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Communications

Rhodium-Catalyzed Norbornenylation of 2-Vinylpyridines *via* C-H Activation

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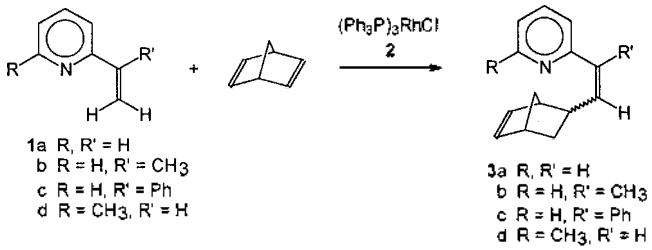
The catalytic alkylation of alkenic C-H bond with olefins *via* C-H bond activation by transition metal complex is a very useful method for the synthetic organic chemistry.[1] This chemistry has economical and environmental merits using cheap alkenes instead of alkyl halides. We have already reported that the alkylation of 2-vinylpyridines,[2a,b] 2-vinylquinolines[2c] and 2-phenylpyridines[3] with terminal alkenes in the presence of rhodium catalysts give the corresponding regioselectively alkylated products. Murai *et al.*[4] and Trost *et al.*[5] also reported the alkylation of the alkenic position by ruthenium complexes, independently. During the course of our studies of the alkylation using rhodium catalysts, we wondered that the coupling reaction was affected by the ability of the coordination of alkene to Rh complex in this coupling reaction. So we examined the alkylation of 2-vinylpyridines with various cyclic alkenes. 2-Vinylpyridines reacted with 2,5-norbornadiene in the presence of the Wilkinson catalyst, $(PPh_3)_3RhCl$, to give the regioselectively norbornenylated products in nearly quantitative yields. Murai and co-workers reported that attempts to catalyze the alkylation of acetophenones with 2,5-norbornadiene by ruthenium complex was unsuccessful.[4b] Cyclohexene and cyclopentene are inactive or give trace amounts of the alkylated product in this alkylation.[2b] Norbornylene, less strained bicyclic alkene than norbornadiene, gave the desired product in 8% isolated yield under the similar reaction conditions. The exceptional reactivities of 2,5-norbornadiene may result from the stabilization of metal complex by η^4 type coordination and release from the ring strain.[6] The low reactivity of other cyclic alkenes probably due to difficulty of coordination on metal complex by steric congestion. The norbornenylated products are easily converted by flash vacuum thermolysis to give butadienylpyridines and heterocyclic compounds. From the above results and the rarity of catalytic functionalization of 2,5-norbornadiene by a transition metal catalyst,[7] we decided the more detailed investigation of the coupling of 2-vinylpyridines with 2,5-norbornadiene as a useful masked acetylene. In this communication, we report the rhodium-catalyzed direct norbornenylation to alkenic moiety by the C-H bond activation.

2-Vinylpyridine **1a** reacted with 2,5-norbornadiene (2 equiv.) in the presence of **2** (5 mol%) in toluene at 120 °C for 20.5 h to give the Z isomer of the regioselective norbornenylated product **3a**[8] in 97% yield: no the *E* isomer was detected in the reaction mixture by ^1H NMR (Scheme 1, Run 3 in Table 1). 2-Vinylpyridines reacted with terminal alkenes to give mixtures of Z (*J* 11 Hz) and E (*J* 15 Hz) isomers above 100 °C.[2a,b] But, this norbornenylation gave only Z isomer (*J* 11 Hz) even at 120 °C. Interestingly, this reaction gave the *exo* isomer as a major product (**3a**, *exo* : *endo*=84 : 16). Use of 5 mol% of **2** and 2 equiv. of 2,5-norbornadiene gave the best results. To obtain higher ratio of *exo* regioisomer, tricyclohexylphosphine (Cy_3P) having larger cone angle than that of triphenylphosphine as a ligand applied. This reaction gave higher *exo*-ratio (*exo* : *endo*=90 : 10) in 22% isolated yield (Run 6). α-Substituted vinylpyri-

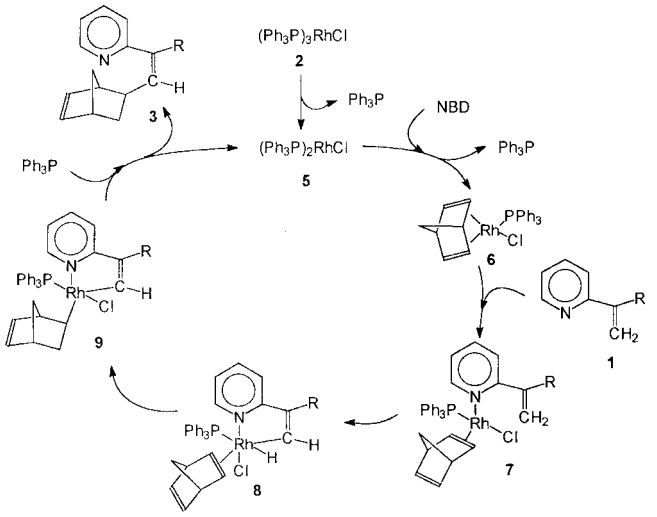


Scheme 1

Table 1. The results of the coupling of 2-vinylpyridines with 2,5-norbornadiene

Run	Substrate	2,5-norbornadiene (equiv.)	**2** (mol%)	Reaction time (h)	Reaction temp. (°C)	Isolated Yield (%)	*Exo* : *Endo*[a]
1	**1a**	5	10	21.5	120	91	83 : 17
2	**1a**	2	10	20.5	115	88	79 : 21
3	**1a**	2	5	20.5	115	97	84 : 16
4	**1a**	2	5	20	130	89	78 : 22
5	**1a**	2	5	20	90-95	52[b]	82 : 18
6	**1a**	2	2.5[c]	21	120-125	22	90 : 10
7	**1b**	2	5	20	120	87	89 : 11
8	**1b**	2	5[d]	20	120	60[b]	-
9	**1c**	2	5	20	120	90	83 : 17
10	**1d**	5	10	24	120	Trace	-

[a] The ratio of isomer was determined by GC and/or ^{1}H NMR. [b] GC-Yield. [c] Use of $[(C_8H_{14})_2RhCl]_2/Cy_3P$ as a catalyst. [d] Use of $[(C_8H_{14})_2RhCl]_2$ as a catalyst.



Scheme 2

dines such as 2-(α-methylvinyl)pyridine **1b** and 2-(α-phenylvinyl)pyridine **1c** were also applied to this coupling reaction. Substrate **1b** gave the norbornenylated products in 87% isolated yield (*exo* : *endo*=89 : 11, Run 7). The methyl group in **1b** enhanced the ratio of *exo* isomer up to 89%. Substrate **1c** gave similar results to **1a** (90% yield, *exo* : *endo*=83 : 17, Run 9).

Other vinylpyridines such as 6-methyl-2-vinylpyridine and 6-methyl-2-(β-methylvinyl)pyridine did not work. Use of chlorobis(cyclooctene)rhodium(I) dimer, $[(C_8H_{14})_2RhCl]_2$ instead of **2**, gave moderate yields (Run 8). This shows that the phosphine ligand plays an important role in the coupling reaction. The results obtained from the norbornenylation of vinylpyridines are listed in Table 1.

A possible mechanism for the reaction may be postulated as shown in Scheme 2. The reaction appears to be initiated by formation of the highly reactive rhodium complex **5** by liberation of one ligand and **5** converts to **6** by ligand-exchanging with 2,5-norbornadiene (NBD).[9] The intermediate **7** forms from **6** by the coordination of **1** and then **8** forms *via* intramolecular C-H bond activation. A hydride in **8** migratory-inserts into the coordinated NBD to give **9** and finally, reductive-eliminates to **3** and **5** by the external ligand.

In conclusion, we have found that the coordinating ability of alkene to rhodium metal was a very important factor in the alkylation of 2-vinylpyridine with cyclic alkenes. The direct norbornenylation of 2-vinylpyridine with 2,5-norbornadiene by a rhodium complex was achieved. The exo norbornenylated products of 2-vinylpyridines were obtained as a major product.

References

1. (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1989. (b) McQuillin, F. J.; Parker, D. G.; Stephenson, G. R. *Transition Metal Organometallics for Organic Synthesis*; Cambridge University Press: Cambridge, 1991.
2. (a) Lim, Y.-G.; Kang, J.-B.; Kim, Y. H. *Chem. Commun.* **1996**, 585. (b) Lim, Y.-G.; Kang, J.-B.; Kim, Y. H. *J. Chem. Soc., Perkin Trans. 1* **1998**, 699. (c) Lim, Y.-G.; Kang, J.-B. *Bull. Korean Chem. Soc.* **1997**, *18*, 1213.
3. (a) Lim, Y.-G.; Kim, Y. H.; Kang, J.-B. *J. Chem. Soc., Chem. Commun.* **1994**, 2267. (b) Lim, Y.-G.; Kang, J.-B.; Kim, Y. H. *J. Chem. Soc., Perkin Trans. 1* **1996**, 2201.
4. (a) Murai, S.; Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N. *Nature* **1993**, *366*, 529. (b) Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N.; Murai, S. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 62. (c) Kakiuchi, F.; Tanaka, Y.; Sato, T.; Chatani, N.; Murai, S. *Chem. Lett.* **1995**, 679. (d) Fujii, N.; Kakiuchi, F.; Chatani, N.; Murai, S. *Chem. Lett.* **1996**, 939 and references therein.
5. Trost, B. M.; Imi, K.; Davies, I. W. *J. Am. Chem. Soc.* **1995**, *117*, 5371.
6. (a) Bennett, M. A.; Wilkinson, G. *J. Chem. Soc.* **1961**, 1418. (b) Robertson, J. J.; Kadziola, A.; Krause, R. A.; Larsen, S. *Inorg. Chem.* **1989**, *28*, 2097. (c) Haarman, H. F.; Bregman, F. R.; Ernsting, J.-M.; Veldman, N.; Spek, A. L.; Vrieze, K. *Organometallics* **1997**, *16*, 54. (d) Behr, A. *Carbon Dioxide Activation by Metal Complexes*, VCH publishers, D-6940 Weinheim, F. R. Germany, **1988**, pp

77-80.
7. (a) Hydroformylation: Botteghi, C.; Paganelli, S.; Perosa, A.; Lazzaroni, R.; Uccello-Barretta, G. *J. Organomet. Chem.* **1993**, *447*, 153. (b) Silylation: Brunner, H.; Prester, F. *J. Organomet. Chem.* **1991**, *411*, C1-C2. (c) Norbornadiene used as a masked acetylene: An, Z. W.; Catellani, M.; Chiusoli, G. P. *J. Organomet. Chem.* **1989**, *371*, C51.
8. **3a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.57 (d, 1H, J=5.0 Hz, 6-H in py), 7.59 (t, 1H, J=7.7 Hz, 4-H in py), 7.24 (d, 1H, J=7.7 Hz, 3-H in py), 7.06 (dd, 1H, J=5.3 Hz, 7.4 Hz, 5-H in py), 6.44 (d, 1H, J=11.8 Hz, α-H-C= to py), 6.07-6.15 [s, 2H, 3',4'-Hs in norbornenyl (nbd)], 5.86 (t, 1H, J=11.4 Hz, β-H-C= to py), 2.88-2.96 (m, 1H, 1'-H in nbd), 2.91 (s, 1H, 2'-H in nbd), 2.67 (s, 1H, 5'-H in nbd), 1.51 (d, 1H, J=8.3 Hz, 6'-H in nbd), 1.36-1.43 (m, 3H, 6', 7'Hs in nbd); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.50, 149.20, 141.97, 137.04, 136.13, 135.70, 127.54, 123.48, 120.96, 48.54, 45.57, 42.12, 37.09, 34.21; MS (m/z) 130 (100), 196 (1.2, M^+-1), 197 (1.3, M^+). **3b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.59-8.63 (m, 1H, 6-H in py), 7.59 (t, 1H, J=7.8 Hz, 4-H in py), 7.18 (d, 1H, J=7.6 Hz, 3-H in py), 7.08-7.15 (m, 1H, 5-H in py), 6.00 (s, 2H, 3',4'-Hs in nbd), 5.60 (d, 1H, J=11.4 Hz, β-H-C= to py), 2.86 (s, 1H, 2'-H in nbd), 2.59 (s, 1H, 5'-H in nbd), 2.16-2.21 (m, 1H, 1'-H in nbd), 2.13 (s, 3H, =C-CH_3), 1.50 (d, 1H, J= 8.02 Hz, 6'-H in nbd), 1.33-1.39 (m, 3H, 6',7'-Hs in nbd); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.04, 149.13, 136.79, 136.20, 135.68, 135.58, 135.33, 123.25, 121.23, 48.44, 45.51, 42.06, 37.53, 34.38, 23.76; MS 130 (26.3), 144 (100), 145 (33.8), 196 (2.5, M^+-CH_3), 211 (3.8, M^+). **3c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (d, 1H, J=4.8 Hz, 6-H in py), 7.64 (t, 1H, J=7.7 Hz, 4-H in py), 7.12-7.29 (m, 7H, 3,5-Hs in py and Hs in ph), 6.00 (s, 2H, 3',4'-Hs in nbd), 6.12 (d, 1H, J=10.2 Hz, β-H-C= to py), 2.88 (s, 1H, 2'-H in nbd), 2.71 (s, 1H, 5'-H in nbd), 2.18 (dt, 1H, J= 3.1 Hz, 9.46 Hz, 1'-H in nbd), 1.56 (d, 1H, J=8.2 Hz, 6-H in nbd), 1.48 (dt, 1H, J=3.5 Hz, 11.7 Hz, 6'-H in nbd), 1.35-1.42 (m, 2H, 7'-H in nbd); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.09, 149.53, 137.41, 136.94, 136.12, 135.83, 128.10, 127.18, 126.87, 125.11, 121.62, 48.53, 45.59, 42.16, 38.28, 34.37.
9. Bennett, M. A.; Longstaff, P. A. *Chem. Ind. (London)* **1965**, 846.

Molecular Simulation Studies for Steric Hindrance Effects through the Circular Pore Entrance

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The fundamental mechanisms which govern the transport properties of gases, vapors and liquids in porous media are of considerable interests in experimental and industrial applications such areas as membrane separations, heterogeneous catalysis, and gel-permeation chromatography. In many situations, and particularly when the size of pore openings is commensurate with that of diffusing molecules into these microporous materials, the significant hindrance effects can arise during mass transport. This highly localized resistance, more specifically at the pore entrance, is often referred to as a surface barrier effect. Such conditions may cause unusual transport properties, for example, the anomalous non-Fickian diffusivity exhibited in some zeolite and carbon molecular sieves.[1]

In most practical porous materials, there is a spatial variation of pore sizes. Experimental methods are based on the assumption that the absolute size of the pore size distributions can reliably be obtained so that the pore cross-sectional shape is known. However, the experimental extraction of an absolute pore distribution is not straightforward, and this assumption may be seriously in error and lead to large uncertainties especially when micropores are presented. As an extremely useful diagnostic tool, molecular-based computer simulations[2] can provide essentially exact experimental data for precisely defined model systems at the fundamental molecular level. Consequently, molecular dynamics (MD) calculations have been carried out for the analysis of surface barrier effects in a variety of pore systems. Vigne-Maeder *et al.*[3] have performed the dynamic simulations of gas molecules passing through the outer surfaces of aluminum-free MFI- and MOR-type zeolite crystals. More recently, Ford and Glandt[4,5] have undertaken the systematic MD simulation studies of hard-sphere and Lennard-Jones systems for a slit pore mouth model in the dilute gas limit. The simulation approaches using attractive potential fields[3,5] have revealed that the primary mechanism for transport was adsorption followed by surface diffusion to the pore entrance, rather than a direct penetration into a pore from the gas phase.

In the present work, we have reported preliminary MD results of hard-spheres passing through a circular pore mouth which acts as a bottleneck. The individual particle