Electronic Supplementary Information

Electron Transfer-Induced Reduction of Organic Halides with Amines

Takahide Fukuyama,† Yuki Fujita,† Hayato Miyoshi,† Ilhyong Ryu,*†‡ Shih-Chieh Kao,‡ and Yen-Ku Wu*‡

†Department of Chemistry, Graduate School of Science, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan
‡Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan

Table of Contents

General Information S2
Typical Procedure for Reduction under Photoirradiation S3
Typical Procedure for Reduction under Heated Conditions S3
Typical Procedure for Reduction 1d and 1i of Using Photo Flow Reactor S4
Spectroscopic Data of Reduced Products S4
Copies of NMR Spectra S10
General Information

$^1$H NMR spectra were recorded on a JEOL ECS400 spectrometer (400 MHz) and referenced to the solvent peak at 7.26 ppm. $^{13}$C NMR spectra were recorded on a JEOL ECS400 spectrometer (100 MHz) and referenced to the solvent peak at 77.0 ppm. Infrared spectra were recorded on a JASCO FT/IR-4100 spectrometer and are reported as wavenumber (cm$^{-1}$). GC analyses were carried out with a Shimadzu GC-2014 gas chromatography equipped with a flame ionization detector using a capillary column (J & W DB-1 or J & W DB-5). GC-MS analyses were performed with a Shimadzu GCMS-QP2010 mass spectrometer. High-resolution mass spectra were recorded with a JEOL JMS-T200GC. Melting points were measured by BÜCHI melting point B-540. Thin layer chromatography (TLC) was performed on Merck pre-coated plates (silica gel 60 F$_{254}$). The products were purified by flash chromatography on silica gel (Kanto Chem. Co. Silica Gel 60N (spherical, neutral, 40-50 µm)) or on alumina (Nacalai Tessque, Inc. Alumina Activated 200). All products excepted for 1-(tert-butyldimethylsilyl)-1H-indole (2r) were compared with the commercially available authentic samples. The product 2r is known compound and the spectral data were identical with the reported values.
**Typical Procedure for Reduction of Alkyl Halides (1a-1a”, 1b, and 1c) under Photo-irradiation**

In a quartz tube were placed 1-bromoadamantane (1c) (0.49 mmol, 105.6 mg), Et$_3$N (5.0 mmol, 502.1 mg), and CH$_3$CN (5 mL). The quartz tube was purged with Ar gas, capped with rubber septum, and sealed. The reaction mixture was irradiated with a 6 W low pressure Hg lamp for 15 h. After the reaction, the mixture was extracted with n-pentane (5 mL x 4) and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (n-pentane) to give adamantane (2c) (62.2 mg, 93%).

**Typical Procedure for Reduction of Alkenyl Halides (1d-1d”, 1e, and 1u) under Photo-irradiation**

In a quartz tube were placed 2-bromo-1-pentadecene (1e) (0.50 mmol, 144.0 mg), Et$_3$N (5.0 mmol, 506.6 mg), and CH$_3$CN (5 mL). The quartz tube was purged with Ar gas, capped with rubber septum, and sealed. The reaction mixture was irradiated with a 6 W low pressure Hg lamp for 15 h. After the reaction, the mixture was extracted with n-pentane (5 mL x 4) and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (n-pentane) to give 1-pentadecene (2e) (92.8 mg, 89%).

**Typical Procedure for Reduction of Aryl Halides (1f-1t, 1v, and 1w) under Photo-irradiation**

In a quartz tube were placed 2-iodobiphenyl (1f) (0.51 mmol, 142.3 mg), Et$_3$N (5.0 mmol, 508.9 mg), and CH$_3$CN (5 mL). The quartz tube was purged with Ar gas, capped with rubber septum, and sealed. The reaction mixture was irradiated with a 6 W low pressure Hg lamp for 15 h. After the reaction, the mixture was extracted with n-pentane (5 mL x 4) and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (n-pentane) to give biphenyl (2f) (67.2 mg, 86%).

**Typical Procedure for Reduction of Aryl Halides (1f, 1i, 1k, and 1l) under Heated Conditions**

A magnetic stirring bar, 4-bromobiphenyl (1l) (115.5 mg, 0.5 mmol), Et$_3$N (507.6 mg, 5.0 mmol) and CH$_3$CN (5 mL) were placed in a stainless steel autoclave lined with a glass liner. The autoclave was closed and heated to 250 °C with stirring for 24 h. After cooling, the mixture was extracted with n-pentane (5 mL x 4). The solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (n-pentane) to give biphenyl (2f) (47.1 mg, 62%). For 2-bromonaphthalene (1i) and 1-bromo-4-tert-butylbenzene (1k), the reaction was conducted without solvent.
Typical Procedure for Reduction of 1d and 1i Using Photo Flow Reactor

Photochemical reactions were carried out in photo-microreactor system, KeyChem-Lumino, provided by YMC Co., Ltd which composed of a single lane channel (1 mm in width, 200 µm in depth, 56 cm in length) caved on stainless steel plate covered with quartz glass. Irradiation was made by low pressure Hg lamps (a wavelength of 254 nm, 1.2 W). An acetonitrile solution (0.025 M, 10 mL) of 1-bromododecene (1d) (65.4 mg, 0.27 mmol) and DABCO (45.5 mg, 0.41 mmol) was placed in a gas tight syringe, and was pumped into the photo-microreactor at a rate of 0.34 mL/h (residence time: 20 min). The reaction mixture eluted from the outlet was discarded for the first 40 min and the subsequent portion was collected for 12 h (4 mL). The yield of product 1-dodecene (2d) was determined to be 94% by GC analysis using nonane as an internal standard.

Dodecane (2a)

Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.88 (t, $J$ = 6.4 Hz, 6H), 1.21-1.35 (m, 20H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.12, 22.71, 29.39, 29.69, 29.72, 31.95.

Adamantane (2c)

White solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.75 (m, 12H), 1.87 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 28.46, 37.87.

1-Dodecene (2d)

Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.89 (t, $J$ = 6.4 Hz, 3H), 1.21-1.41 (m, 16H), 2.04 (q, $J$ = 6.8 Hz, 2H), 4.92-4.94 (m, 1H), 4.97-5.02 (m, 1H), 5.82 (ddt, $J$ = 16.8, 10.0, 6.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.27, 22.87, 29.13, 29.34, 29.53, 29.69, 29.81, 32.10, 34.01, 114.22, 139.41.

1-Pentadecene (2e)

Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.88 (t, $J$ = 6.4 Hz, 3H), 1.21-1.41 (m, 22H), 2.04 (q, $J$ = 6.8 Hz, 2H), 4.92-4.94 (m, 1H), 4.97-5.02 (m, 1H), 5.82 (ddt, $J$ = 16.8, 10.0, 6.4 Hz, 1H); A few aliphatic carbon signals are missing due to peak overlap.$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.35, 22.92, 29.17, 29.39, 29.59, 29.75, 29.85, 29.91, 32.15, 34.06, 114.28, 139.49.
Biphenyl (2f)

![Biphenyl structure]

White solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35 (m, 2H), 7.45 (m, 4H), 7.60 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 127.15, 127.23, 128.74, 141.21.

Naphthalene (2h)

![Naphthalene structure]

White solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.48 (dd, $J$ = 6.2, 3.2 Hz, 4H), 7.85 (dd, $J$ = 6.2, 3.2 Hz, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 125.95, 128.02, 133.56.

2-Methylnaphthalene (2j)

![2-Methylnaphthalene structure]

Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.52 (s, 3H), 7.32 (dd, $J$ = 8.4, 1.6 Hz, 1H), 7.42 (m, 2H), 7.61 (s, 1H), 7.77 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 21.86, 125.08, 125.99, 126.96, 127.35, 127.72, 127.81, 128.25, 131.80, 133.77, 135.57.

t-Butylbenzene (2k)

![t-Butylbenzene structure]

Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.33 (s, 9H), 7.18 (t, $J$ = 6.8 Hz, 1H), 7.31 (t, $J$ = 7.6 Hz, 2H), 7.40 (d, $J$ = 6.8 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 31.51, 34.79, 125.38, 125.56, 128.20, 151.20.

tert-Butyl phenylcarbamate (2m)

![tert-Butyl phenylcarbamate structure]

White solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38 – 7.26 (m, 4H), 7.03 (t, $J$ = 7.2 Hz, 1H), 6.63 (s, 1H), 1.53 (s, 9H); $^{13}$C NMR (400 MHz, CDCl$_3$) $\delta$ 152.8, 138.4, 128.9, 123.0, 118.6, 80.5, 28.4.
1,3-Benzodioxole (2n)

Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.84-6.83 (m, 4H), 5.94 (s, 2H); $^{13}$C NMR (400 MHz, CDCl$_3$) $\delta$ 147.4, 121.6, 108.7, 100.6.

N-Methylbenzamide (2o)

White solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.77 (d, $J$ = 7.2 Hz, 2H), 7.44 (t, $J$ = 7.2 Hz, 1H), 7.34 (t, $J$ = 7.6 Hz, 2H), 6.90 (br, 1H), 2.93 (d, $J$ = 4.8 Hz, 3H); $^{13}$C NMR (400 MHz, CDCl$_3$) $\delta$ 168.5, 134.5, 131.2, 128.4, 126.9, 26.8.

Ethyl benzoate (2p)

Yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.05 (d, $J$ = 8.0 Hz, 2H), 7.55 (t, $J$ = 7.6 Hz, 1H), 7.44 (t, $J$ = 7.6 Hz, 2H), 4.37 (q, $J$ = 7.2 Hz, 2H), 1.39 (t, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (400 MHz, CDCl$_3$) $\delta$ 166.6, 132.8, 130.5, 129.5, 128.3, 60.9, 14.3.

Acetophenone (2q)

Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.62 (s, 3H), 7.47 (t, $J$ = 8.0 Hz, 2H), 7.57 (t, $J$ = 6.8 Hz, 1H), 7.97 (d, $J$ = 8.0 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 26.73, 128.40, 128.67, 133.22, 137.18, 198.29.
1-(tert-Butyldimethylsilyl)-1H-indole (2r)^1

Colorless oil; \(^{1}\text{H NMR (400 MHz, CDCl}_3\) \(\delta\) 7.76 (d, \(J = 7.6\) Hz, 1 H), 7.65-7.63 (d, \(J = 8.4\) Hz, 1 H), 7.30–7.21 (m, 3 H), 6.74-6.73 (d, \(J = 3.2\) Hz, 1 H), 1.05 (s, 9 H), 0.71 (s, 6 H); \(^{13}\text{C NMR (400 MHz, CDCl}_3\) \(\delta\) 141.0, 131.4, 131.0, 121.4, 120.7, 119.8, 113.9, 104.8, 26.4, 19.6, –3.9.

9H-Carbazole (2s)

White solid; \(^{1}\text{H NMR (400 MHz, CDCl}_3\) \(\delta\) 8.09 (d, \(J = 8.0\) Hz, 2H), 8.03 (s, 1H), 7.45- 7.40 (m, 4H), 7.27-7.23 (m, 2H); \(^{13}\text{C NMR (400 MHz, CDCl}_3\) \(\delta\) 139.5, 125.8, 123.3, 120.3, 119.4, 110.5.

Dibenzofuran (2t)

Colorless oil; \(^{1}\text{H NMR (400 MHz, CDCl}_3\) \(\delta\) 7.35 (m, 2H), 7.46 (m, 2H), 7.58 (d, \(J = 8.4\) Hz, 2H), 7.97 (d, \(J = 8.0\) Hz, 2H), \(^{13}\text{C NMR (100 MHz, CDCl}_3\) \(\delta\) 111.81, 120.79, 122.81, 124.34, 127.26, 156.29

2-Pentadecene (2u)

Obtained as an inseparable mixture (\(E/Z\)= 55/45); Colorless oil; \(E\) isomer: \(^{1}\text{H NMR (400 MHz, CDCl}_3\) \(\delta\) 0.88 (t, \(J = 6.8\) Hz, 3H), 1.21-1.41 (m, 20H), 1.64 (m, 3H), 1.95 (m, 2H), 5.41 (m, 2H); A few aliphatic carbon signals are missing due to peak overlap. \(^{13}\text{C NMR (100 MHz, CDCl}_3\) \(\delta\) 14.28, 18.08, 22.88, 29.40, 29.49, 29.55, 29.76, 29.85, 29.87, 32.11, 32.81, 124.66, 131.85; \(Z\) isomer: \(^{1}\text{H NMR (400 MHz, CDCl}_3\) \(\delta\) 0.88 (t, \(J = 6.8\) Hz, 3H), 1.21-1.41 (m, 20H), 1.60 (m, 3H), 2.02 (m, 2H), 5.41 (m, 2H); A few aliphatic carbon signals are missing due to
peak overlap. $^{13}$C NMR (100 MHz, CDCl$_3$) δ 12.89, 14.28, 22.88, 27.01, 29.40, 29.49, 29.55, 29.76, 29.85, 29.87, 32.11, 123.72, 131.06.

**Anisole (2v)**

![Anisole](image)

Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.32-7.28 (m, 2H), 6.97-6.90 (m, 3H), 3.82 (s, 3H); $^{13}$C NMR (400 MHz, CDCl$_3$) δ 159.5, 129.4, 120.6, 113.9, 55.1.

**α-Butylbenzenemethanol (2w)**

![α-Butylbenzenemethanol](image)

Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.37- 7.32 (m, 3H), 7.29-7.26 (m, 1H), 4.65 (dd, $J$ =7.5, 5.9, 1H), 2.08 (br, 1H), 1.84-1.66 (m, 2H), 1.45-1.21 (m, 4H), 0.89 (t, $J$ =7.2 Hz, 3H); $^{13}$C NMR (400 MHz, CDCl$_3$) δ = 144.9, 128.4, 127.4, 125.9, 74.7, 38.8, 28.0, 22.6, 14.0.

**2,6-Dichloroaniline (2x)**

![2,6-Dichloroaniline](image)

Pale yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.17 (d, $J$ = 8.0 Hz, 2H), 6.61 (t, $J$ = 8.0 Hz, 1H), 4.45 (br, 2H); $^{13}$C NMR (400 MHz, CDCl$_3$) δ = 140.1, 127.7, 119.6, 118.0.

**2-Chloroaniline (2x’)**

![2-Chloroaniline](image)

Pale yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.24 (d, $J$ = 8.4 Hz, 1H), 7.06 (t, $J$ = 7.6 Hz,1H), 6.76 (d, $J$ = 8.0 Hz, 1H), 6.69 (t, $J$ = 7.6 Hz, 1H), 4.04 (br, 1H); $^{13}$C NMR (400 MHz, CDCl$_3$) δ = 142.9, 129.4, 127.6, 119.2, 119.0, 115.8.
N$_2$N$_2$N$_3$N$_3$-Tetraethylbutane-2,3-diamine (4)

Yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 2.56-2.22 (m, 10 H), 0.98 (t, $J = 6.8$ Hz, 12 H), 0.92 (t, $J = 6.4$ Hz, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 57.5, 43.7, 14.6, 9.9; IR (neat) 2958, 2925, 1270, 1678, 1660, 1615, 1486, 1459, 1378, 1288, 1237, 1207, 1189, 1160, 1121, 1080, 1041, 969, 804, 736 cm$^{-1}$; HRMS (FI): calcd for C$_6$H$_{14}$N$_1$ (M$^+$/2): 100.1126, found: 100.1121 (100, M$^+$/2).

Reference

X : parts per Million : Proton
X : parts per Million : Carbon13
X: parts per Million: Proton
The image contains a graph with labeled axes and a molecular structure. The x-axis is labeled "X: parts per Million: Carbon13" and the y-axis is labeled "abundance." The graph shows a peak at approximately 141.213 ppm with a peak at 128.735 ppm and another at 127.236 ppm. The structure depicted is labeled "2f."
X : parts per Million : Carbon13
CARBON_01
kao-msi-dioxy proton carbon

\[-2\Phi\]

\[
\begin{array}{c}
  O \\
  O \\
  2n \\
\end{array}
\]
PROTON_01
kao-nsi1-dioxy-proton carbon

\[ \text{2n} \]

\[ \text{2o} \]
X: parts per Million: Carbon13

![Graph showing the abundance of Carbon13 with various peaks at specific ppm values.](image-url)
X : parts per Million : Carbon13

2t
NH₂

2x'
CARBON_D1
kao-m51-tea dimer

4