Eosin Y-Catalyzed Photooxidation of Triarylphosphines under Visible Light Irradiation and Aerobic Conditions

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Electronic Supplementary Information

<table>
<thead>
<tr>
<th>Electronic Supplementary Information</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental Section</td>
<td>S2</td>
</tr>
<tr>
<td>NMR Spectra</td>
<td>S10</td>
</tr>
<tr>
<td>References</td>
<td>S35</td>
</tr>
</tbody>
</table>
Experimental Section

General information

All reactions were carried out using a 23 W household lamp at a distance of 3-5 cm with the reactor. $^1$H (400 MHz), $^{13}$C (100 MHz), $^{31}$P (162 MHz), $^{19}$F (376 MHz) NMR spectra of samples in CDCl$_3$ were recorded on an AVANCE III 400 spectrometer. Melting points were determined on a SGWX-4 Micro Melting Point Apparatus. Compounds 1a, 1b, 1d, 1e, 1f, 1j, 1k, and 1o were commercial available. Compounds 1c, 1g, 1h, 1i, 1l, 1m, 1n, and 1p were prepared according to literature procedures. Quantum yield was determined using the phenylglyoxylic acid chemical actinometer system.

Typical Procedure I for the photoreaction

Synthesis of triphenylphosphine oxide (2a)

$^1$a (54 mg, 0.21 mmol), Eosin Y (2 mg, 0.0031 mmol), CH$_2$Cl$_2$ (2.5 mL), and CH$_3$OH (0.5 mL) were added to a pyrex reaction flash which was equipped with a magnetic stirrer. The mixture was irradiated by a 23 W household lamp at rt under air atmosphere. The photoreaction was completed after 3.5 hours as monitored by TLC (eluent: petroleum ether). The solvent was removed and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1→1/1→EA) to afford 2a as a solid (52 mg, 95%); mp 157.3-157.8 °C (petroleum ether/ethyl acetate); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.71-7.63 (m, 6 H), 7.58-7.51 (m, 3 H), 7.50-7.42 (m, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 132.5 (d, $J_{PC}$ = 104.1 Hz), 132.1 (d, $J_{PC}$ = 9.8 Hz), 131.9 (d, $J_{PC}$ = 1.9 Hz), 128.5 (d, $J_{PC}$ = 12.1 Hz); $^{31}$P NMR (162 MHz, CDCl$_3$) δ 29.8 ppm.

The following compounds were prepared according to Typical Procedure I.

(1) Tris(4-methoxyphenyl)phosphine oxide (2b)
The reaction of \(1b\) (72 mg, 0.20 mmol), Eosin Y (2 mg, 0.0031 mmol), \(\text{CH}_2\text{Cl}_2\) (2.5 mL), and \(\text{CH}_3\text{OH}\) (0.5 mL) afforded \(2b\) as a solid (68 mg, 92%); mp 141.7-142.4 °C (petroleum ether/ethyl acetate); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.56 (dd, \(J = 11.6, 8.8 \text{ Hz}, 6 \text{ H}), 6.96 (dd, \(J = 6.8, 2.0 \text{ Hz}, 6 \text{ H}), 3.84 (s, 9 \text{ H}); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 162.2 (d, \(J_{\text{PC}} = 2.8 \text{ Hz}), 133.7 (d, \(J_{\text{PC}} = 11.2 \text{ Hz}), 124.1 (d, \(J_{\text{PC}} = 110.7 \text{ Hz}), 113.9 (d, \(J_{\text{PC}} = 13.1 \text{ Hz}), 55.2; \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) 32.0 ppm.

(2) Tris(4-ethoxyphenyl)phosphine oxide (2c)

The reaction of \(1c\) (79 mg, 0.20 mmol), Eosin Y (2 mg, 0.0031 mmol), \(\text{CH}_2\text{Cl}_2\) (2.5 mL), and \(\text{CH}_3\text{OH}\) (0.5 mL) afforded \(2c\) as a solid (81 mg, 99%); mp 151.2-151.5 °C (petroleum ether/ethyl acetate); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.54 (dd, \(J = 11.6, 8.8 \text{ Hz}, 6 \text{ H}), 6.93 (dd, \(J = 8.8, 2.0 \text{ Hz}, 6 \text{ H}), 4.06 (q, J = 7.0 \text{ Hz}, 6 \text{ H}), 1.42 (t, J = 7.0 \text{ Hz,} 9 \text{ H}); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 161.6, 133.7 (d, \(J_{\text{PC}} = 11.1 \text{ Hz}), 124.1 (d, \(J_{\text{PC}} = 111.0 \text{ Hz}), 114.3 (d, \(J_{\text{PC}} = 13.1 \text{ Hz}), 63.5, 14.6; \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) 29.3 ppm.

(3) Tris(4-methylphenyl)phosphine oxide (2d)
The reaction of 1d (61 mg, 0.20 mmol), Eosin Y (2 mg, 0.0031 mmol), CH₂Cl₂ (2.5 mL), and CH₃OH (0.5 mL) afforded 2d as a solid (57 mg, 89%); mp 142.4-142.9 °C (petroleum ether/ethyl acetate); ¹H NMR (400 MHz, CDCl₃) δ 7.54 (dd, J = 11.6, 8.0 Hz, 6 H), 7.25 (d, J = 7.2 Hz, 6 H), 2.39 (s, 9 H); ¹³C NMR (100 MHz, CDCl₃) δ 142.1, 132.0 (d, JₚC = 10.2 Hz), 129.6 (d, JₚC = 107.5 Hz), 129.1 (d, JₚC = 12.4 Hz), 21.5; ³¹P NMR (162 MHz, CDCl₃) δ 30.2 ppm.

(4) Tris(3-methylphenyl)phosphine oxide (2e)¹

The reaction of 1e (61 mg, 0.20 mmol), Eosin Y (2 mg, 0.0031 mmol), CH₂Cl₂ (2.5 mL), and CH₃OH (0.5 mL) afforded 2e as a solid (61 mg, 95%); mp 112.3-112.8 °C (petroleum ether/ethyl acetate); ¹H NMR (400 MHz, CDCl₃) δ 7.58 (d, J = 12.4 Hz, 3 H), 7.40-7.31 (m, 9 H), 2.36 (s, 9 H); ¹³C NMR (100 MHz, CDCl₃) δ 138.3 (d, JₚC = 11.8 Hz), 132.5, 132.45 (d, JₚC = 102.8 Hz), 132.37 (d, JₚC = 9.4 Hz) 129.1 (d, JₚC = 10.2 Hz), 128.1 (d, JₚC = 12.8 Hz), 21.3; ³¹P NMR (162 MHz, CDCl₃) δ 30.0 ppm.

(5) Tris(2-methylphenyl)phosphine oxide (2f)¹₀
The reaction of 1f (61 mg, 0.20 mmol), Eosin Y (2 mg, 0.0031 mmol), CH₂Cl₂ (2.5 mL), and CH₃OH (0.5 mL) afforded 2f as a solid (58 mg, 91%); mp 153.6-154.1 °C (petroleum ether/ethyl acetate); ¹H NMR (400 MHz, CDCl₃) δ 7.45-7.40 (m, 3 H), 7.34-7.28 (m, 3 H), 7.17-7.07 (m, 6 H), 2.50 (s, 9 H); ¹³C NMR (100 MHz, CDCl₃) δ 143.5 (d, JPC = 7.5 Hz), 132.8 (d, JPC = 12.6 Hz), 131.9 (d, JPC = 10.3 Hz), 131.8 (d, JPC = 1.6 Hz), 130.6 (d, JPC = 100.7 Hz), 125.4 (d, JPC = 12.6 Hz), 21.9 (d, JPC = 3.7 Hz); ³¹P NMR (162 MHz, CDCl₃) δ 30.0 ppm.

(6) Tris(4-ethylpheny)phosphine oxide (2g)¹

The reaction of 1g (71 mg, 0.21 mmol), Eosin Y (2 mg, 0.0031 mmol), CH₂Cl₂ (2.5 mL), and CH₃OH (0.5 mL) afforded 2g as a solid (60 mg, 83%); mp 154.6-155.0 °C (petroleum ether/ethyl acetate); ¹H NMR (400 MHz, CDCl₃) δ 7.58 (dd, J = 11.8, 8.2 Hz, 6 H), 7.31-7.23 (m, 6 H), 2.68 (q, J = 7.6 Hz, 6 H), 1.24 (t, J = 7.6 Hz, 9 H); ¹³C NMR (100 MHz, CDCl₃) δ 148.3, 132.2 (d, JPC = 10.1 Hz), 130.0 (d, JPC = 105.7 Hz), 127.9 (d, JPC = 12.3 Hz), 28.9, 15.2; ³¹P NMR (162 MHz, CDCl₃) δ 29.3 ppm.

(7) Tris(4-(tert-butyl)pheny)phosphine oxide (2h)¹

The reaction of 1h (88 mg, 0.20 mmol), Eosin Y (2 mg, 0.0031 mmol), CH₂Cl₂ (2.5 mL), and CH₃OH (0.5 mL) afforded 2h as a solid (77 mg, 87%); mp 282.5-282.9 °C (petroleum ether/ethyl acetate); ¹H NMR (400 MHz, CDCl₃) δ 7.61 (dd, J = 11.6, 8.4 Hz, 6 H), 7.31-7.23 (m, 6 H), 2.68 (q, J = 7.6 Hz, 6 H), 1.24 (t, J = 7.6 Hz, 9 H); ¹³C NMR (100 MHz, CDCl₃) δ 148.3, 132.2 (d, JPC = 10.1 Hz), 130.0 (d, JPC = 105.7 Hz), 127.9 (d, JPC = 12.3 Hz), 28.9, 15.2; ³¹P NMR (162 MHz, CDCl₃) δ 29.3 ppm.
Hz, 6 H), 7.46 (dd, J = 8.4, 2.4 Hz, 6 H), 1.32 (s, 27 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 155.1, 131.9 (d, $J_{PC} =$ 10.2 Hz), 129.7 (d, $J_{PC} =$ 105.9 Hz), 125.4 (d, $J_{PC} =$ 12.3 Hz), 35.0, 31.1; $^{31}$P NMR (162 MHz, CDCl$_3$) δ 31.1 ppm.

(8) Tris(4-phenylphenyl)phosphine oxide (2i)$^{11}$

The reaction of 1i (97 mg, 0.20 mmol), Eosin Y (2 mg, 0.0031 mmol), CH$_2$Cl$_2$ (2.5 mL), and CH$_3$OH (0.5 mL) afforded 2i as a solid (96 mg, 95%); mp 231.4-231.8 °C (petroleum ether/ethyl acetate); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.91-7.77 (m, 6 H), 7.76-7.68 (m, 6 H), 7.67-7.57 (m, 6 H), 7.52-7.35 (m, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 144.8, 139.9, 132.6 (d, $J_{PC} =$ 10.2 Hz), 131.2 (d, $J_{PC} =$ 105.0 Hz), 128.9, 128.1, 127.3, 127.2; $^{31}$P NMR (162 MHz, CDCl$_3$) δ 28.8 ppm.

(9) Tris(4-fluorophenyl)phosphine oxide (2j)$^{12}$

The reaction of 1j (63 mg, 0.20 mmol), Eosin Y (2 mg, 0.0031 mmol), CH$_2$Cl$_2$ (2.5 mL), and CH$_3$OH (0.5 mL) afforded 2j as a solid (63 mg, 95%); mp 139.5-140.0 °C (petroleum ether/ethyl acetate); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.91-7.77 (m, 6 H), 7.76-7.68 (m, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.2 (d, $J_{PC} =$ 253.0 Hz), 134.4 (dd, J = 11.0, 9.3 Hz), 128.1 (d, $J_{PC} =$ 107.7 Hz), 116.1 (dd, J = 21.3, 13.4 Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) δ -105.9; $^{31}$P NMR (162 MHz, CDCl$_3$) δ 27.3 ppm.

(10) Tris(4-chlorophenyl)phosphine oxide (2k)$^{13}$
The reaction of 1k (73 mg, 0.20 mmol), Eosin Y (2 mg, 0.0031 mmol), CH₂Cl₂ (2.5 mL), and CH₃OH (0.5 mL) afforded 2k as a solid (70 mg, 92%); mp 174.3-174.7 °C (petroleum ether/ethyl acetate); ¹H NMR (400 MHz, CDCl₃) δ 7.62-7.54 (m, 6 H), 7.50-7.44 (m, 6 H); ¹³C NMR (100 MHz, CDCl₃) δ 139.1 (d, JₚC = 2.9 Hz), 133.3 (d, JₚC = 10.8 Hz), 130.2 (d, JₚC = 106.0 Hz), 129.1 (d, JₚC = 12.8 Hz); ³¹P NMR (162 MHz, CDCl₃) δ 30.5 ppm.

(11) Tris(3-(trifluoromethyl)phenyl)phosphine oxide (2l)¹⁴

The reaction of 1l (95 mg, 0.20 mmol), Eosin Y (2 mg, 0.0031 mmol), CH₂Cl₂ (2.5 mL), and CH₃OH (0.5 mL) afforded 2l as a solid (98 mg, 99%); mp 103.4-103.9 °C (petroleum ether/ethyl acetate); ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, J = 12.4 Hz, 3 H), 7.92-7.78 (m, 6 H), 7.73-7.65 (m, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 135.0 (d, JₚC = 10.0 Hz), 132.5 (d, JₚC = 104.6 Hz), 131.7 (dd, J = 33.3, 12.8 Hz), 129.6, 129.5, 128.8-128.5 (m), 123.3 (q, JₚC = 272.9 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -63.0; ³¹P NMR (162 MHz, CDCl₃) δ 27.6 ppm.

(12) Tris(4-cyanophenyl)phosphine oxide (2m)¹⁵
The reaction of 1m (67 mg, 0.20 mmol), Eosin Y (2 mg, 0.0031 mmol), CH₂Cl₂ (2.5 mL), and CH₃OH (0.5 mL) afforded 2m as a solid (66 mg, 94%); mp 198.3-198.7 °C (petroleum ether/ethyl acetate); ¹H NMR (400 MHz, CDCl₃) δ 7.90-7.73 (m, 12 H); ¹³C NMR (100 MHz, CDCl₃) δ 135.4 (d, JₚC = 101.8 Hz), 132.5 (d, JₚC = 12.1 Hz), 132.4 (d, JₚC = 9.9 Hz), 117.3, 116.9; ³¹P NMR (162 MHz, CDCl₃) δ 24.8 ppm.

(13) Tris(4-(methoxycarbonyl)phenyl)phosphine oxide (2n)¹⁶

The reaction of 1n (87 mg, 0.20 mmol), Eosin Y (2 mg, 0.0031 mmol), CH₂Cl₂ (2.5 mL), and CH₃OH (0.5 mL) afforded 2n as a solid (86 mg, 95%); mp 173.6-174.1 °C (petroleum ether/ethyl acetate); ¹H NMR (400 MHz, CDCl₃) δ 8.14 (dd, J = 8.4, 2.8 Hz, 6 H), 7.75 (dd, J = 12.0, 8.4 Hz, 6 H), 3.95 (s, 9 H); ¹³C NMR (100 MHz, CDCl₃) δ 166.0, 136.1 (d, JₚC = 101.6 Hz), 133.7 (d, JₚC = 2.8 Hz), 132.0 (d, JₚC = 10.1 Hz), 129.7 (d, JₚC = 12.3 Hz), 52.6; ³¹P NMR (162 MHz, CDCl₃) δ 26.9 ppm.

(14) Tris(naphthalen-2-yl)phosphine oxide (2o)¹
The reaction of 1o (83 mg, 0.20 mmol), Eosin Y (2 mg, 0.0031 mmol), CH₂Cl₂ (2.5 mL), and CH₃OH (0.5 mL) afforded 2o as a solid (77 mg, 90%); mp 248.3-248.7 °C (petroleum ether/ethyl acetate); ¹H NMR (400 MHz, CDCl₃) δ 8.37 (d, ³J = 14.0 Hz, 3 H), 7.96-7.84 (m, 9 H), 7.78-7.71 (m, 3 H), 7.63-7.51 (m, 6 H); ¹³C NMR (100 MHz, CDCl₃) δ 134.7, 134.1 (d, ³J_P_C = 9.4 Hz), 132.4 (d, ³J_P_C = 13.3 Hz), 129.6 (d, ³J_P_C = 104.1 Hz), 128.9, 128.4 (d, ³J_P_C = 1.2 Hz), 128.2, 127.8, 126.9, 126.8; ³¹P NMR (162 MHz, CDCl₃) δ 29.8 ppm.

(15) Tris(thiophen-2-yl)phosphine oxide (2p)¹⁷

The reaction of 1p (56 mg, 0.20 mmol), Eosin Y (2 mg, 0.0031 mmol), CH₂Cl₂ (2.5 mL), and CH₃OH (0.5 mL) afforded 2p as a solid (53 mg, 90%); mp 128.4-128.8 °C (petroleum ether/ethyl acetate); ¹H NMR (400 MHz, CDCl₃) δ 7.79-7.74 (m, 3 H), 7.63-7.57 (m, 3 H), 7.23-7.18 (m, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 136.7 (d, ³J_P_C = 11.3 Hz), 134.6 (d, ³J_P_C = 127.2 Hz), 134.2 (d, ³J_P_C = 5.6 Hz), 128.2 (d, ³J_P_C = 15.0 Hz); ³¹P NMR (162 MHz, CDCl₃) δ 6.6 ppm.
NMR Spectra

2a

2a
References