SUPPORTING INFORMATION

Iridium-Catalyzed Ring Cleavage Reaction of Cyclobutanone *O*-Benzoyloximes Providing Nitriles

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General Methods. ^{1}H NMR spectra were obtained in $CDCl_3$ at 270, 300, or 400 MHz with Me_4Si as an internal standard. ^{13}C NMR spectra were obtained at 67.8, 75.5, or 100 MHz. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

Materials. All commercially available organic and inorganic compounds were used without further purification except for the solvent, which was distilled by the known method before use. Cyclobutanone *O*-benzoyloximes were prepared according to the reported procedures from the corresponding cyclobutanones.[S1] Cyclobutanones were produced by the reduction of α,α-dichlorocyclobutanones synthesized from the corresponding alkenes by the reported procedure[S2] in the presence of Zn-powder and AcOH.[S3]

3-Methyl-3-phenylcyclobutanone *O*-benzoyloxime (1a). White solid; mp 81.0–81.5 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.59 (s, 3H), 3.15–3.37 (m, 2H), 3.38–3.58 (m, 2H), 7.23–7.34 (m, 3H), 7.37 (t, J = 6.9 Hz, 2H), 7.47 (t, J = 6.9 Hz, 2H), 7.59 (t, J = 6.9 Hz, 1H), 8.07 (d, J = 7.3 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 30.9, 38.0, 44.8, 125.0, 126.3, 128.4, 128.5, 128.9, 129.5, 133.1, 147.8, 163.8, 165.0. Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13; N, 5.01. Found: C, 77.27; H, 6.14; N, 4.99.

Benzoic acid 3-phenylcarboxyimino-1-methylcyclobutylmethyl ester (1c). White solid; mp 59.1–59.3 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.44 (s, 3H), 2.92 (d, J = 18.8 Hz, 2H), 3.22 (d, J = 18.8 Hz, 2H), 4.34 (s, 2H), 7.38–7.64 (m, 6H), 8.04 (d, J = 7.3 Hz, 4H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 23.8, 33.7, 40.8, 70.3, 128.4, 128.8, 129.5, 133.2, 163.7, 164.2, 166.2. Anal. Calcd for $C_{20}H_{19}NO_4$: C, 71.20; H, 5.68; N, 4.15. Found: C, 71.26; H, 5.81; N, 4.09.

2-Benzyloxymethyl-3,3-dimethylcyclobutanone *O*-benzoyloxime (4a, *E/Z* mixture). Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23 (s, 2.1H), 1.27 (s, 0.9H), 1.33 (s, 0.9H), 1.36 (s, 2.1H), 2.70–2.85 (m, 2H), 3.30–3.36 (m, 1H), 3.71–3.98 (m, 2H), 4.48–4.55 (m, 2H), 7.22–7.50 (m, 7H), 7.53–7.65 (m, 1H), 7.90–8.04 (m, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 22.6, 22.7, 29.9, 30.1, 33.0, 33.7, 43.5, 43.8, 54.1, 55.3, 66.3, 66.9, 73.1, 73.2, 127.5, 127.6, 127.6, 128.3, 128.4, 128.4, 128.8, 129.0, 129.4, 129.5, 133.0, 133.1, 137.8, 138.0, 163.8, 166.0, 166.9. Anal. Calcd for $C_{21}H_{23}NO_3$: C, 74.75; H, 6.87; N, 4.15. Found: C; 74.73, H; 6.95, N; 4.11.

1-Phenylbicyclo[3.2.0]heptan-6-one *O*-benzoyloxime (4b, *E/Z* mixture). Colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.76–2.46 (m, 6H), 3.05–3.19 (m, 1H), 3.43 (d, J = 18.1 Hz, 2H) 3.85–3.92 (m, 1H), 7.20–7.62 (m, 8H), 8.03–8.08 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 26.3, 26.4, 30.8, 32.7, 41.8, 41.9, 42.4, 42.4, 48.2, 49.0, 55.6, 55.9, 125.5, 126.3, 128.5, 128.5, 128.6, 129.1, 129.1, 129.6, 133.2, 133.3, 146.6, 146.6, 163.9, 168.9, 169.6. Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59. Found: C; 78.96, H; 6.36, N; 4.48.

Typical Procedure for the Synthesis of 3-Methyl-3-phenylbutyronitrile. A mixture of $[IrCl(cod)]_2$ (0.0024 mmol), BnBPA (0.0050 mmol), K_2CO_3 (0.10 mmol), 9,10-dihydroanthracene (0.12 mmol), and DMF (0.30 mL) in a 20-mL Schlenk tube was stirred at room temperature under N_2. After 15 min, 3-methyl-3-phenylcyclobutanone *O*-benzoyloxime (**1a**) (0.10 mmol) in DMF (0.20 mL) was added, and the resulting mixture was stirred at 50 °C for 48 h. The reaction mixture was cooled down to room temperature, and then filtered through a pad of Florisil. The filtrate was concentrated under vacuum to leave a colorless oil, which was subjected to column chromatography on SiO_2 with EtOAc-hexane (3/97) as eluent.

3-Benzyl-3-methyl-4-phenylbutyronitrile (2b). Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (s, 3H), 2.04 (s, 2H), 2.74 (d, J = 13.5 Hz, 2H), 2.83 (d, J = 13.5 Hz, 2H), 7.15–7.37 (m, 10H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 23.6, 26.4, 38.0, 46.0, 118.8, 126.7, 128.3, 130.5, 136.7. HRMS (FAB): calcd for $C_{18}H_{20}N$ ($M+H^+$), 250.1596; found, 250.1596. Anal. Calcd for $C_{18}H_{19}N$: C, 86.70; H, 7.68; N, 5.62. Found: C, 86.16; H, 7.70; N, 5.44.

Benzoic acid 3-cyano-2,2-dimethylpropyl ester (2c). Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ

1.22 (s, 6H), 2.46 (s, 2H), 4.16 (s, 2H), 7.43–7.51 (m, 2H), 7.55–7.63 (m, 1H), 8.02–8.07 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 24.2, 27.9, 34.2, 55.7, 117.7, 128.5, 129.6, 129.7, 133.3, 166.1. HRMS (FAB): calcd for $C_{14}H_{16}NO_2$ ($M+H^+$), 218.1181; found, 218.1183. Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.79; H, 7.00; N, 6.21.

5-Benzyloxy-3,3-dimethylpentanenitrile (5a). Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10 (s, 6H), 1.71 (t, J = 6.2 Hz, 2H), 2.34 (s, 2H), 3.56 (t, J = 6.2 Hz, 2H), 4.49 (s, 2H), 7.25–7.40 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 27.2, 30.8, 32.5, 40.4, 66.8, 73.1, 118.6, 127.6, 127.6, 128.4, 138.2. Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.51; H, 8.82; N, 6.30.

1-Phenylcyclopentylacetonitrile (5b). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.77–1.83 (m, 4H), 2.05–2.09 (m, 4H), 2.58 (s, 2H), 7.23–7.42 (m, 5H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 23.1, 30.4, 37.2, 49.2, 118.3, 126.4, 126.8, 128.5, 145.5. HRMS (FAB): calcd for $C_{13}H_{15}N$ ($M+H^+$), 186.1283; found, 186.1288.

Typical Procedure for the Reaction of 3-Methyl-3-phenylcyclobutanone *O*-Benzoyloxime (1a) with Diphenyldisulfide. A mixture of $[IrCl(cod)]_2$ (0.0125 mmol), BnBPA (0.025 mmol), K_2CO_3 (0.50 mmol), and ethylene carbonate (0.50 mL) in a 20-mL Schlenk tube was stirred at 50 °C under N_2. After 15 min, 3-methyl-3-phenylcyclobutanone *O*-benzoyloxime (**1a**) (0.50 mmol) and diphenyl disulfide (0.75 mmol) in ethylene carbonate (0.50 mL) were added, and the resulting mixture was stirred at 50 °C for 24 h. The reaction mixture was cooled down to room temperature, and then filtered through a pad of Florisil. The filtrate was concentrated under vacuum to leave a yellow oil, which was subjected to column chromatography on SiO_2 with EtOAc-hexane (3/97) as eluent.

3-Methyl-3-phenyl-4-(phenylthio)butyronitrile (6). Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.56 (s, 3H), 2.77 (d, J = 16.5 Hz, 1H), 2.85 (d, J = 16.5 Hz, 1H), 3.30 (d, J = 13.0 Hz, 1H), 3.31 (d, J = 13.0 Hz, 1H), 7.06–7.32 (m, 10H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 25.4, 29.5, 41.7, 47.0, 117.7, 125.6, 126.6, 127.4, 128.7, 129.0, 130.3, 136.3, 142.8. HRMS (FAB); calcd for $C_{17}H_{17}NS$ (M^+), 267.1082; found, 287.1083. Anal. Calcd for $C_{17}H_{17}NS$: C, 76.36; H, 6.41; N, 5.24. Found: C, 76.31; H, 6.38; N, 5.24.

3-Methyl-3-phenyl-4-(phenylseleno)butyronitrile (7). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.62 (s, 3H), 2.82 (d, J = 16.6 Hz, 1H), 2.91 (d, J = 16.6 Hz, 1H), 3.33 (d, J = 12.7 Hz, 1H), 3.40 (d, J =

12.7 Hz, 1H), 7.18–7.35 (m, 8H), 7.42–7.44 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 25.7, 30.0, 41.5, 41.7, 117.7, 125.5, 127.2, 127.3, 128.6, 129.0, 130.3, 133.2, 142.9. Anal. Calcd for $C_{17}H_{17}NSe$: C, 64.97; H, 5.45; N, 4.46. Found: C, 65.05; H, 5.50; N, 4.28.

3-Methyl-3-phenyl-4-(phenyltellro)butyronitrile (8). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67 (s, 3H), 2.85 (d, J = 16.1), 2.91 (d, J = 16.6), 3.33 (d, J = 12.2), 3.49 (d, J = 12.2), 7.14–7.35 (m, 10H), 7.64–7.66 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.2, 26.8, 31.4, 41.3, 117.9, 125.3, 127.3, 127.9, 128.7, 129.2, 138.9, 143.5. Anal. Calcd for $C_{17}H_{17}NTe$: C, 56.26; H, 4.72; N, 3.86. Found: C, 56.34; H, 4.78; N, 3.79.

References

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