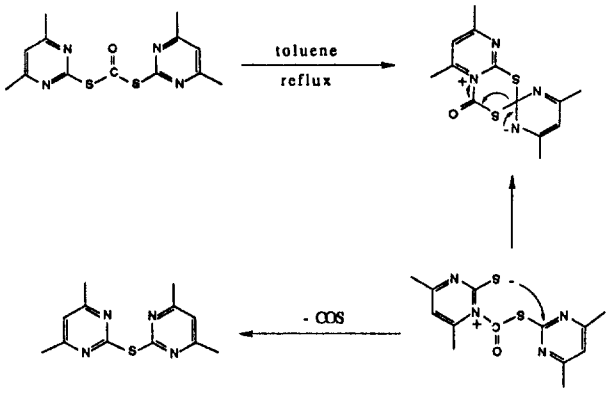

Scheme 1.

2-pyridinyl) sulfide derivatives have been reported,[3,6] we consider the present method as an useful addition to them.

The present reaction might be rationalized by the three-step sequence, as shown in Scheme 1. Thermal rearrangement of DPDC into N-acylpyrimidinum species might initiate the present reaction. A similar rearrangement has been noted with di-2-pyridyl thionocarbonate.[7] Thermal rearrangement might be followed by nucleophilic addition and elimination of carbon oxysulfide.

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References

1. S. Kim and K. Y. Yi, *Bull. Korean Chem. Soc.*, **7**, 1987 (1986).
2. S. Kim and S. S. Kim, *Synthesis*, 1017 (1986).
3. V. S. Reznik, N. G. Rashkurov, R. R. Shagidullin, and R. A. Bulgakova, *Chem. Abstract.*, **70**, 87716e (1968).
4. S. Kim, J. I. Lee and K. Y. Ko, *Tetrahedron Lett.*, 4943 (1984).
5. It was easily prepared by the reaction of oxalyl chloride with 2 equiv of 4,6-dimethyl-2-pyrimidinethiol hydrochloride in the presence of 4 equiv of triethylamine in dichloromethane.
6. (a) J. Renault, *Ann. Chim.*, **10**, 135 (1955). (b) W. Winfried, K. Schermanz, K. Schweiger, and A. Fuchsgruber, *Monatsh Chem.*, **114**, 1371 (1983).
7. S. Kim and K. Y. Yi, *J. Org. Chem.*, **51**, 2613 (1986).

C-H Bond and Ring-Strain-Induced C-C Bond Activation by Rh(I): Formation of Cycloalkylcarbinyl group and Ring-Opening Reaction of Cyclobutyl Group

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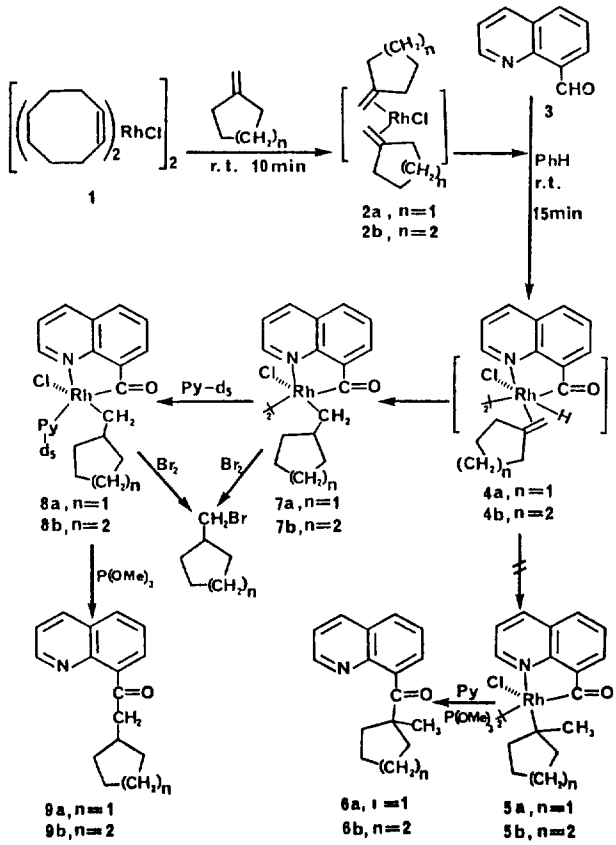
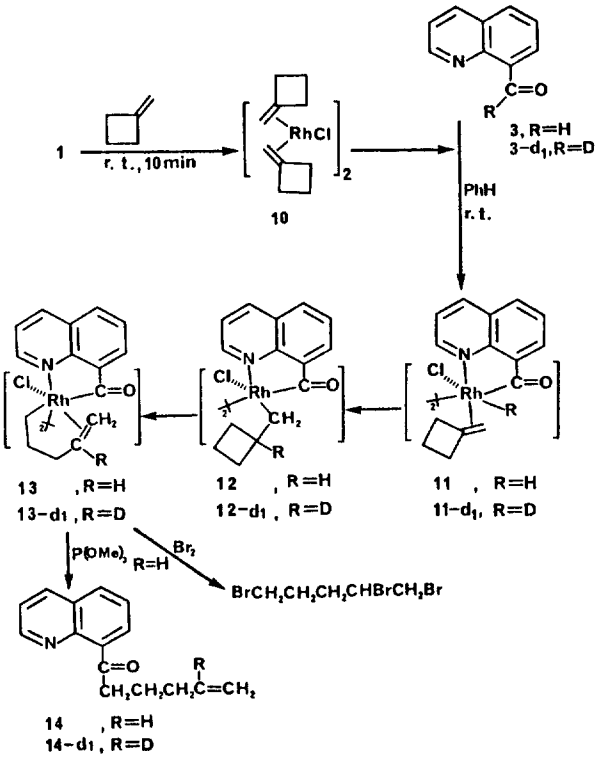
One of the characteristic features of transition metal complexes is the coordination of olefins to these metals[1]. Even some transition metals can coordinate to the exocyclic olefin of strained small rings without showing any C-C bond cleavage[2]. It is noted that some strained molecules such as cyclopropane are themselves sufficiently strained for their rings to be cleaved by certain metals[3]. Also other kinds of C-H and C-C bond activations of unstrained substrates having quinoline moieties by cyclometallation have been reported[4]. The hydride generated by C-H bond activation inserts into the coordinated olefin and diolefin to form acylrhodium(III) alkyl complexes[5] and acylrhodium(III) allyl complexes[6], which are reductive-eliminated to give alkyl ketones and β,γ-unsaturated ketones respectively. Recently there have been many interests to make cycloalkylcarbinyl system, since 5-hexenyl and 6-heptenyl radicals can be cyclized to form cyclopentylcarbinyl and cyclohexylcarbinyl groups[7]. Herein are described new formation of cycloalkylcarbinyl groups through the hydride-insertion into the exocyclic olefin of unstrained cyclic molecules and ring-opening reaction of mildly strained cyclobutyl molecule.

A number of stable methylenecyclopropane complexes of Rh, Ir and Pt have been reported[2]. Coordination of Rh with other methylenecycloalkanes such as methylenecyclohexane, methylenecyclopentane, methylenecyclobutane, were applied to olefin exchange reaction. Methylenecyclopentane was added to chlorobis(cyclooctene)rhodium(I) at room temperature for 10 min to give a red solution, which was supposed to be 2a(Scheme 1). Without isolation of 2a, it reacted with 8-quinolinecarboxaldehyde 3 in benzene at room temperature for 15 min to give an insoluble chlorine-bridged dimer 7a, which was isolated with pentane in 92% yield. Compound 7a can be solubilized by pyridine-d_5 to give acylrhodium(III) cyclopentylcarbinyl complex 8a: ^{1}H NMR ($CDCl_3$) δ(ppm) 10.6(d, 1H, quinoline C-2), 8.5-7.3(m, quinoline ring), 2.3(dd, J = 6, 3.3Hz, 2H, α-CH_2), 2.0-0.5(m, 9H, cyclopentyl group). The IR band of the carbonyl in 3 at 1690 cm^{-1} shifted to 1640 cm^{-1} in 7a. Treatment of the chlorine-bridged dimer 7a or the monomer 8a with Br_2 generated cyclopentylcarbinylbromide identified by ^{1}H NMR spectrum. The carbinyl group appears as doublet at 3.4 ppm (J = 6.8 Hz). Trimethylphosphite caused facile ligand-promoted reductive-elimination of both 8a and 7a to 9a in 46% yield: 9a; ^{1}H NMR($CDCl_3$), δ(ppm), 8.9(dd, 1H, H of quinoline C-2), 8.2-7.3 (m, 5H, quinoline), 3.35 (d, J-7.05 Hz, 2H, δ-CH_2), 2.1-0.9 (brm, 9H, cyclopentyl group); IR (neat) 3020, 2950, 1720, 1685, 1590, 1570, 1495, 1170, 1020,



Scheme 1. Synthesis of cycloalkylcarbinyl ketones *via* C-H bond activation.



Scheme 2. Ring-opening reaction of cyclobutyl group mediated by Rh.

830, 790, 760 cm^{-1}; mass spectra, *m/z*(assignment, relative intensity) 239(M^+, 34) 238 (M^+-1,14), 171(43), 156 (quinoinyl CO^+, 100), 129 (quinoline$^+$, 71); TLC R_f = 0.48, hexane: ethylacetate = 5:2, SiO_2.

Same treatments of methyleneyclohexane instead of methylenecyclopentane gave 7b in 94% yield, which was solubilized by pyridine-d_5 giving 8b. Addition of Br_2 to 7b or 8b produced cyclohexylcarbinylbromide. Reductive-elimination of 8b with trimethylphosphite gave 9b in 68% yield after chromatographic isolation: 9b; ^1H NMR($CDCl_3$) δ(ppm) 8.9(dd, 1H, H of quinoline C-2), 8.2-7.3(m, 5H, quinoline ring), 3.2(d, J = 6.55Hz, 2H, α-CH_2), 2.0-0.9(brm, 11H, cyclohexyl group); IR(neat) 3020, 2920, 1730, 1685, 1590, 1770, 1492, 1445, 1170, 1050, 940, 830, 790 cm^{-1}; mass spectra, *m/z* (assignment, relative intensity) 253(M^+, 38), 171(90), 156(quinolinyl CO^+, 100), 129(quinoline$^+$, 68); TLC R_f = 0.41, hexane:ethylacetate = 5:2, SiO_2.

The reaction of 3 and 2a(2b) would lead to 4a(4b) as an intermediate via C-H bond activation. The next step is the formation of acylrhodium(III) cycloalkylcarbinyl complexes 7a(7b) by 1,2-addition of the Rh-H bond in 4a(4b) across the exocyclic double bond of methylenecycloalkanes. There are two possible ways of hydride-insertion into the exocyclic double bond: one follows Markownikoff's rule to form 5a(5b) and the other anti-Markownikoff's rule to form 7a(7b). The formations of 9a(9b), not 6a(6b), by reductive-elimination and cycloalkylcarbinylbromide by bromination of the metal complexes confirm that the hydride insertion occurs in accord with anti-Markownikoff's rule. The reason for these results is that 5a(5b) is thermodynamically very unstable, that is, the tertiary carbon-Rh bond must be much weaker than the primary carbon-Rh bond, possibly due to a steric hindrance of 5a(5b)[8]. Any ring-opened product was not isolated in this reaction differently from that the reaction of platinum(II) hydride and methylenecyclopropane derivatives would lead to ring-opened product rather than cyclopropylcarbinyl platinum(II) complexes[9]. The result can be explained by assuming a large difference of ring strain energy between cyclopropyl group and both cyclopentyl and cyclohexyl groups[10].

Compound 3 reacted with 10, prepared from 1 and methyl enecyclobutane at room temperature for 10 min *in situ*, followed by reductive-elimination of the resulting metal complex to give 8-quinolinyl pent-4'-enyl ketone 14, the ring-opened product, in 86% yield after chromatographic isolation (Scheme 2): 14; ^1H NMR ($CDCl_3$) δ(ppm) 8.9(dd, 1H, H of quinoline C-2), 8.3-7.2(m, 5H, quinoline ring), 5.6 (m, 1H, -CH=), 5.0 (tm, 2H, CH_2=), 3.3(t, 2H, α-CH_2), 2.3-1.7 (m, 4H, -CH_2CH_2-); IR(neat) 3070, 2930, 1685, 1640, 1595, 1570, 1495, 1250, 970, 910, 827, 740, 695 cm^{-1}; mass spectra, *m/z* (assignment, relative intensity) 225 (M^+, 16), 224 (M^+-1,16), 184 (M^+-allyl, 46), 171(15), 156 (quinolinyl CO^+, 100), 128 (quinoline$^+$, 40); TLC Rf = 0.50, hexane: ethylacetate = 5:2. When 10 was formed by olefin-exchange reaction of 1 and methylenecyclobutane, ring-opening reaction of cyclobutyl group did not occur since only liberating methylenecyclobutane was detected with addition of triphenylphosphine to 10. Any ring-opened molecule such as 1,4-pentadiene was not observed by ^1H NMR spectrum. Strained olefins have a tendency to form stable metal complexes due to partial strain relief upon complexation[1]. Although the pre-

cursor for 14 is supposed to be acylrhodium(III) pent-4'-enyl complex 13, attempts to characterize this complex failed: addition of pyridine-d_5 in $CDCl_3$ in order to solubilize a chlorine-bridged dimer complex gave complicated ^1H NMR spectrum. The IR band of the carbonyl in 3 at 1690 cm^{-1} moved to 1640 cm^{-1} in 13 similar to 7a (7b). Addition of Br_2 to the metal complex generated 1,2,5-tribromopentane, which was confirmed by comparison with the authentic specimen obtained by the reaction of 5-bromopentene and Br_2. Rearrangement of 12 to 13 is the key step in this work. Some ring opening reactions of strained ring molecules, especially cyclobutylcarbinyl group, were reported[12]. Since a vacant coodination site as well as a ring strain of the cyclobutyl group is generated in 12, a 16-electron Rh(III) species formed by hydride-insertion into a coodinated olefin in 11, C-C bond activation becomes very facile[13].

In an attempt to trace the aldehyde-proton in 3, the reaction was carried out by using 3-d_1[14] as a substrate for C-H bond activation giving 14-d_1. The deuterium resides only in the 4-position in 4-pentenyl group. None has been incorporated into the aliphatic CH_2 or the terminal CH_2 group. From this result, ring-opening reaction can be explained by β-alkyl elimination of the cyclobutylcarbinyl system[15]. Most of the numerous studies devoted to ring opening reactions have been concerned with cycloalkylcarbinyl radicals[16]. Although the mechanism is not clear, some evidences previously showed that the bond homolysis for this kind of Rh-alkyl complexes produced alkyl radicals[17] Relative low isolated yields of 9a and 9b compared with that of 14 may come from little amount of formation of 2a and 2b respectively since bulky alkyl groups seem to retard facile coordination of the exocyclic olefin to Rh rather than small size cyclobutyl group[12a].

Detailed kinetic and other mechanistic investigations of C-H bond and C-C bond activations are under way.

References

1. "Advanced Inorganic Chemistry", F. A. Cotton, G. Wilkinson, 4th Ed., New York: John Wiley, p. 95 (1980).
2. M. Green, J. A. K. Howard, R. P. Hughes, S. C. Kellett, P. Woodward, *J. Chem. Soc., Dalton Trans.*, 2007 (1975).
3. K. C. Bishop III, *Chem. Rev.*, **76**, 461 (1976).
4. (a) J. W. Suggs, *J. Am. Chem. Soc.*, **100**, 640 (1978); (b) J. W. Suggs, S. D. Cox, *J. Organomet. Chem.*, **221**, 199 (1980); (c) J. W. Suggs, C. H. Jun, *ibid.*, **106**, 3054 (1984); (d) J. W. Suggs, C. H. Jun, *J. Chem. Soc., Chem. Comm.* 92 (1985).
5. J. W. Suggs, M. Wovkulich, S. D. Cox, *Organometallics*, **4**, 1101 (1985).
6. C. H. Jun, J. B. Kang, *Bull. Korean Chem. Soc.*, **10**(1), 114 (1989).
7. D. P. Curran, *Synthesis*, 417 (1988).
8. P. D. stoutland, R. G. Bergman, S. P. Nolan, C. D. Hoff, *Polyhedron*, **7**, 1429 (1988).
9. T. G. Attig, *Inorg. Chem.*, **17**(11), 3097 (1978).
10. "Stained Organic Molecules", A. Greenberg, J. F. Liebman, London: Academic Press, p. 66 (1978).
11. (a) T. G. Traynham, J. R. Olechowski, *J. Am. Chem. Soc.*, **81**, 571 (1959); (b) M. A. Muhs, F. T. Weiss, *ibid.*, **84**, 4697 (1962).
12. (a) A. Hill, H. G. Richey Jr, R. C. Rees, *J. Org. Chem.*, **28**, 2161 (1963); (b) A. Hill, J. A. Davidson, *J. Am. Chem. Soc.*, **86**, 4603 (1964).
13. (a) R. A. Periana, R. G. Bergman, *J. Am. Chem. Soc.*, **106**, 7272 (1984); (b) *ibid.*, **108**, 7346 (1986).
14. J. W. Suggs, G. D. N. Pearson, *J. Org. Chem.*, **45**, 1514 (1980).
15. (a) T. C. Flood, J. A. Statler, *Organometallics*, **3**, 1795 (1984); (b) T. C. Flood, S. P. Bitler, *J. Am. Chem. Soc.*, **106**, 6070 (1984); (c) P. L. Watson, D. C. Roe, *ibid.*, **14**, 6471 (1982).
16. (a) M. Castaing, M. Pereyre, M. Ratier, P. M. Blum, A. G. Davies, *J. Chem. Soc., Perkin II*, 287 (1979); (b) A. L. . Beckwith, G. Moad, *ibid.*, 1083 (1980).
17. J. W. Suggs, C. H. Jun, *J. Am. Chem. Soc.*, **108**, 4679 (1986).

Permanganate Colorimetric Rapid Method for Chemical Oxygen Demand in Seawater

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Recently, there has been considerable interest in simplifying the rather tedious standard chemical oxygen demand(COD) procedure for the dichromate reflux method which has limitations for the samples of low to moderate COD with chloride concentrations approaching that of seawater[1,2] However, no one has ever made such an attempt to eliminate that tedious and insensitive detection procedure for the alkaline-permanganate method[3] which is superior to dichromate reflux method in which chloride interference is largely prevented by complexing method.[4]

Herein we report a rapid and sensitive method that is consistent with the official procedure[3] for the determination of COD in seawater, a typical sample of low COD. In this experiment, the COD in a 5-m*l* sample was determined by measuring the excess permanganate spectrophotometrically at 535nm after digestion in alkaline medium. Since we expect