Investigation of Electronic Effects of Rh(II)-Mediated α-Methyl-Substituted Carbenoid Intramolecular C−H Insertion

Jianbo Wang,* Fengting Liang, and Bei Chen

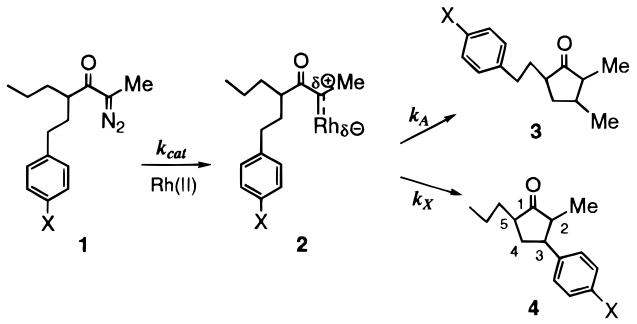
Department of Chemistry, Peking University, Beijing 100871, People's Republic of China

Received June 30, 1998

The electronic effects of Rh(II)-mediated carbenoid intramolecular C−H insertion have been intensively investigated. The chemo-, regio-, and stereoselectivity of the reaction have been observed to be affected by the electrophilicity of the carbene−Rh intermediate, the substituents on the carbon at which the C−H insertion occurs, and steric and conformational factors.[1] It has been well documented that the electronic properties of the ligands of the Rh(II) catalyst have a marked influence over the electrophilicity of carbene−Rh intermediate.[1c,e,2] In addition, the α-substituent on the carbenoid carbon is expected to exert a similar effect on the reactivity of carbene−Rh complex.[2c,3] According to the reaction mechanism proposed by Doyle, an electron-donating α-substituent decreases the electrophilicity of the carbene−Rh complex and causes the C−H insertion to occur with a later transition state, while an electron-withdrawing α-substituent operates in the opposite way.[1c] However, this prediction lacks solid support by experimental data. The α-substituent effect, although important, is generally subtle and may be readily overridden by other effects, such as steric and conformational effects.[3b] Most of the studies on the electronic effects have so far been concentrated on electron-withdrawing α-substituents, such as ester or acetyl groups. We have recently reported a linear free energy correlation study of the carbenoid C−H insertion.[4] In the study, the electronic effects are evaluated under the condition where possible steric and conformational interference is minimized through the measurement of the relative reactivity of the carbenoid insertion into a series of para-substituted benzylic C−H bonds. We envisaged that the same approach could be employed to address the problem of α-substituent effects. We report in this paper the study on the Hammett correlation of the α-methyl-substituted carbenoid C−H insertion.

Diazo compounds **1a**−**e**, in which the α-substituent is a methyl group rather than an ester group, are employed in this study (Scheme 1). By assuming that k_A is constant through the series of insertion reactions, the relative reactivity of the para-substituted benzylic C−H to nonsubstituted benzylic C−H, k_X/k_A, is obtained by the ratio **4**/**3**.

Scheme 1



a, X = NO_2; **b**, X = Cl; **c**, X = H; **d**, X = Ph; **e**, X = OMe.

$$k_X/k_H = \frac{k_X/k_A}{k_H/k_A} = \frac{[\mathbf{4/3}]_X}{[\mathbf{4/3}]_H}$$

The syntheses of diazo compounds **1a**−**e** is outlined in Scheme 2. Acid **5**[4] was converted into the corresponding acyl chloride, followed by treatment with diazoethane to give **1a**. To synthesize **1b**,**d**,**e**, acid **5** was first converted to its corresponding methyl ester, which was further subjected to reduction to give the corresponding amino compound **6**. To prepare **1b**, **6** was subjected to a Sandmeyer reaction[5] to yield the 4-chloro compound **7**, followed by hydrolysis, acylation, and diazoethane treatment to give **1b**. **1d** was prepared by phenylation[6] of **6** to give the 4-phenyl compound **8**, followed by the same procedure as that used for the preparation of **1a**. To prepare **1e**, **6** was first hydroxylated,[7] followed by methylation to yield **9**. Further hydrolysis and diazo transfer gave **1e**. **1c** was synthesized in a different way. Diethyl propylmalonate **10** was alkylated with 2-phenylethyl bromide, followed by hydrolysis, acidification, and decarboxylation to give acid **11**. Acylation and diazo transfer gave **1c** (Scheme 3).

Rh(II)-mediated C−H insertion reactions were conducted at room temperature under standard conditions as previously reported.[4] The remaining catalyst was removed by a short column of silica gel, and the crude reaction mixture was carefully analyzed by ^{1}H NMR (400 MHz) and GC−MS.

It was intended that the Hammett approach be applied to the model compounds **1a**−**e** with three typical Rh(II) catalysts, rhodium(II) acetate, rhodium(II) trifluoroacetate, and rhodium(II) acetamide. However, we found the diazo decomposition of **1a** with $Rh_2(OAc)_4$ or $Rh_2(acam)_4$ did not give the expected C−H insertion products **3a** and **4a**; an unstable yellow compound was instead isolated as the main product (Scheme 4). The structure

(1) (a) Taber, D. F.; Ruckle, R. E., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 7686. (b) Stork, G.; Nakatani, K.*Tetrahedron Lett.* **1988**, *29*, 2283. (c) Doyle, M. P.; Westrum, L. J.; Wolthuis, W. N. E.; See, M. M.; Boone, W. P.; Bagheri, V.; Pearson, M. M. *J. Am. Chem. Soc.* **1993**, *115*, 958. (d) Wang, P.; Adams, J. *J. Am. Chem. Soc.* **1994**, *116*, 3296. (e) Pirrung, M. C.; Morehead, A. T., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 8991.

(2) (a) Padwa, A.; Austin, D. J.; Hornbuckle, S. F.; Semones, M. A.; Doyle, M. P.; Protopopova, M. N. *J. Am. Chem. Soc.* **1992**, *114*, 1874. (b) Padwa, A.; Austin, D. J.; Price, A. T.; Semones, M. A.; Doyle, M. P.; Protopopova, M. N.; Winchester, W. R.; Tran, A. *J. Am. Chem. Soc.* **1993**, *115*, 8669. (c) Wee, A. G. H.; Yu, Q. *J. Org. Chem.* **1997**, *62*, 3324. (d) Padwa, A.; Austin, D. J.; Hornbuckle, S. F. *J. Org. Chem.* **1996**, *61*, 63. (e) Doyle, M. P.; Dyatkin, A. B. *J. Org. Chem.* **1995**, *60*, 3035.

(3) (a) Doyle, M. P.; Bagheri, V.; Pearson, M. M.; Edwards, J. D. *Tetrahedron Lett.* **1989**, *30*, 7001. (b) Wee, A. G. H.; Liu, B.; Zhang, L. *J. Org. Chem.* **1992**, *57*, 4404.

(4) Wang, J.; Chen, B.; Bao, J. *J. Org. Chem.* **1998**, *63*, 1853.

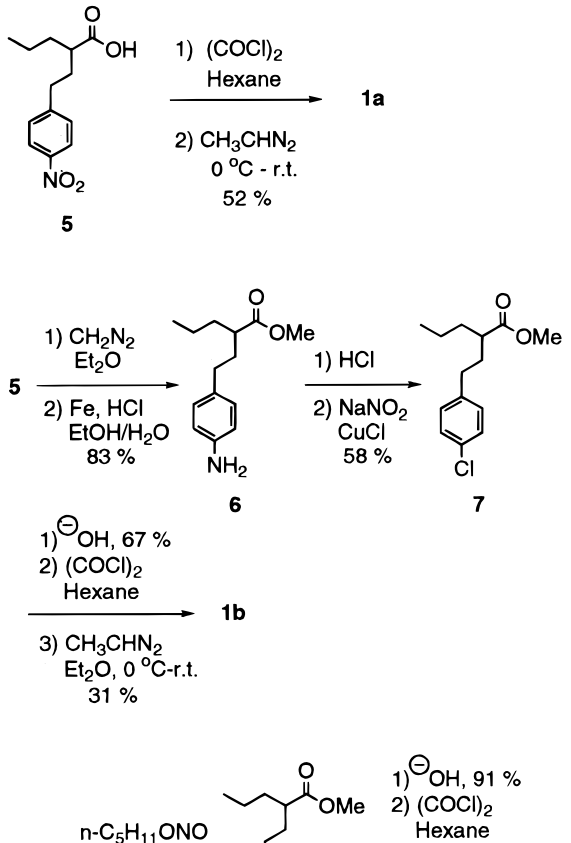
(5) Marvel, C. S.; McElvain, S. M. *Organic Syntheses*; Wiley: New York, 1941; Vol. I, p 170.

(6) Cadogan, L. I. G. *J. Chem. Soc.* **1962**, 4257.

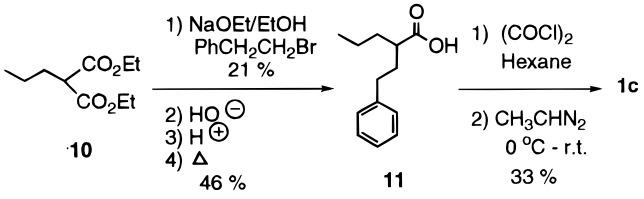
(7) Icke, R. N.; Redemann, C. E.; Wisegarver, B. B.; Alles, G. A. *Organic Syntheses*; Wiley: New York, 1955; Vol. III, p 564.

10.1021/jo981279t CCC: $15.00
Published on Web 10/27/1998

Scheme 2



Scheme 3



of this compound was assigned as azine **12** by inspection of the spectra data. Similar results have been obtained with other diazo compounds **1b**−**e**. The formation of azine in the Rh(II)-mediated decomposition of α-methyl-substituted diazocarbonyl compounds has been previously reported by Taber.[8] On the other hand, when the reaction was catalyzed by $Rh_2(O_2CCF_3)_4$, the expected C−H insertion products were isolated as major products.

(8) Taber, D. F.; Hennessy, M. J.; Louey, J. P. *J. Org. Chem.* **1992**, *57*, 436.

Scheme 4

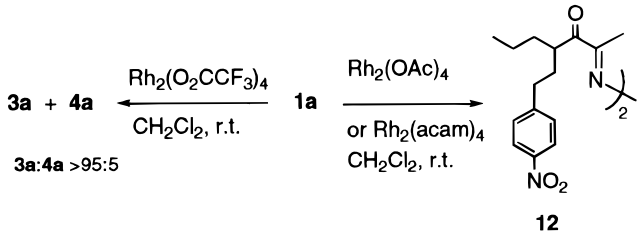


Table 1. $Rh_2(O_2CCF_3)_4$-Catalyzed Reaction of Diazo Compounds 1a−e[a]

	X	yield (%, **3** + **4**)	**4**/**3**[b]	k_X/k_H
1a	NO_2	83	<5:95	
1b	Cl	73	23.2:76.8	0.55
1c	H	84	35.6:64.4	1.00
1d	Ph	82	38.9:61.1	1.15
1e	OMe	59	54.3:45.7	2.13

[a] All reactions were run at room temperature in CH_2Cl_2. [b] The relative yields for **4b**−**e** and **3b**−**e** were determined by GC−MS analysis, and an average was taken from two runs in each case. Average standard deviation is 0.5%.

^{1}H NMR of the crude reaction mixture indicates that the **3a**/**4a** ratio is greater than 95:5. Diazo decomposition of **1b**−**e** with $Rh_2(O_2CCF_3)_4$ gave C−H insertion products **3b**−**e** and **4b**−**e** as main products.

In contrast to the intramolecular C−H insertions by metal carbenes with α-carboxylate ester substituents in which the reactions show high stereoselectivity,[1a,4] **3a**−**e** and **4b**−**e** in this study were obtained as a mixture of distereoisomers. Since the insertion products were not separable by column chromatography, structure identification was first provided by inspection of the ^{1}H NMR (400 MHz) spectra of the reaction mixture. For benzylic secondary C−H insertion products, the chemical shift of the 3-H in the five-membered ring of **4b**−**e** is characteristically located in the range between 3.40 and 3.60 ppm, while for the corresponding 3-H of aliphatic secondary insertion products **3a**−**e**, the chemical shifts are below 3.0 ppm.[9] The structure for each isomer was further established by GC−MS analysis. The mixtures of **3a**−**e** and **4b**−**e** were separable by gas chromatography, and the mass spectrum for each isomer was thus obtained by GC−MS. The characteristic McLafferty rearrangement[10] gave different fragment ions for **3a**−**e** and **4b**−**e**, thus unambiguously establishing the structure for each insertion product. The product ratio was determined by GC−MS.[11] The **3**/**4** ratios and the relative rate constants, k_X/k_H, are collected in Table 1.

The relative rates are then fitted to the Hammett equation with both σ and σ^+.[12] Better linear correlation is found with σ than with σ^+, giving reaction constants of −1.18 (with σ, $r = 0.99$) and −0.58 (with σ^+, $r = 0.93$),

(9) Similarly, we found in our previous study that, in the diazo decomposition of α-ester diazo compounds, the chemical shift for the corresponding 3-H in the benzylic secondary C−H insertion products locates considerably downfield in the range between 3.60 and 3.90 ppm, while for the corresponding 3-H in the aliphatic secondary C−H insertion products, the chemical shifts are below 3.0 ppm; see ref 4.

(10) (a) He, X.; Chen, B.; Wang, J.; He, M. *Rapid. Commun. Mass Spectrom.* **1997**, *11*, 1818. (b) Chen, B.; Liang, F.; Chen, H.; Wang, J. *J. Chem. Res., Synop.* **1998**, 410.

(11) The product ratio was also analyzed by ^{1}H NMR (400 MHz) of the reaction mixture in each case, and the results obtained were comparable to those from GC−MS.

(12) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

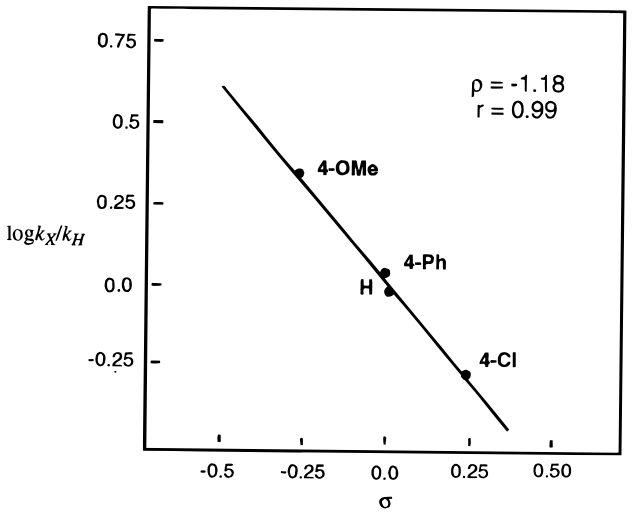


Figure 1. Plot of log k_X/k_H against σ for the C−H insertions of an $Rh_2(O_2CCF_3)_4$-catalyzed reaction.

respectively (Figure 1).[13] The relatively small and negative value of the reaction constant suggests that the C−H insertion proceeds through a transition state with a small positive charge buildup at the carbon where the insertion occurs. In our previous study, $Rh_2(O_2CCF_3)_4$-catalyzed C−H insertion with diazo β-ketoester gives a reaction constant of −0.66 with σ.[4] The numerical difference of the ρ values is marked, and the larger value of the reaction constant obtained in the C−H insertion with α-methyl-substituted substrates **1b**−**e** suggests that the carbene−Rh intermediate in this case is less reactive toward the C−H bond, thus giving higher sensitivity to the substituent effect. In other words, the partial positive charge at the benzylic carbon is more developed, and the C−H insertion occurs at a relatively later transition state compared to the $Rh_2(O_2CCF_3)_4$-catalyzed C−H insertion with diazo β-ketoester (Hammond postulate). This is consistent with the prediction based on Doyle's model.[1c]

The formation of azine as a major product in the $Rh_2(OAc)_4$- or $Rh_2(acam)_4$-catalyzed reaction might be related to the decrease of electrophilicity of the carbene−Rh complex. Since both the electron-donating α-substituent and the electron-releasing ligand from Rh can decrease the electrophilicity of the carbene−Rh complex, the reactivity of the carbene−Rh complex formed from **1a**−**e** and $Rh_2(OAc)_4$ or $Rh_2(acam)_4$, whose ligands are relatively less electron withdrawing compared to $Rh_2(O_2CCF_3)_4$, is so decreased that C−H insertion cannot compete with the other reaction pathway.[14] In contrast, for the $Rh_2(O_2CCF_3)_4$-catalyzed reaction, the decease of the Rh(II)−carbene reactivity due to α-methyl substitution is counterbalanced by the strong electron-withdrawing ligand. As a result, the C−H insertion in this case can occur, but as shown by the reaction constant, the reaction proceeds with a relatively later transition state compared to the $Rh_2(O_2CCF_3)_4$-catalyzed reaction with diazo β-ketoester.

In conclusion, the α-substituent effects of the intramolecular C−H insertion by Rh(II)-mediated carbenoids have been investigated through linear free energy correlation analysis. The study has confirmed that electron donation from the α-methyl group decreases the electrophilicity of the carbene−Rh complex and leads to the increase of its selectivity.

Experimental Section

General. For the details of the general procedure, see our previous report.[4] ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded with a Varian Mercury 200 spectrometer. Diazoethane was prepared from *N*-ethyl-*N*-nitrosourea according to a literature procedure.[15] GC−MS analysis was performed with an HP 5971A-5890II GC−MSD. Elemental analyses were performed at the Institute of Chemistry, Chinese Academy of Sciences.

2-Diazo-6-(4-nitrophenyl)-4-propyl-3-hexanone (1a). To a solution of 4-(4-nitrophenyl)-2-propylbutanoic acid **5** (200 mg, 0.8 mmol) in anhydrous hexane was added oxalyl chloride (0.7 mL, 8.0 mmol), and the solution was heated under gentle reflux for 1.5 h. The solvent and excess oxalyl chloride were removed by distillation, and the residue was kept in vacuo for 1 h. The acyl chloride was then dissolved in anhydrous hexane (5 mL) and was added dropwise to a solution of diazoethane (8.0 mmol) in Et_2O (50 mL) at −10 °C. The solution was stirred at 0 °C for 1 h and at room temperature overnight. The solvent and excess diazoethane were removed under reduced pressure. The residue was subjected to column chromatography with 15:1 petroleum ether/EtOAc to give a yellow oil, **1a** (120 mg, 52%): R_f = 0.41 (petroleum ether/EtOAc = 4:1); ^{1}H NMR (400 Hz) δ 0.80 (t, J = 7.0 Hz, 3H), 1.15−1.40 (m, 4H), 1.50−1.78 (m, 2H), 1.86−2.10 (m, 1H), 1.90 (s, 3H), 2.50−2.72 (m, 2H), 7.24 (d, J = 8.7 Hz, 2H), 8.06 (d, J = 8.7 Hz, 2H); ^{13}C NMR (50 MHz) δ 7.89, 13.70, 20.04, 33.02, 33.18, 34.95, 45.18, 62.79, 123.29, 128.73, 146.07, 149.25, 197.01; IR 2905, 2050, 1610, 1505, 1330, 1275 cm^{-1}; MS (*m*/*z*, relative intensity) 261 [$(M - N_2)^+$, 18], 218 (58), 144 (20), 122 (22), 111 (64); HRMS $(M - N_2)^+$ calcd for $C_{15}H_{19}NO_3$ 261.1365, found 261.1370.

2-Diazo-6-(4-chlorophenyl)-4-propyl-3-hexanone (1b). Acid **5** was first converted to its corresponding methyl ester by treatment with an ethereal solution of diazomethane. Methyl 4-(4-nitrophenyl)-2-propylbutanoate: R_f = 0.47 (petroleum ether/EtOAc = 7:1); ^{1}H NMR (200 MHz) δ 0.89 (t, J = 7.2 Hz, 3H), 1.21−2.10 (m, 6H), 2.36−2.48 (m, 1H), 2.62−2.76 (m, 2H), 3.70 (s, 3H), 7.33 (d, J = 8.5 Hz, 2H), 8.14 (d, J = 8.5 Hz, 2H); ^{13}C NMR (50 MHz) δ 14.43, 21.00, 33.94, 34.15, 35.15, 45.29, 52.03, 124.10, 129.64, 147.00, 150.10, 176.74; IR 2925, 1720, 1590, 1505, 1330 cm^{-1}.

The methyl ester (8.83 g, 33 mmol) was dissolved in 80% EtOH/H_2O (120 mL), followed by addition of 20 drops of concentrated aqueous HCl and ion powder (18.6 g, 330 mmol). The mixture was heated under reflux for 1 h while being stirred with a mechanical stirrer. After completion of the reduction, the black powder in the reaction mixture was removed by filtration. EtOH was then removed in vacuo. The residue was extracted with Et_2O (3 × 50 mL), and the combined ethereal solution was washed with H_2O and dried over anhydrous $MgSO_4$. Removal of the solvent gave an oil of methyl 4-(4-aminophenyl)-2-propylbutanoate, **6** (6.53 g, 83%). **6** was used in the next step without further purification: R_f = 0.43 (petroleum ether/EtOAc = 2:1); ^{1}H NMR (200 MHz) δ 0.87 (t, J = 7.2 Hz, 3H), 1.20−2.00 (m, 6H), 2.30−2.52 (m, 3H), 3.50 (s, br. 1H), 3.66 (s, 3H), 6.60 (d, J = 8.4 Hz, 2H), 6.94 (d, J = 8.4 Hz, 2H); ^{13}C NMR (50 MHz) δ 14.50, 21.09, 33.35, 34.97, 35.15, 45.41, 51.85, 115.75, 129.67, 132.18, 144.90, 177.33; IR 3450, 3380, 2940, 1720, 1625, 1515, 1275, 1160 cm^{-1}; MS (*m*/*z*, relative intensity) 235 (M^+, 19), 204 (3), 119 (42), 106 (100); HRMS calcd for $C_{14}H_{21}O_2N$ 235.1572, found 235.1576.

(13) The nitro group was not included in the Hammett analysis, since the accurate value of the product ratio could not be obtained. If we introduce in the Hammett plot the roughly estimated **4**/**3** ratio of 2.2:97.8 from ^{1}H NMR analysis of the reaction mixture, we can get a ρ value of −1.66 with σ (r = 0.99).

(14) The mechanism for the azine formation in this case is not clear. Eguchi has also reported an example in which $Rh_2(acam)_4$ more effectively promotes azine formation compared with $Rh_2(O_2CCF_3)_4$ in Rh(II)-catalyzed diazo decomposition; see: Ohno, M.; Itoh, M.; Umeda, M.; Furuta, R.; Kondo, K.; Eguchi, S. *J. Am. Chem. Soc.* **1996**, *118*, 7075.

(15) Wilds, A. L.; Meader, A. L., Jr. *J. Org. Chem.* **1948**, *13*, 763.

To **6** (2.7 g, 11.5 mmol) were added H_2O (20 mL) and concentrated HCl (2.7 mL, 33 mmol). The mixture was warmed for 10 min until it became a homogeneous solution. A TLC check of the mixture indicated that all free amine had been changed to its salt. The solution was then cooled to 0 °C with an ice bath, and a solution of $NaNO_2$ (1.18 g, 17.2 mmol) was added dropwise with stirring. The solution was further stirred between 0 and 5 °C for 1 h, and then urea (0.34 g, 5.7 mmol) was added to remove excess $NaNO_2$. The mixture was added dropwise to CuCl [freshly prepared from $CuSO_4 \cdot 5H_2O$ (8.56 g, 34.5 mmol)] at 0 °C with stirring. The mixture was allowed to warm to room temperature. After being stirred at room temperature for 1 h, the mixture was heated between 50 and 60 °C for 45 min. After cooling, the mixture was extracted with Et_2O (3 × 150 mL). The combined ethereal solution was washed with 5% aqueous NaOH, H_2O, concentrated H_2SO_4, and H_2O and finally dried over anhydrous $MgSO_4$. Removal of the solvent gave a crude product (2.2 g), which was subjected to column chromatography, eluting with 25:1 petroleum ether/EtOAc to give methyl 2-(4-chlorophenyl)-2-propylbutanoate, **7** (1.7 g, 58%): R_f = 0.54 (petroleum ether/EtOAc = 10:1); ^{1}H NMR (200 MHz) δ 0.88 (t, J = 7.1 Hz, 3H), 1.20−2.05 (m, 6H), 2.34−2.65 (m, 3H), 3.68 (s, 3H), 7.09 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.2 Hz, 2H); ^{13}C NMR (50 MHz) δ 13.61, 20.18, 32.73, 33.59, 34.29, 44.47, 51.07, 128.08, 129.39, 131.27, 139.74, 176.15; IR 2955, 1725, 1485, 1450, 1200, 1160 cm^{-1}; MS (*m*/*z*, relative intensity) 254 (M^+, 6), 138 (11), 125 (30), 116 (81), 87 (100); HRMS calcd for $C_{14}H_{19}ClO_2$ 254.1074, found 254.1066.

Methyl ester **7** (1.96 g, 7.7 mmol) was dissolved in MeOH (40 mL), to which was added aqueous NaOH (770 mg, 19 mmol). The mixture was refluxed for 6 h. MeOH was removed, and the usual workup gave 4-(4-chlorophenyl)-2-propylbutanoic acid as an oily product (1.24, 67%): ^{1}H NMR (200 MHz) δ 0.90 (t, J = 7.0 Hz, 3H), 1.24−2.08 (m, 6H), 2.32−2.79 (m, 3 H), 7.01 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4, 2H); ^{13}C NMR (50 MHz) δ 14.56, 21.05, 33.56, 34.22, 34.92, 45.29, 129.08, 130.39, 132.00, 140.56, 183.38; IR 3000 (br), 1700, 1450, 1240 cm^{-1}. The acid was used in the next step without further purification.

The same procedure was followed as for the preparation of **1a**, and the acid (1.22 g, 5.08 mmol) was converted to diazo compound **1b** (440 mg, 31%): R_f = 0.50 (petroleum ether/EtOAc = 6:1); ^{1}H NMR (400 MHz) δ 0.86 (t, J = 7.2 Hz, 3H), 1.22−1.34 (m, 2H), 1.38−1.42 (m, 1H), 1.62−1.73 (m, 2H), 1.95 (s, 3H), 1.93−2.06 (m, 1H), 2.44−2.51 (m, 1H), 2.54−2.67 (m, 2H), 7.07 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz) δ 8.29, 14.07, 20.45, 32.95, 33.87, 35.30, 45.51, 63.06, 128.45, 129.60, 131.65, 140.07, 197.85; IR 2920, 2060, 1620, 1450, 1280 cm^{-1}; MS (*m*/*z*, relative intensity) 250 [$(M - N_2)^+$, 8], 235 (3), 207 (12), 152 (11), 140 (20), 125 (100); HRMS $(M - N_2)^+$ calcd for $C_{15}H_{19}OCl$ 250.1124, found 250.1119.

2-Diazo-6-(4-phenylphenyl)-4-propyl-3-hexanone (1d). A solution of amino compound **6** (2.23, 9.5 mmol) and *n*-pentylnitrite (1.75 g, 15 mmol) in benzene (40 mL) was stirred for 20 min, until gas evolution had stopped. The solution was then refluxed for 1.5 h. The solvent was removed in vacuo, and the residue was subjected to column chromatography, eluting with 5:1 petroleum ether/EtOAc to give methyl 4-(4-phenylphenyl)-2-propylbutanoate, **8**, as a light-yellow oil (1.60 g, 57%): R_f = 0.52 (petroleum ether/EtOAc = 10:1); ^{1}H NMR (200 MHz) δ 0.89 (d, J = 7.1 Hz, 3H), 1.20−2.10 (m, 6H), 2.33−2.71 (m, 3H), 3.68 (s, 3H), 7.15−7.64 (m, 9H); ^{13}C NMR (50 MHz) δ 13.95, 20.54, 33.35, 34.04, 34.64, 44.97, 51.40, 126.96, 127.06, 128.37, 128.68, 128.79, 138.86, 140.80, 141.03, 176.63; IR 2960, 1730, 1460, 1200, 1161 cm^{-1}. The methyl ester (1.38 g, 4.66 mmol) was hydrolyzed in aqueous MeOH with NaOH to give 4-(4-phenylphenyl)-2-propylbutanoic acid (1.2 g, 91%): ^{1}H NMR (200 MHz) δ 0.92 (t, J = 7.0 Hz, 3H), 1.24−2.15 (m, 6H), 2.38−2.57 (m, 1H), 2.59−2.82 (m, 2H), 7.20−7.67 (m, 9H); ^{13}C NMR (50 MHz) δ 13.98, 20.46, 33.23, 33.79, 34.34, 44.61, 125.95, 127.00, 127.12, 128.38, 128.70, 128.84, 140.67, 141.00, 181.34; IR 3000 (br), 1700, 1460, 1245 cm^{-1}.

The same procedure was followed as for the preparation of **1a**, and the acid (1.1 g, 3.9 mmol) was converted to diazo compound **1d** (450 mg, 36%): R_f = 0.42 (petroleum ether/EtOAc = 6:1); ^{1}H NMR (400 MHz) δ 0.87 (t, J = 7.2 Hz, 3H), 1.23−1.36 (m, 2H), 1.40−1.48 (m, 1H), 1.60−1.79 (m, 2H), 1.95 (s, 3H), 2.02−2.11 (m, 1H), 2.50−2.60 (m, 1H), 2.61−2.71 (m, 1H), 7.22 (d, J = 8.2 Hz, 2H), 7.30−7.37 (m, 1H), 7.40−7.47 (m, 2H), 7.51 (d, J = 8.2 Hz, 2H), 7.58−7.61 (m, 2H); ^{13}C NMR (100 MHz) δ 8.28, 14.13, 20.51, 33.23, 34.08, 35.31, 45.60, 63.16, 126.98, 127.04, 127.12, 128.72, 128.72, 138.90, 140.74, 141.03, 198.05; IR 2915, 2055, 1620, 1445, 1280, 1040 cm^{-1}; MS (*m*/*z*, relative intensity) 292 [$(M - N_2)^+$, 35], 235 (11), 180 (89), 167 (100); HRMS $(M - N_2)^+$ calcd for $C_{21}H_{24}O$ 296.1776, found 296.1766.

2-Diazo-6-(4-methoxyphenyl)-4-propyl-3-hexanone (1e). To amino compound **6** (1.24 g, 5.27 mmol) in H_2O (20 mL) was added aqueous H_2SO_4 (0.5 M, 36 mL), and the mixture was warmed until it became homogeneous. A TLC check of the mixture indicated that all of the free amine had been changed to its salt. After the mixture cooled to 0 °C, a solution of $NaNO_2$ (545 mg, 7.9 mmol) was added dropwise while the temperature was maintained between 0 and 5 °C. The resulting solution was stirred at 5 °C for another 1.5 h after the addition. Urea (158 mg, 2.6 mmol) was added to remove excess $NaNO_2$. Aqueous H_2SO_4 (0.5 M, 20 mL) was added dropwise, and the solution was refluxed for 30 min. The mixture was cooled to room temperature, and the usual workup gave methyl 4-(4-hydroxyphenyl)-2-propylbutanoate as an oily product: R_f = 0.34 (petroleum ether/EtOAc = 4:1); ^{1}H NMR (200 MHz) δ 0.87 (t, J = 7.1 Hz, 3H), 1.20−2.02 (m, 6H), 2.37−2.48 (m, 1H), 2.49 (t, J = 7.4 Hz, 2H), 3.68 (s, 3H), 5.73 (s, 1H), 6.75 (d, J = 8.2 Hz, 2H), 7.00 (d, J = 8.2 Hz, 2H); ^{13}C NMR (50 MHz) 13.90, 20.51, 32.78, 34.27, 34.60, 44.93, 51.53, 115.18, 129.39, 133.47, 153.92, 177.33. IR 3400 (br), 2960, 1700, 1600, 1520, 1440, 1380, 1220 cm^{-1}. The hydroxyl compound was used in the next step without further purification.

The hydroxyl compound was dissolved in DMF (20 mL). To the solution was added NaH (15.8 mmol), and the mixture was stirred at room temperature for 1 h. MeI (0.98 mL, 15.8 mmol) was then added, and the solution was stirred overnight. Et_2O (150 mL) was added to the solution, and then H_2O (150 mL) and 5% aqueous HCl (4 mL) were added. The ethereal layer was separated, washed with H_2O twice, and then dried over anhydrous $MgSO_4$. Removal of the drying agent and solvent gave a crude oil, which was purified with column chromatography, eluting with 20:1 petroleum ether/EtOAc to give methyl 4-(4-methoxyphenyl)-2-propylbutanoate, **9**, as oily product (998 mg, 76% from 6): R_f = 0.56 (petroleum ether/EtOAc = 8:1); ^{1}H NMR (200 Hz) δ 0.88 (t, J = 7.0 Hz, 3H), 1.22−2.00 (m, 6H), 2.33−2.70 (m, 3H), 3.68 (s, 3H), 3.78 (s, 3H), 6.81 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H); ^{13}C NMR (50 MHz) δ 13.63, 20.21, 32.46, 34.01, 34.30, 44.54, 51.01, 54.88, 113.41, 128.94, 133.41, 157.46, 176.37; MS (*m*/*z*, relative intensity) 250 (26), 219 (8), 134 (81), 121 (100); HRMS calcd for $C_{15}H_{22}O_3$ 250.1569, found 250.1586.

The methyl ester **9** (785 mg, 3.14 mmol) was hydrolyzed in aqueous MeOH with NaOH to give 4-(4-methoxyphenyl)-2-propylbutanoic acid (586 mg, 79%), which was converted to diazo compound **1e** (209 mg, 33%) by the same procedure as that used for the preparation of **1a**. **1e**: R_f = 0.43 (petroleum ether/EtOAc = 6:1); ^{1}H NMR (400 MHz) δ 0.86 (t, J = 7.2 Hz, 3H), 1.22−1.33 (m, 2H), 1.38−1.49 (m, 1H), 1.60−1.72 (m, 2H), 1.95 (s, 3H), 1.93−2.05 (m, 1H), 2.40−2.47 (m, 1H), 2.52−2.70 (m, 2H), 3.77 (s, 3H), 6.81 (d, J = 8.4 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz) δ 8.28, 14.12, 20.52, 32.66, 34.38, 35.25, 45.54, 55.26, 63.14, 113.79, 129.18, 133.67, 157.80, 198.19; IR 2920, 2055, 1620, 1500, 1445, 1240 cm^{-1}; HRMS (*m*/*z*, relative intensity) 246 (M^+, 14), 134 (7), 121 (100); HRMS $(M - N_2)^+$ calcd for $C_{16}H_{22}O_2$ 246.1586, found 246.1603.

2-Diazo-6-phenyl-4-propyl-3-hexanone (1c). To absolute EtOH (60 mL) was added sodium (3.4 g, 148 mmol). When the formation of sodium ethoxide was complete, diethyl propylmalonate **10** (20 mL, 99 mmol) was added dropwise over 1.5 h. A solution of (2-bromoethyl)benzene (37 g, 200 mmol) in 20 mL of absolute EtOH was added dropwise. The mixture was stirred for 20 h under reflux. EtOH was removed by distillation, and ice water was added to the residue. The mixture was extracted with Et_2O (3 × 200 mL). The combined ethereal solution was washed with H_2O and dried over anhydrous $MgSO_4$. Removal of the drying agent and solvent gave a crude product, which was distilled under vacuum to yield diethyl 2-propyl-(2-phenylethyl)-malonate (6.3 g, 21%): bp 134−136 °C, 0.17 mmHg; ^{1}H NMR (200 MHz) 0.94 (t, J = 7.0 Hz, 3H), 1.26 (t, J = 7.2 Hz, 6H), 1.90−2.00 (m, 2H), 2.15−2.22 (m, 2H), 2.42−2.58 (m, 2H), 4.19

(q, J = 7.2 Hz, 4H), 7.12−7.34 (m, 5H); ^{13}C NMR (50 MHz) 14.69, 14.99, 18.03, 31.24, 34.97, 35.41, 58.13, 61.61, 126.55, 128.89, 128.95, 142.13, 172.22; IR 2995, 1725, 1460, 1370, 1200 (br), 1040 cm^{-1}. The diester was then subjected to hydroxylation and decarboxylation by the conventional method, as previously reported, to provide 4-phenyl-2-propylbutanoic acid, **11** (3.2 g, 46%): ^{1}H NMR (200 MHz) δ 0.90 (t, J = 7.2 Hz, 3H), 0.79−1.10 (m, 1H), 1.20−2.19 (m, 6H), 2.28−2.80 (m, 2H), 7.02−7.56 (m, 5H); ^{13}C NMR (50 MHz) δ 13.59, 20.43, 33.59, 33.76, 34.29, 44.79, 125.92, 128.35, 128.40, 141.52, 183.20; MS (*m*/*z*, relative intensity) 206 (M$^+$, 14), 105 (82), 91 (53), 73 (100); HRMS calcd for $C_{13}H_{18}O_2$ 206.1307, found 206, 1307.

The acid **11** (400 mg, 1.94 mmol) was converted to diazo compound **1c** (250 mg, 53%): R_f = 0.57 (petroleum ether/EtOAc = 6:1); ^{1}H NMR (200 MHz) δ 0.79 (t, J = 7.2 Hz, 3H), 1.08−1.39 (m, 3H), 1.44−1.76 (m, 3H), 1.88 (s, 3H), 2.38−2.62 (m, 3H), 6.95−7.22 (m, 5H); ^{13}C NMR (50 MHz) δ 8.23, 14.05, 20.44, 33.50, 34.02, 35.20, 45.46, 63.25, 125.85, 128.23, 128.32, 141.55, 198.10; MS (*m*/*z*, relative intensity) 216 [(M − N$_2$)$^+$, 12], 173 (17), 111 (21), 104 (24), 91 (100); HRMS (M − N$_2$)$^+$ calcd for $C_{15}H_{22}O$ 216.1514, found 216.1528.

General Procedure for Rh(II)-Catalyzed Dinitrogen Extrusion from Diazo Compounds 1a−e. 1a−e (2.0 mmol) in CH_2Cl_2 (20 mL) was added to a stirring solution of CH_2Cl_2 (20 mL) containing 1.0 mol % Rh(II) at room temperature under a nitrogen atmosphere. The homogeneous solution was stirred for 10−14 h until complete disappearance of the diazo compound was observed. The catalyst was removed by a short column of silica gel, and the crude C−H insertion products were analyzed with ^{1}H NMR (400 MHz) and GC−MS for the product ratio determination and structure characterization.

Rh(II)-Catalyzed Dinitrogen Extrusion of 2-Diazo-6-(4-nitrophenyl)-4-propyl-3-hexanone (1a). The diazo decomposition of **1a** with $Rh_2(OAc)_4$ gave an unstable yellow oil of azine **12** (74%) as the major product. **12**: R_f = 0.64 (petroleum ether/EtOAc = 10:1); ^{1}H NMR (200 MHz) δ 0.88 (t, J = 7.2 Hz, 6H), 1.19−2.12 (m, 12H), 2.33 (s, 6H), 2.63 (t, J = 8.0 Hz, 4H), 3.32−3.47 (m, 2H), 7.30 (d, J = 8.7 Hz, 4H), 8.13 (d, J = 8.7 Hz, 4H); ^{13}C NMR (50 MHz) δ 13.68(CH_3), 20.11(CH_2), 23.69(CH_3), 31.40(CH_2), 33.06(CH_2), 33.25(CH_2), 42.73(CH), 123.35(CH), 128.80(CH), 146.16(C), 148.96(C), 197.49(C=O or C=N), 201.71(C=O or C=N); IR 2920, 1705, 1600, 1515, 1340 cm^{-1}; MS (*m*/*z*, relative intensity) 234 (33), 206 (26), 160 (31), 150 (22), 131 (26), 57 (100).

The diazo decomposition of **1a** with $Rh_2(O_2CCF_3)_4$ as a catalyst gave C−H insertion products in 83% isolated yield. An ^{1}H NMR spectrum of the crude product indicated that it was a mixture of diastereomeric isomers of aliphatic C−H insertion products **3a** and a tiny amount of benzylic C−H insertion product **4a** was detected (δ 0.68, d, J = 7.5 Hz). **3a** to **4a** ratio was estimated to be greater than 95:5. The mixture of **3a** was not separable by TLC or column chromatography. The mixture gave the following analytical data: ^{1}H NMR (400 MHz): δ 0.87 (d, J = 7.2 Hz), 0.94 (d, J = 7.4 Hz), 1.11 (d, J = 6.4 Hz), 1.06 (d, J = 6.9 Hz), 1.08 (d, J = 6.5 Hz), 1.15 (d, J = 5.7 Hz), 1.24−1.45 (m, 1H), 1.57−1.66 (m, 2H), 2.02−2.40 (m, 4H), 2.76−2.84 (m, 2H), 7.35 (d, J = 8.6 Hz, 2H), 8.14 (d, J = 8.6 Hz, 2H); IR 2960, 1730, 1600, 1515, 1455, 1340 cm^{-1}. Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 69.10; H, 7.17; N, 5.39. GC−MS analysis of the mixture gave three peaks, which were labeled as **3a-1**, **3a-2**, and **3a-3**. The ratio of **3a-1**/**3a-2**/**3a-3** is 71:10:19. MS (*m*/*z*, relative intensity) **3a-1**: 261 (M$^+$, 2), 112 [(M − *p*-$NO_2C_6H_4CH{=}CH_2$)$^+$, 100], 97 (12). **3a-2**: 261 (M$^+$, 2), 112 [(M − *p*-$NO_2C_6H_4CH{=}CH_2$)$^+$, 100], 97 (13). **3a-3**: 261 (M$^+$, 2), 112 [(M − *p*-$NO_2C_6H_4CH{=}CH_2$)$^+$, 100], 97 (13).

Rh(II)-Catalyzed Dinitrogen Extrusion of 2-Diazo-6-(4-chlorophenyl)-4-propyl-3-hexanone (1b). The diazo decomposition of **1b** with $Rh_2(O_2CCF_3)_4$ as a catalyst gave C−H insertion products in 73% isolated yield. An ^{1}H NMR spectrum of the product indicated that it was a mixture of diastereomeric isomers of aliphatic C−H insertion products **3b** and benzylic C−H insertion products **4b**. The mixture was not separable by TLC or column chromatography. The mixture gave the following analytical data: ^{1}H NMR (400 MHz) δ 0.67 (d, J = 7.8 Hz), 0.85 (d, J = 7.2 Hz), 0.92 (d, J = 7.5 Hz), 0.95 (t, J = 7.0 Hz), 0.99 (d, J = 7.1 Hz), 1.00 (d, J = 6.5 Hz), 1.06 (d, J = 6.6 Hz), 1.14 (d, J = 6.0 Hz) 1.15 (d, J = 6.0 Hz), 1.28−1.79 (m), 1.85−2.00 (m), 2.02−2.48 (m), 2.58−2.76 (m), 3.48−3.58 (m, 0.23 H, **4b**), 7.12 (d, J = 8.4 Hz), 7.11 (d, J = 8.4 Hz), 7.22 (d, J = 8.4 Hz), 7.30 (d, J = 8.4 Hz); IR 2960, 1730, 1490, 1460, 1160, 1090 cm^{-1}. Anal. Calcd for $C_{15}H_{19}ClO$: C, 71.85; H, 7.64. Found: C, 72.18; H, 7.62. GC−MS analysis of the mixture gave five peaks, which were labeled as **3b-1**, **3b-2**, **3b-3**, **4b-1**, and **4b-2**. The following product ratios were obtained from GC−MS: **3b-1**/**3b-2**/**3b-3** = 62:11:27; **4b-1**/**4b-2** = 65:35; (**4b-1** + **4b-2**)/(**3b-1** + **3b-2** + **3b-3**) = 23.2:76.8. MS (*m*/*z*, relative intensity) **3b-1**: 250 (M$^+$, 9), 127 (5), 112 [(M − *p*-$ClC_6H_4CH{=}CH_2$)$^+$, 100], 97 (15). **3b-2**: 250 (M$^+$, 12), 127 (6), 112 [(M − *p*-$ClC_6H_4CH{=}CH_2$)$^+$, 100], 97 (10). **3b-3**: 250 (M$^+$, 11), 127 (6), 112 [(M − *p*-$ClC_6H_4CH{=}CH_2$)$^+$, 100], 97 (17). **4b-1**: 250 (M$^+$, 14), 208 [(M − $CH_3CH{=}CH_2$)$^+$, 100], 193 (6), 179 (8), 152 (16), 139 (8), 117 (20). **4b-2**: 250 (M$^+$, 20), 221 (5), 208 [(M − $CH_3CH{=}CH_2$)$^+$, 100], 193 (4), 179 (8), 165 (3), 151 (20), 115 (20).

Rh(II)-Catalyzed Dinitrogen Extrusion of 2-Diazo-6-phenyl-4-propyl-3-hexanone (1c). The diazo decomposition of **1c** with $Rh_2(O_2CCF_3)_4$ as a catalyst gave C−H insertion products in 84% isolated yield. An ^{1}H NMR spectrum of the product indicated that it was a mixture of diastereomeric isomers of aliphatic C−H insertion products **3c** and benzylic C−H insertion products **4c**. The mixture was not separable by TLC or column chromatography. The mixture gave the following analytical data: ^{1}H NMR (400 MHz): δ 0.68 (d, J = 7.8 Hz), 0.85 (d, J = 7.2 Hz), 0.92 (d, J = 7.5 Hz), 0.96 (t, J = 7.0 Hz), 1.00 (d, J = 7.1 Hz), 1.01 (d, J = 6.4 Hz), 1.06 (d, J = 6.5 Hz), 1.13 (d, J = 6.1 Hz), 1.14 (d, J = 6 Hz), 1.22−1.75 (m), 1.82−2.46 (m), 2.60−2.78 (m), 3.42−3.58 (m, 0.32 H, **4c**), 7.15−7.35 (m, 5H); IR 2960, 1730, 1600, 1495, 1455, 1375, 1160 cm^{-1}. Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 82.99; H, 9.36. GC−MS analysis of the mixture gave six peaks, which were labeled as **3c-1**, **3c-2**, **3c-3**, **4c-1**, **4c-2** and **4c-3**. The following product ratios were obtained from GC−MS: **3c-1**/**3c-2**/**3c-3** = 53:11:36; **4c-1**/**4c-2**/**4c-3** = 35:6:59; (**4c-1** + **4c-2** + **4c-3**)/(**3c-1** + **3c-2** + **3c-3**) = 35.6:64.4. MS (*m*/*z*, relative intensity) **3c-1**: 216 (M$^+$, 18), 112 [(M−$C_6H_4CH{=}CH_2$)$^+$, 100], 97 (18), 91 (26). **3c-2**: 216 (M$^+$, 20), 112 [(M − $C_6H_4CH{=}CH_2$)+, 100], 97 (21), 91 (35). **3c-3**: 216 (M$^+$, 22), 112 [(M − $C_6H_4CH{=}CH_2$)$^+$, 100], 97 (22), 91 (32). **4c-1**: 216 (M$^+$, 11), 174 [(M − $CH_3CH{=}CH_2$)$^+$, 100], 159 (12), 145 (17), 131 (8), 117 (45), 91 (26). **4c-2**: 216 (M$^+$, 15), 174 [(M − $CH_3CH{=}CH_2$)$^+$, 100], 145 (14), 117 (53), 91 (30). **4c-3**: 216 (M$^+$, 17), 174 [(M − $CH_3CH{=}CH_2$)$^+$, 100], 145 (20), 117 (69), 91 (36).

Rh(II)-Catalyzed Dinitrogen Extrusion of 2-Diazo-6-(4-phenylphenyl)-4-propyl-3-hexanone (1d). The diazo decomposition of **1d** with $Rh_2(O_2CCF_3)_4$ as a catalyst gave C−H insertion products in 82% isolated yield. An ^{1}H NMR spectrum of the product indicated that it was a mixture of diastereomeric isomers of aliphatic C−H insertion products **3d** and benzylic C−H insertion products **4d**. The mixture was not separable by TLC or column chromatography. The mixture gave the following analytical data: ^{1}H NMR (400 MHz): δ 0.72 (d, J = 7.8 Hz), 0.85 (d, J = 7.1 Hz), 0.93 (t, J = 7.5 Hz), 0.97 (d, J = 7.0 Hz), 1.00 (d, J = 6.3 Hz), 1.05 (d, J = 6.4 Hz), 1.06 (d, J = 6.3 Hz), 1.13 (d, J = 5.8 Hz), 1.14 (d, J = 6.0 Hz), 1.22−1.52 (m), 1.58−1.80 (m), 1.82−2.08 (m), 2.10−2.48 (m), 2.59−2.80 (m), 3.49−3.58 (m, 0.38 H, **4d**), 7.23−7.27 (m, 2H), 7.28−7.36 (m, 1H), 7.38−7.46 (m, 2H), 7.48−7.53 (m, 1H), 7.54−7.61 (m, 3H); IR 2950, 1720, 1480, 1440, 1140 cm^{-1}. Anal. Calcd for $C_{21}H_{24}O$: C, 86.26; H, 8.27. Found: C, 85.88; H, 8.37. GC−MS analysis of the mixture gave six peaks, which were labeled as **3d-1**, **3d-2**, **3d-3**, **3d-4**, **4d-1**, and **4d-2**. The following product ratios were obtained from GC−MS: **3d-1**/**3d-2**/**3d-3**/**3d-4** = 45:26:9:20; **4d-1**/**4d-2** = 13:87; (**4d-1** + **4d-2**)/(**3d-1** + **3d-2** + **3d-3** + **3d-4**) = 38.9:61.1. MS (*m*/*z*, relative intensity) **3d-1**: 292 (M$^+$, 8), 180 [(*p*-$C_6H_5C_6H_4CHCH_2$)$^+$, 100], 167 (13), 152 (3), 112 [(M-*p*-$PhC_6H_4CH{=}CH_2$)$^+$, 2.5]. **3d-2**: 292 (M$^+$, 8), 180 [(*p*-$PhC_6H_4CH{=}CH_2$)$^+$, 100], 167 (13), 152 (3), 112 [(M − *p*-$PhC_6H_4CH{=}CH_2$)$^+$, 3.2]. **3d-3**: 292 (M$^+$, 9), 180 [(*p*-$PhC_6H_4CH{=}CH_2$)$^+$, 100], 167 (13), 152 (3), 112 [(M − *p*-$PhC_6H_4CH{=}CH_2$)$^+$, 4.2]. **3d-4**: 292 (M$^+$, 9), 180 [(*p*-$PhC_6H_4CH{=}CH_2$)$^+$, 100], 167 (100), 151 (2), 112 [(M − *p*-$PhC_6H_4CH{=}CH_2$)$^+$, 2.5]. **4d-1**: 292 (M$^+$, 100), 250 [(M − $CH_3CH{=}CH_2$)$^+$, 94], 193 (47), 178 (40), 167 (33), 152 (11). **4d-2**: 292 (M$^+$, 100), 250 [(M − $CH_3CH{=}CH_2$)$^+$, 97], 221 (18), 193 (68), 178 (45), 167 (38).

Rh(II)-Catalyzed Dinitrogen Extrusion of 2-Diazo-6-(4-methoxyphenyl)-4-propyl-3-hexanone (1e). The diazo de-

composition of **1e** with $Rh_2(O_2CCF_3)_4$ as a catalyst gave C−H insertion products in 59% isolated yield. An ^{1}H NMR spectrum of the product indicated that it was a mixture of diastereomeric isomers of aliphatic C−H insertion products **3e** and benzylic C−H insertion products **4e**. The mixture was found to be not separable by TLC or column chromatography. The mixture gave following analytical data: ^{1}H NMR (400 MHz): δ 0.67 (d, J = 7.8 Hz), 0.85 (d, J = 7.2 Hz), 0.94 (t, J = 7.3 Hz), 0.96 (d, J = 7.0 Hz), 1.00 (d, J = 7.2 Hz), 1.01 (d, J = 6.4 Hz), 1.04 (d, J = 7.1 Hz), 1.06 (d, J = 6.4 Hz), 1.14 (d, J = 6.0 Hz), 1.15 (d, J = 6.0 Hz), 1.22−1.70 (m), 1.80−1.96 (m), 2.02−2.42 (m), 2.52−2.70 (m), 3.40−3.54 (m, 0.55 H, **4e**), 3.78 (s, 1.60 H), 3.80 (s, 1.40 H), 6.82 (d, J = 8.6 Hz), 6.88 (d, J = 8.6 Hz), 6.96 (d, J = 8.6 Hz), 7.10 (d, J = 8.6 Hz), 7.11 (d, J = 8.6 Hz), 7.17 (d, J = 8.6 Hz); IR 2960, 1730, 1605, 1505, 1465, 1240 cm^{-1}. Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 78.28; H, 8.95. GC−MS analysis of the mixture gave six peaks, which were labeled as **3e-1**, **3e-2**, **3e-3**, **3e-4**, **4e-1**, and **4e-2**. The following product ratios were obtained from GC−MS: **3e-1**/**3e-2**/**3e-3**/**3e-4** = 34:24:9:33; **4e-1**/**4e-2** = 56:44; (**4e-1** + **4e-2**)/(**3e-1** + **3e-2** + **3e-3** + **3e-4**) = 54.3:45.7. MS (*m*/*z*, relative intensity) **3e-1**: 246 (M^+, 8), 134 [(*p*-$MeOC_6H_4CH{=}CH_2)^+$, 100], 112 [(M − *p*-$MeOC_6H_4$-$CH{=}CH_2)^+$, 2.4], 121 (21). **3e-2**: 246 (M^+, 13), 134 [(*p*-$MeOC_6H_4$-$CH{=}CH_2)^+$, 100], 112 [(M − *p*-$MeOC_6H_4CH{=}CH_2)^+$, 2.1], 121 (23). **3e-3**: 246 (M^+, 9), 134 [(*p*-$MeOC_6H_4CH{=}CH_2)^+$, 100], 112 [(M-*p*-$MeOC_6H_4CH{=}CH_2)^+$, 2.2], 121 (21). **3e-4**: 246 (M^+, 9), 134 [(*p*-$MeOC_6H_4CH{=}CH_2)^+$, 100], 112 [(M − *p*-$MeOC_6H_4CH{=}CH_2)^+$, 2.0]. 121 (22). **4e-1**: 246 (M^+, 100), 204 [(M − $CH_3CH{=}CH_2)^+$, 77], 189 (18), 175 (14), 162 (18), 147 (60), 135 (42), 121 (56). **4e-2**: 246 (M^+, 100), 204 [(M − $CH_3CH{=}CH_2$), 68), 203 (74), 189 (24), 175 (17), 162 (19), 147 (64), 135 (38), 121 (57).

Acknowledgment. Financial support by the State Education Commission of China (Excellent Young Teacher's Foundation to J.W.) and NSFC (Grant No. 29702002) is gratefullly acknowledged. We thank the Bioorganic Molecular Engineering Laboratory of Peking University and Ms. Yufang Sun for GC−MS measurement.

Supporting Information Available: Hammett plot (with σ^+), copies of ^{1}H and ^{13}C NMR spectra for all title compounds, and the GC−MS data for insertion products (34 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO981279T