, 81.17; H, 7.57; N, 5.26. Found: C, 81.70; H, 7.49; N, 5.10. TLC R_f=0.77, hexane : ethylacetate=5 : 2, SiO_2.

Stoichiometric Hydroacylation of Dimethylmateate (6) with 1 Using Complex 5. To 0.1 g (0.28 mmol) of chlorobis(cyclooctene)rhodium (I), $[RhCl(C_8H_{14})_2]_2$ (**5**), in a 5 m*l* vial was added 0.5 g (3.5 mmol) of **6** at ambient temperature under nitrogen. The mixture was stirred at room temperature for 10 min. To this suspension was rapidly added 0.044 g (0.279 mmol) of **1** in 3 m*l* of benzene. A white-yellow precipitate formed on addition of aldehyde solution. After the reaction was allowed to proceed for 30 min, 0.5 m*l* of pyridine and 0.5 m*l* of trimethylphosphite were added, successively, during which time the precipitate was dissolved to give a clear red solution. The solution was evaporated to dryness at 80℃ under reduced pressure. The crude residue was purified by column chromatography to give 0.063 g (75% overall yield) of **10**. **10**: ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 8.92 (dd, J=1.84 Hz & 4.14 Hz, 1H, H-2 in quinoline group), 8.25-7.4 (m, 5H, quinoline group), 5.54 (t, J=7.1 Hz, 1H, α-CH to CO), 3.66 (s, 3H, MeO), 3.63 (s, 3H, MeO), 3.12 (dd, 2H, two diastereotropic protons of CH_2); ^{13}C-NMR (50.5 MHz, $CDCl_3$) δ (ppm) 198 (C=O to quinioline), 172 (CO-OMe), 170 ($\underline{C}$O-OMe), 150-121 (C's of quinoline group), 5.54 (α-$\underline{C}$H to QCO), 52.3 (-O$\underline{C}H_3$), 51.9 (-O$\underline{C}H_3$), 33.0 ($\underline{C}H_2$); IR (neat) 2980, 2940, 1730 (s, O-$\underline{C}$=O), 1680 (s, $\underline{Q}$CO), 1560, 1490, 1430, 1330, 1270, 1220, 960, 1020, 940, 830, 790 cm^{-1}; mass spectrum m/e (assignment, relative intensity) 301 (M^+, 8.21), 242 (M^+-CO_2Me, 18.1), 228 (M^+-CH_2CO_2Me, 9.3), 210 ($QCOC_2H_4CO^+$, 48.9), 182 ($QCOC_2H_4^+$, 9.5), 156 (QCO^+, 100.0), 128 (Q^+, 48.6). Anal. Calcd for $C_{16}H_{15}NO_5$: C, 63.78; H, 5.02; N, 4.65. Found: C, 63.95; H, 5.03; N, 4.64. TLC R_f=0.30, hexane : ethylacetate=5 : 2, SiO_2.

Stoichiometric Hydroacylation of Triethoxyvinylsilane (11) with 1 Using Complex 5. Under the identical reaction conditions with stoichiometric experimental section using 0.5 g (2.63 mmol) of **11** instead of **6**, the reaction proceeded. The final crude residue was purified by column chromatography to give 0.052 g (54% overall yield) of **13**. **13**: ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 8.94 (dd, J=1.83 Hz & 4.19 Hz, 1H, H-2 in quinoline group), 8.20-7.39 (m, 5H, quinoline group), 3.85 (q, J=7.0 Hz, 6H, $SiOCH_2$), 3.43 (2H, α-CH_2 to CO), 1.23 (t, J=7.0 Hz, 9H, CH_3), 1.14 (β-CH_2 to CO); ^{13}C-NMR (50.5 MHz, $CDCl_3$) δ (ppm) 206.8 (C=O), 150-121 (C's of quinoline group), 58.4 (α-$\underline{C}H_2$ to QCO), 38.1 (β-$\underline{C}H_2$ to CO); 18.2 (O-$\underline{C}H_2$), 4.5 ($\underline{C}H_3$); IR (neat) 2970, 2922, 2890, 1680 (s, $\underline{Q}$CO), 1565, 1492, 1387, 1290, 1250, 1190, 1165, 1100, 1075, 960 790 cm^{-1}; mass spectrum m/e (assignment, relative intensity) 347 (M^+, 8.21), 332 (M^+-CH_3, 50.6), 301 (M^+-$HOCH_2CH_3$, 54.1), 184 ($QCOC_2H_4^+$, 21.7), 156 (QCO^+, 100.0),

128 (Q^+, 34.6). Anal. Calcd for $C_{18}H_{25}NO_4Si$: C, 62.22; H, 7.25; N, 4.03. Found: C, 62.29; H, 7.34; N, 4.10. TLC R_f=0.57, hexane : ethylacetate=5 : 2, SiO_2.

Stoichiometric Hydroacylation of Methyl Vinyl Ketone (12) with 1 Using Complex 5. Under the identical reaction conditions with stoichiometric experimental section using 0.5 g (7.1 mmol) of **12** instead of **6**, the reaction proceeded. The final crude residue was purified by colum chromatography to give 0.027 g (37% overall yield) of **14**. **14** ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 8.96 (dd, J=1.89 Hz & 4.33 Hz, 1H, H-2 in quinoline group), 8.23-7.40 (m, 5H, quinoline group), 3.64 (t, J=6.3 Hz, 2H, α-CH_2 to QCO), 2.98 (t, J=6.3 Hz, 2H, β-CH_2 to QCO); 2.26 (s, 3H, CH_3); ^{13}C-NMR (50.5 MHz, $CDCl_3$) δ (ppm) 150-121 (C's of quinoline group), 38.8 (α-$\underline{C}H_2$ to QCO), 37.9 (β-$\underline{C}H_2$ to QCO), 30.0 ($\underline{C}H_3CO$); IR (neat) 2920, 2840, 1720-1670 (s, $\underline{Q}CO$), 1565, 1429, 1460, 1350, 1250, 1160, 830, 790 cm^{-1}; mass spectrum m/e (assignment, relative intensity) 227 (M^+, 0.17), 184 (M^+-CH_3CO, 100), 156 (QCO^+, 61.0), 128 (Q^+, 30). Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.1; H, 5.56 N, 6.29. TLC R_f=0.13, hexane : ethylacetate=5 : 2, SiO_2.

Stoichiometric Hydroacylation of Styrene (2a) with 1 Using Complex 5. Under the identical reaction conditions with stoichiometric experimental section using 0.5 g (4.8 mmol) of **2a** instead of **6**, the reaction proceeded. The final crude residue was purified by colum chromatography to give 0.042 g (62% overall yield) of a mixure of 8-quinolinyl α-methylbenzyl ketone (**19b**) and **4b** in a 64 : 36 ratio. **19a**: ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 8.97 (dd, J=1.82 Hz & 4.2 Hz, 1H, H-2 in quinoline group), 8.1-7.1 (m, 10H, quinoline & phenyl group), 5.25 (q, J=6.98 Hz, 1H, α-CH to CO), 1.66 (d, J=6.98 Hz, 3H, CH_3 to CO); ^{13}C-NMR (50.5 MHz, $CDCl_3$) δ (ppm) 207.3 (C=O), 150.4-121.3 (C's of quinoline & phenyl group), 53.2 (α-$\underline{C}H$ to CO), 17.9 ($\underline{C}H_3$); IR (neat) 1680 cm^{-1} (s, CO); mass spectrum m/e (assignment, relative intensity) 261 (M^+, 25.3), 156 (QCO^+, 100.0), 128 (Q^+, 24.0). Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 81.99; H, 5.80; N, 5.31. TLC R_f=0.64, hexane : ethylacetate=5 : 2, SiO_2.

Stoichiometric Hydroacylation of 2,3,4,5,6-Pentafluorostyrene (2b) with Using Complex 5. Under the identical reaction conditions with stoichiometric experimental section using 0.5 g (2.6 mmol) of **2b** instead of **6**, the reaction proceeded. The final crude residue was purified by colum chromatography to give 0.051 g (52% overall yield) of a mixure of 8-quinolinyl α-methyl-pentafluorobenzyl ketone (**19b**) and **4b** in a 35 : 65 ratio. **19b**: ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 8.93 (dd, J=1.85 Hz & 4.2 Hz, 1H, H-2 in quinoline group), 8.1-7.5 (m, 5H, quinoline), 5.83 (q, J=7.2 Hz, 1H, α-CH to CO), 1.56 (d, J=7.2 Hz, 3H, CH_3 to CO); ^{13}C-NMR (50.5 MHz, $CDCl_3$) δ (ppm) 207 (C=O), 150-121 (C's of quinoline & pentafluorophenyl group), 53.2 (α-$\underline{C}H$ to CO), 17.9 ($\underline{C}H_3$ to CO); IR (neat) 1685 cm^{-1} (s, CO); mass spectrum m/e (assignment, relative intensity) 351 (M^+, 0.6), 331 (M^+-F-1, 1.9), 195 ($C_6F_5CH_2CH^{2+}$, 1.9), 156 (QCO^+, 100.0), 128 (Q^+, 27.2). Anal. Calcd for $C_{18}H_{10}F_5NO$: C, 61.54; H, 2.85; N, 3.99. Found: C, 61.98; H, 2.57; N, 3.75. TLC R_f=0.69, hexane : ethylacetate=5 : 2, SiO_2.

Stoichiometric Hydroacylation of Vinylcyclohexane (2c) with 1 Using Complex 5. Under the identical reaction conditions with stoichiometric experimental section using 0.5 g (4.55 mmol) of **2c** instead of **6**, the reaction proceeded. The final crude residue was purified by colum chromatography to give 0.058 g (78% overall yield) of **4c**.

Stoichiometric Hydroacylation of 1-Hexene (22) with 1 Using Comple 5. Under the identical reaction conditions with stoichiometric experimental section using 0.5 g (2.6 mmol) of **22** instead of **6**, the reaction proceeded. The final crude residue was purified by colum chromatography to give 0.0539 g (80.2% overall yield) of 8-quinolinyl 1-hexyl ketone (**23**) which was contaminated with trace amount (1.6% based on **23**) of 8-quinolinyl hex-2-yl ketone (**24**), determined by GC-MSD and **24** cannot be clearly characterized. **23**: ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 8.94 (dd, J=1.6 Hz & 4.0 Hz, 1H, H-2 in quinoline group), 8.2-7.4 (m, 5H, quinoline), 3.3 (t, 2H, J=7.1 Hz, α-CH_2 to CO), 1.8-1.3 (m, 8H, -$(CH_2)_4$-), 0.9 (t, J=7.0 Hz, 3H, -CH_3); ^{13}C-NMR (50.5 MHz, $CDCl_3$) δ (ppm) 150-121 (C's of quinoline), 45 (α-$\underline{C}H_2$ to CO), 31.7, 29.0, 24.4 & 22.5 (-$(\underline{C}H_2)_4$-), 14.0 (-$\underline{C}H_3$); IR (neat) 2970, 2940, 2870, 1690 (C=O), 1600, 1560, 1505, 1472, 1365, 1275, 1250, 1170, 1120, 1065, 830, 785, 720, 540 cm^{-1}; mass spectrum m/e (assignment, relative intensity) 241 (M^+, 6), 231 (M^+-CO, 8), 198 (M^+-C_3H_7), 184 (M^+-C_4H_9, 67), 171 ($QC(OH)=CH_2$, 21), 156 (QCO^+, 100.0), 128 (Q^+, 39), TLC R_f=0.67, hexane : ethylacetate=5 : 2, SiO_2.

Stoichiometric Hydroacylation of α-Methylstyrene (26) with 1 Using Complex 5. Under the identical reaction conditions with stoichiometric experimental section using 0.5 g (4.2 mmol) of **26** instead of **6**, the reaction proceeded. The final crude residue was purified by colum chromatography to give 0.0324 g (42% overall yield) of 8-quinolinyl 2-phenypropyl ketone (**27**) **27**: ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 8.95 (dd, J=1.80 Hz & 4.2 Hz, 1H, H-2 in quinoline group), 8.2-7.1 (m, 10H, quinoline & phenyl group), 3.8-3.4 (m, 3H, CH_2-CH), 1.35 (d, J=6.7 Hz, 3H, CH_3); ^{13}C-NMR (50.5 MHz, $CDCl_3$) δ (ppm) 207 (C=O), 150-121 (C's of quinoline & phenyl group), 53.0 (α-$\underline{C}H_2$ to CO), 35.9 (β-$\underline{C}H$ to CO), 22.1 ($\underline{C}H_3$); IR (neat) 3020, 2960, 2920, 1685 (s, C=O), 1590, 1565, 1490, 1450, 1270, 1165, 1050, 1010, 975, 828, 790, 760, 700 cm^{-1}; mass spectrum m/e (assignment, relative intensity) 275 (M^+, 17), 170 ($QCOCH_2^+$, 41.8), 156 (QCO^+, 49), 129 (QH^+, 100). Anal. Calcd for $C_{14}H_{13}NO_2$: C, 82.88; H, 6.23; N, 5.09. Found: C, 82.90; H, 6.27; N, 5.21. TLC R_f=0.64, hexane : ethylacetate=5 : 2, SiO_2.

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Simultaneous Determination of Diffusion Coefficient and Concentration by Chronoamperometry at a Microdisk Electrode

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Two unknown values among three electrochemical values, *i.e.* electrode area, diffusion coefficient, and concentration, are simultaneously obtained by nonlinear regression analysis of a single chronoamperometric faradaic current curve at a microdisk electrode. The approach is an analytical application of the semi-empirical equation presented by Shoup and Szabo for the chronoamperometric response at a disk electrode. To demonstrate the usefulness and accuracy of this approach, the chronoamperometric current at a platinum disk electrode of 50 μm radius in solutions of $Ru(NH_3)_6^{3+}$, ferrocene, $Fe(CN)_6^{3-}$, and C_{60}, were analyzed.

Introduction

The chronoamperometric response at a disk electrode has been studied for determination of the diffusion coefficient of electroactive species[1-4]. In most cases, at least two separate measurements and the approximate expressions for chronoamperometric current were used. In this study, two unknown parameters among diffusion coefficient (D), concentration (C), and electrode radius (a), are simultaneously determined from a single chronomperometric faradaic current at a disk electrode of small radius.

In general, the physicochemical unknowns are obtained by the endeavor to fit the experimental data with the proposed model. Therefore, if the equation for the model is proven to be accurate, it can be applied to obtain unknown values. The diffusion controlled chronoamperometric response at a disk electrode was solved by Ksenzhek *et al.*[5] and Aoki *et al.*[6,7]. The former describes the current function as an integral equation of the 1st order Bessel function and the latter describes that as a serial sum of Gamma function. The calculation itself of these functions may be challenging. Therefore, both are hardly applicable to fit the experimental data. A simple semi-empirical nonlinear equation which is accurate to 0.6% in arbitrary time domain was presented by Shoup and Szabo[8]. In the electrochemical experiment where 1% error is allowed, it may be regarded as a de facto solution.

In principle, since the accurate equation is known, it can be applied to the experimental data for the analytical purpose. It can be easily analyzed by the nonlinear curve fitting or the nonlinear regression analysis using ubiquitous personal computers in electrochemical laboratories, especially a computer with a data acquisition board. In the potential step experiment, the charging current is not negligible at the beginning time, but quickly (exponentially) decreases with time[9], *i.e.* $i_c \propto \exp(-t/(R_sC_d))$ where R_s is the solution resistance and C_d is the double layer capacitance. Therefore, the time domain for dominated faradaic current can be adjusted to fit the Shoup and Szabo equation which describes the faradaic current at a disk electrode. The time domain can be extended to very short time for the high concentration of electroactive species and electrolytes. For the arbitrary concentrated solutions, the chronoamperometric faradaic current should be obtained by the total current subtracted by nonfaradaic current which can be approximated from the current in the same electrolyte solution without the electroactive species and in the same experimental conditions. In this work, the latter method is employed.

To demonstrate the usefulness and accuracy of the nonlinear regression approach, it is applied to the chronoamperometric faradaic current at a platinum disk electrode of 50 μm radius in various solutions. In result, we report values of diffusion coefficients of ferricyanide in aqueous solution,