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Synthesis of Cycloalkanones from Dienes and Allylamines through C-H and C-C Bond Activation Catalyzed by Rhodium(I) Complex

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General Method. NMR spectra were recorded in $CDCl_3$ on Bruker Avance DPX 250 spectrometer (^1H NMR, 250 MHz; ^{13}C NMR, 62.5 MHz) spectrometer, and the chemical shift was expressed in ppm relative to TMS. IR spectra were recorded on Nicolet Impact 400 spectrometer. GC analyses were conducted using Donam DS 2000 Gas Chromatography. Mass spectra were obtained using G1800A GCD System. Commercially available compounds are used as received except toluene, which was purified according to the known procedure.[1] $[(C_8H_{14})_2RhCl]_2$ (**4**) was prepared as described in the literature.[2]

Materials. *N*-(3-Methyl-2-pyridyl)-*N*-[(E)-3-phenyl-2-propenyl]amine (**1a**) was prepared by the reaction of cinnamyl chloride and *N*-lithium-2-amino-3-picoline, generated from 2-amino-3-picoline and *n*BuLi in THF, according to the known procedure.[3] *N*-cinnamylaniline (**1b**)[4] was also prepared by same method using aniline instead of 2-amino-3-picoline by the same manner, and identified by ^1H NMR, ^{13}C NMR, IR, and MS spectra.

Among dienes, 1,4-pentadiene (**2a**), 1,5-hexadine (**2b**), 2-methyl-1,5-hexadine (**2c**), 2-methyl-1,4-pentadiene (**2g**), and piperylene (**2h**) were purchased from Aldrich Co., and used as received. 1,1-Divinylcyclohexane (**2e**)[5] and 3,3-dimethyl-1,4-pentadiene (**2f**)[6] was prepared following the known procedures. Other dienes were prepared as follows,

[1] W. L. F. Armarego, D. D. Perrin, *Purification of Laboratory Chemicals*, 4th ed., Butterworth-Heinemann, Oxford, **1996**.
[2] J. A. Osborn, G. Wilkinson, in *Reagents for Transition Metal Complex and Organometallic Synthesis, Vol. 28* (Ed.: R. Angelich), Wiley, New York, **1989**, pp. 90-91.
[3] C.-H. Jun, H. Lee, J.-B. Park, D.-Y. Lee, *Org. Lett.* **1999**, *1*, 2161.
[4] B. C. Ranu, A. Majee, A. Sarkar, *J. Org. Chem.* **1998**, *63*, 370.
[5] P. Elibracht, M. Acker, I. Hädrich, I. *Chem. Ber.* **1988**, *121*, 519.
[6] P. Elibracht, M. Acker, W. Totzauer, *Chem. Ber.* **1983**, *116*, 238.

and identified by the comparison of the known spectral data.

2,2-Dimethyl-4,5-divinyl-1,3-dioxolan (2d).[7] To a solution of 1,5-hexadiene-3-4-diol (0.706 g, 6.18 mmol, a mixture of *meso* and (±), purchased from Aldrich Co.) and 2,2-dimethoxypropane (1.294 g, 12.42 mmol) in 10 mL of acetone was added molecular sieve (4 Å) and *p*-TsOH (0.120 g, 0.613 mmol). After stirred at rt for 6h, the solution was diluted with 50 mL of Et_2O, washed with 1N NaOH. The aqueous layer was extracted with Et_2O and CH_2Cl_2. The organic extracts were collected, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by Kugelohr distillation to give **2d** as a mixture of *meso* and (±) compounds (0.704 g, 74 %, *meso*/(±)=45/55). **2d**: ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.84-5.69 (m), 5.39-5.21 (m), 4.61 (d, *J* = 6.7 Hz, 2H, 3- and 4-H in *meso* isomer), 4.07 (m, 2H, 3- and 4-H in (±) isomer), 1.53 (s, 3H, CH_3 in *meso* isomer), 1.45 (s, 6H, two CH_3s in (±) isomer), 1.41 (s, 3H, CH_3 in *meso* isomer). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 144.5, 141.8, 128.4, 128.4, 128.3, 127.5, 126.0, 125.8, 73.6, 40.4, 32.0. IR (neat): 3376, 3061, 3027, 2925, 2860, 1603, 1494, 1453, 1202, 1058, 915, 748, 699 cm^{-1}. MS (EI): m/z (relative intensity) 212 (M^+, 8), 194 (40), 107 (100), 91 (24), 79 (46).

3-Benzyloxy-1,5-hexadiene (2i).[8] To the slurry of NaH (1.33 g, 33 mmol) in 33 mL of THF was added 1,5-hexadien-3-ol (2.33 g, 23.8 mmol) for 10 min, then the reaction

[7] a) K. B. Wiberg, J. R. Snoonian, *J. Org. Chem.* **1998**, *63*, 1402; b) H. D. Scharf, H. Plum, J. Fleischhauer, W. Schleker, *Chem. Ber.* **1979**, *112*, 862.
[8] a) N. M. Kablaoui, S. L. Buchwald, *J. Am. Chem. Soc.* **1996**, *118*, 3182; b) G. A. Molander, J. O. Hoberg, *J. Am. Chem. Soc.* **1992**, *114*, 3123; c) G. A. Molander, P. J. Nichols, *J. Am. Chem. Soc.* **1995**, *117*,

mixture was heated at reflux for 1h. The solution was cooled to rt, then placed in ice-salt bath, and benzyl bromide (2.8 mL, 23.8 mmol) was added dropwise for 10min. After reflux for 12h, the reaction was quenched with 40 mL of water, acidified with 4N HCl solution, and then extracted with Et_2O. The organic layers were combined, washed with saturated $NaHCO_3$ solution and brine, and then dried over $MgSO_4$. After concentrated under reduced pressure, the resulting residue was purified by column chromatography (n-Hexane/Ethyl acetate = 70/1) to give **2i** (3.40 g, 76 %). **2i**: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.33-7.23 (m, 5H), 5.83-5.71 (m, 2H), 5.25-5.03 (m, 4H), 4.59 (d, *J* = 11.9 Hz, 1H), 4.36 (d, *J* = 11.9 Hz,1H), 3.79 (q, *J* = 6.7 Hz, 1H), 2.38 (m, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 138.6, 138.3, 134.5, 128.2, 127.6, 127.4, 117.3, 116.8, 80.0, 70.0, 40.0. IR (neat): 3076, 3031, 2982, 2929, 2898, 2853, 1650, 2599, 1458, 1423, 1325, 1209, 1080, 995, 924, 741, 701 cm^{-1}. MS (EI): m/z (relative intensity) 188 (M^+, 2), 147 (11), 91 (100), 65 (6).

Typical Procedures for the Catalytic Reactions. The Reaction of Allylamine (1a) and 1,5-hexadiene (2b). (Table 1, entry 2, and Figure 1) A screw-capped pressure vial (1 mL) was charged with allylamine **1a** (56.0 mg, 0.250 mmol), 1,5-hexadiene (**2b,** 61.5 mg, 0.75 mmol), $[(C_8H_{14})_2RhCl]_2$ (**4**, 4.5 mg, 0.0063 mmol), tricyclohexylphosphine (**5,** 10.8 mg, 0.039 mmol), and the reaction mixture was dissolved by 100 mg of toluene. It was stirred in an oil bath that was

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preheated at 150 °C varying the reaction time. After the reaction, the reaction mixture was hydrolyzed by 1N HCl at rt for 3h, extracted with Et_2O and CH_2Cl_2. The organic layers were combined, dried over $MgSO_4$. The conversion rate and the ratio of the products were determined by GC analyses (Table S1). Among the products, cycloheptanone (**3c**),[9] 2-methylcyclohexanone (**3d**),[9] and 2-ethylcyclopentanone (**3e**)[10] were identified by the comparison with authentic specimens using GC and GCD. Alkenyl ketones **8a** and **8b** were identified as 1-phenyl-3-nonanone (**14**)[11] and 7-tridecanone (**15**)[9] after hydrogenation using Pd/C catalyst.

[9] Commercially available compound.
[10] C.-H. Jun, H. Lee, S.-G. Lim, *J. Am. Chem. Soc.* **2001**, *123*, 751.
[11]C.-H. Jun, H. Lee, J.-B. Park, D.-Y. Lee, *Org. Lett.* **1999**, *1*, 2161.

Table S1. The Reaction of Allylamine (1a) and 1,5-Hexadiene (2b)

Entry	Time	Conversion rate (%)	Total yield Of cycloalkanones (%, GC yield)	The ratio of Cycloalkanones(%)			The yield of alkenyl ketones (%)	
				3c	**3d**	**3e**	**8a**[a]	**8b**[b]
1	5 min	63	21	100	0	0	23	19
2	15 min	100	41	86	10	4	30	29
3	30 min	100	56	74	18	8	23	21
4	1 h	100	64	57	27	16	15	21
5	2 h	100	85	38	40	22	9	9
6[c]	6 h	100	85	26	52	22	3	12
7[c]	12 h	100	88	15	62	23	0	12

[a] Identified as **14** after hydrogenation. [b] Identified as **15** after hydrogenation [c] Very trace amount (~2 %) of 2,4-dimethylcyclopentanone was observed by GC

Among the other products, commercially available compounds such as cyclohexanone (**3a**) and 2-methylcyclopentanone (**3b**) were identified by comparison with authentic specimens. Other cycloalkanones such as 3-methylcycloheptanone (**3f**),[12] 2,2-dimethylhexahydro-cyclohepta[1.3]diozaol-6-one (**3g**),[13] spiro[5.5]undecan-3-one (**3h**),[14] 4,4-dimethylcyclohexanone (**3i**),[15] 3-

[12] J. Cossy, N. Furet, S. BouzBouz, *Tetrahedron* **1995**, *51*, 11751.
[13] D. Batty, D. Crich, *J. Chem. Soc., Perkin Trans. 1.* **1992**, 3193.
[14] B. B. Snider, N. H. Vo, B. M. Foxman, *J. Org. Chem.* **1993**, *58*,

methylcyclohexanone (**3j**),[12] and 4-benzyloxy-2-methylcyclohexanone (**3l**)[16] have already been reported, and were identified by ^{1}H NMR, ^{13}C NMR, IR, and MS spectra. All new compounds are characterized below.

4-Benzyloxycycloheptanone (3k). ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.39, 2.38 (t, *J* = 7.7 Hz, *J* =7.3 Hz, 4H), 1.71-1.64 (br, 5H), 1.65-1.50 (m, 2H), 1.46 (dt, *J* = 7.6, 7.4 Hz, 2H), 1.23-1.14 (br m, 4H), 0.91 (t, *J* = 7.4 Hz, 3H), 0.85-0.80 (br m, 2H). ^{13}C NMR (62.5MHz, $CDCl_3$): δ 211.6, 44.6, 40.3, 37.2, 33.0, 31.1, 26.5, 26.2, 17.2, 13.7. IR (neat): 2925, 2852, 1715, 1450, 1412, 1372, 1267, 1128, 1040, 888 cm^{-1}. MS (EI): *m/z* (relative intensity) 182 (M^+, 10), 139 (30), 121, (100), 96 (94), 87 (60), 81 (35), 67 (25), 58 (76), 55 (69), 43 (76). HRMS (EI): *m/z* calcd. for $C_{12}H_{22}O$ (M^+) 182.1671, found 182.1684.

8-Methyl-1-phenylnon-8-en-3-one (8c). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.52 (d, *J* = 1.1 Hz, 1H), 7.42-7.31 (m, 5H), 2.80 (t, *J* = 7.5 Hz, 2H), 2.06 (d, *J* = 1.3 Hz, 3H), 1.67 (m, 2H), 1.39-1.26 (br m, 6H), 0.90 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (62.5MHz, $CDCl_3$): δ 202.7, 176.6, 138.3, 137.4, 136.1, 129.7, 128.4, 37.7, 31.7, 29.1, 25.0, 22.5, 14.0, 13.2. IR

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[15] 1) W. L. Meyer, M. J. Brannon, C. Burgos, T. E. Goodwin, R. W. Howard, *J. Org. Chem.* **1985**, *50*, 438; 2) F. J. Weigert, J. D. Robert, *J. Am. Chem. Soc.* **1970**, *92*, 1347.
[16] M. Chini, P. Crotti, L. A. Flippin, F. Macchina, *Tetrahedron Lett.*

(neat): 3057, 3025, 2955, 2928, 2857, 1668, 1626, 1493, 1447, 1366, 1299, 1198, 1058, 1030, 927, 850, 750, 697 cm^{-1}. MS (EI): m/z (relative intensity) 230 (M^+, 11), 215 (4), 160 (33), 145 (100), 117 (54), 115 (32), 91 (14). HRMS (EI): *m/z* calcd. for $C_{16}H_{22}O$ (M^+) 230.1671, found 230.1660.

2,12-Dimethyltrideca-1,12-dien-7-one (8d). ^1H NMR (250 MHz, $CDCl_3$): δ 4.70 (d, *J* = 4.1 Hz, 2H), 2.42-2.38 (t, *J* = 5.6 Hz, 2H), 2.04-1.99 (t, *J* = 7.2 Hz, 2H), 1.70(s, 3H), 1.60-1.51 (m, 2H), 1.48-1.38 (m, 2H); ^{13}C NMR (62.5MHz, $CDCl_3$): δ 211.7, 146.1, 128.8, 110.5, 43.4, 38.0, 27.6, 23.9, 22;0; IR (neat): 2937, 2861, 1715, 1654, 1455, 1375 cm^{-1}. MS (EI): m/z (relative intensity). HRMS (EI): *m/z* calcd. for $C_{15}H_{26}O$ (M^+)222.1984, found 222.1984.

1989, *30*, 6563.