Supporting Information for

Photoinduced 1,2,3,4-tetrahydropyridine ring conversions

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Experimental and analytical data
Methods and instruments
The reaction products were analysed by $^1$H and $^{13}$C NMR spectra registered on a Bruker DMX 500 spectrometer. The progress of the photochemical reaction of 1 was monitored by $^1$H NMR spectra on a Bruker WH 90 spectrometer.
Cyclic voltammetry was recorded using Advanced Electrochemical System PARSTAT 2273.
UV spectra were recorded on Camspec M501 Single Beam Scanning UV/Visible Spectrophotometer.
Infrared spectra were recorded on a Perkin-Elmer 580B spectrometer.
GC-MS spectra were obtained by Hewlett-Packard Model GC 6890 gas chromatograph coupled with mass selective detector.
Elemental analyses were performed at EA 1106 (Carlo Erba Instruments).
Melting points were obtained on a BÜCHI 535.
X-ray crystallographic analysis were done on Nonius Kappa CCD.

Experimental section
3,5-Diethoxycarbonyl-2,6-dimethyl-4-phenyl-1,2,3,4-tetrahydropyridine (1) was synthesized from the corresponding 1,4-dihydropyridine according to a general procedure¹.
$^1$H NMR (500 MHz, CDCl$_3$, δ): 0.71 (t, $J$= 7.0 Hz, 3-COOCH$_2$CH$_3$, 3H), 1.03 (t, $J$= 7.0 Hz, 5-COOCH$_2$CH$_3$, 3H), 1.11 (d, $J$= 7.0 Hz, 2-CH$_3$, 3H), 2.30 (d, $J$= 1.0 Hz, 6-CH$_3$, 3H), 2.42 (t, $J$= 10.0 Hz, 3-H, 1H), 3.52 (m, $J$= 10.0 & 7.0 & 1.0 Hz, 2-H, 1H), 3.71 (dq, $J$= 7.0 & 1.2 Hz, 3-COOCH$_2$CH$_3$, 2H), 3.94 (broad s, NH, 1H), 3.98 (q, $J$= 7.0 Hz, 5-COOCH$_2$CH$_3$, 2H), 4.06 (broad d, $J$= 10.0 Hz, 4-H, 1H), 7.08 (m, ArH, 5H) ppm.
Mp 144-146 °C.

X-ray structure (CCDC 667862)

Oxidation of 1 in solutions saturated by dioxygen

3,5-Diethoxycarbonyl-2,6-dimethyl-3-hydroperoxy-4-phenyl-3,4,5,6-tetrahydropyridine (2)

0.12080 g (0.36 mmol) of 3,5-diethoxycarbonyl-2,6-dimethyl-4-phenyl-1,2,3,4-tetrahydropyridine (1) was dissolved in 20 mL CHCl₃. Oxygen was intensively blew through the solution, therefore the volumetric flask of bigger volume (50 mL) was preferred. The solution was exposed to direct sunlight. After 35 min CHCl₃ was evaporated due to the continuous flow of dioxygen and crystals of hydroperoxy 2 suitable for X-ray diffraction analysis were obtained.

1H NMR (500 MHz, CDCl₃, δ): 0.97 (t, J= 7.0 Hz, 5-COOCH₂CH₃, 3H), 1.07 (t, J = 7.0 Hz, 3-COOCH₂CH₃, 3H), 1.45 (d, J= 7.0 Hz, 6-CH₃, 3H), 2.09 (d, J= 2.1 Hz, 2-CH₃, 3H), 3.41 (dd, J= 13.3 & 9.8 Hz, 5-H, 1H), 3.85 (m, J= 9.8 & 7.0 & 2.1 Hz, 6-H, 1H), 3.95 (AB m, J= 7.0 Hz, 5-COOCH₂CH₃, 2H), 3.98 (q, J= 7.0 Hz, 3-COOCH₂CH₃, 2H), 4.06 (d, J= 13.3 Hz, 4-H, 1H), 7.20 (m, ArH, 5H), 9.43 (bs, OOH, 1H) ppm.

13C NMR (50 MHz, CDCl₃, δ): 13.67 (5-COOCH₂CH₃), 13.83 (3-COOCH₂CH₃), 21.60 (6-CH₃), 21.66 (2-CH₃), 43.71 (4-C), 49.01 (5-C), 56.67 (6-C), 60.64 (5-COOCH₂CH₃), 62.00 (3-COOCH₂CH₃), 87.85 (3-C), 127.58 & 127.99 & 128.86 & 135.92 (ArC), 163.78 (2-C), 166.28 (3-COOCH₂CH₃), 172.63 (5-COOCH₂CH₃) ppm.


X-ray structure (CCDC 667861)
$^1$H NMR spectra in CDCl$_3$ of 2

S4
${}^{13}$C NMR spectra in CDCl$_3$ of 2
II Oxidation of 1 in air saturated solutions

1.13955 g (3.44 mmol) of 3,5-diethoxycarbonyl-2,6-dimethyl-4-phenyl-1,2,3,4-tetrahydropyridine (1) was dissolved in 50 mL CDCl₃. The solution was stirred in a opened glass flask exposed to the direct sunlight. The reaction was controlled by ¹H NMR spectroscopy. After completion of the reaction (t ~ 1 h) the solvent was evaporated, the crude product was charged on a silica gel (0.035–0.07 mm Acros Organics) column (h = 28 cm, d = 2 cm) and eluted using chloroform/petroleum ether/acetone (9:7:1); 10 mL fractions were collected. Combined fractions 12–18 following after the dead volume (110 mL) contained 0.29315 g (0.81 mmol) of pure 3,5-diethoxycarbonyl-2,6-dimethyl-3-hydroxy-4-phenyl-1,2-epoxypiperidine (4) which was concentrated in vacuum to obtain a white solid. Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a hexane solution.

Fractions 21–30 that contained a mixture of 3,5-diethoxycarbonyl-2,6-dimethyl-3-hydroxy-4-phenyl-3,4,5,6-tetrahydropyridine (3) and N-acetyl-2,4-diethoxycarbonyl-2-hydroxy-4-methyl-3-phenylpyrrolidine (5) were combined and after solvent removal (rotary evaporator) a pale yellow oil (0.8377 g) was obtained. Pure 5 was isolated from the oil by crystallization from diethyl ether/hexane. The white precipitate 0.4453 g (1.23 mmol) was removed by filtration. Crystals for X-ray diffraction analysis were grown from hexane.

The filtrate containing a mixture of 3,5-diethoxycarbonyl-2,6-dimethyl-3-hydroxy-4-phenyl-3,4,5,6-tetrahydropyridine (3) and N-acetyl-2,4-diethoxycarbonyl-2-hydroxy-4-methyl-3-phenylpyrrolidine (5) was concentrated in vacuum and analysed by 1D and 2D NMR spectra. The isolation of the products is the same if ethyl acetate/hexane (1:1) was used as an eluent (4 Rᵣ 0.48; 3 Rᵣ 0.16; 5 Rᵣ 0.15) for column chromatography.

3,5-Diethoxycarbonyl-2,6-dimethyl-3-hydroxy-4-phenyl-3,4,5,6-tetrahydropyridine (3)

¹H NMR (500 MHz, CDCl₃, δ): 0.94 (t, J = 7.0 Hz, 5-COOCH₂CH₃; 3H), 1.36 (t, J = 7.0 Hz, 3-COOCH₂CH₃; 3H), 1.46 (d, J = 7.3 Hz, 6-CH₃; 3H), 1.95 (d, J = 2.1 Hz, 2-CH₃; 3H), 3.43 (dd, J = 13.4 & 9.5 Hz, 5-H; 1H), 3.51 (d, J = 13.4 Hz, 4-H; 1H), 3.78 (s, OH; 1H), 3.94 (m, J = 9.5 & 7.3 & 2.1 Hz, 6-H; 1H), 3.96 (AB m, J = 7.0 Hz, 5-COOCH₂CH₃; 2H), 4.20 (AB m, J = 7.0 Hz, 3-COOCH₂CH₃; 2H), 7.20 (m, ArH, 5H) ppm.

¹³C NMR (125 MHz, CDCl₃, δ): 13.6 (5-COOCH₂CH₃), 13.8 (3-COOCH₂CH₃), 21.7 (6-CH₃), 21.9 (2-CH₃), 49.3 (5-C), 49.8 (4-C), 56.8 (6-C), 60.4 (5-COOCH₂CH₃), 63.2 (3-COOCH₂CH₃), 77.3 (3-C), 129.0 & 129.5 & 135 (ArC), 162.8 (2-C), 170.8 (3-COOCH₂CH₃), 171.9 (5-COOCH₂CH₃) ppm.
IR (dry film, cm$^{-1}$): 3490 (br), 1730 (s), 1670 (m).

GC–MS spectrum of 3 and 5
GC–MS spectrum of 3 and 5
$^1$H NMR spectra in CDCl$_3$ of 3 and 5
HMBC spectra in CDCl$_3$ of 3 and 5
HSQC spectrum in CDCl$_3$ of 3 and 5
NOESY spectrum in CDCl$_3$ of 3 and 5
3,5-Diethoxycarbonyl-2,6-dimethyl-3-hydroxy-4-phenyl-1,2-epoxypiperidine (4)

$^1$H NMR (500 MHz, CDCl$_3$, δ): 0.87 (t, $J= 7.0$ Hz, 5-COOCH$_2$CH$_3$, 3H), 1.39 (t, $J= 7.0$ Hz, 3-COOCH$_2$CH$_3$, 3H), 1.45 (s, 2-CH$_3$, 3H), 1.49 (d, $J= 7.3$ Hz, 6-CH$_3$, 3H), 3.28 (s, 3-OH, 1H), 3.36 (dd, $J= 13.4$ & 10.0 Hz, 5-H, 1H), 3.62 (d, $J= 13.4$ Hz, 4-H, 1H), 3.70 (dq, $J= 10.0$ & 7.3 Hz, 6-H, 1H), 3.86 (AB m, $J= 7.0$ Hz, 5-COOCH$_2$CH$_3$, 2H), 4.34 (q, $J= 7.0$ Hz, 3-COOCH$_2$CH$_3$, 2H), 7.12 (d, $J= 8.0$ Hz, ArH, 2H), 7.26 (m, ArH, 3H), 7.25 (m, 5H, H$_{arom}$) ppm.

$^{13}$C NMR (125 MHz, CDCl$_3$, δ): 13.5 (5-COOCH$_2$CH$_3$), 13.9 (3-COOCH$_2$CH$_3$), 19.0 (2-CH$_3$), 20.2 (6-CH$_3$), 45.4 (4-C), 50.0 (5-C), 56.5 (6-C), 60.5 (5-COOCH$_2$CH$_3$), 62.9 (3-COOCH$_2$CH$_3$), 78.4 (3-C), 83.4 (2-C), 127.8 & 128.0 & 128.8 & 134.8 (ArC), 170.5 (5-COOCH$_2$CH$_3$), 170.6 (3-COOCH$_2$CH$_3$) ppm.

IR (dry film, cm$^{-1}$): 3500 (br), 1740 (br).


X-ray structure (CCDC 667860)
GC–MS spectrum of 4
$^{15}$N NMR spectrum in CDCl$_3$ of 4

NOESY spectrum in CDCl$_3$ of 4
HMBC spectrum in CDCl$_3$ of 4
**N-Acetyl-2,4-diethoxycarbonyl-2-hydroxy-4-methyl-3-phenylpyrrolidine (5)**

$^1$H NMR (500 MHz, CDCl$_3$, δ): 1.08 (t, J = 7.0 Hz, 4-COOCH$_2$CH$_3$, 3H), 1.33 (t, J = 7.0 Hz, 3-COOCH$_2$CH$_3$, 3H), 1.63 (d, J = 6.1 Hz, 5-CH$_3$, 3H), 2.12 (s, COCH$_3$, 3H), 3.46 (dd, J = 12.8 & 7.9 Hz, 4-H, 1H), 3.99 (d, J = 12.8 Hz, 3-H, 1H), 4.09 (q, J = 7.0 Hz, 4-COOCH$_2$CH$_3$, 2H), 4.17 (s, OH, 1H), 4.27 (dq, J = 7.9 & 6.1 Hz, 5-H, 1H), 4.28 (AB m, J = 7.0 Hz, 2-COOCH$_2$CH$_3$, 2H), 7.20 (m, ArH, 5H) ppm.

$^{13}$C NMR (125 MHz, CDCl$_3$, δ): 13.81 (4-COOCH$_2$CH$_3$), 13.90 (2-COOCH$_2$CH$_3$), 21.03 (COCH$_3$), 22.94 (5-CH$_3$), 54.72 (4-C), 55.05 (3-C), 56.62 (5-C), 61.10 (4-COOCH$_2$CH$_3$), 62.63 (2-COOCH$_2$CH$_3$), 89.34 (2-C), 129.03 & 129.21 & 132.91 (ArC), 169.10 (COCH$_3$), 169.62 (2-COOCH$_2$CH$_3$), 171.31 (4-COOCH$_2$CH$_3$) ppm.

IR (Nujol, cm$^{-1}$): 3200 (br), 1750 (s), 1725 (s), 1635 (s).

Anal. Calcd for C$_{19}$H$_{25}$NO$_6$: C, 62.80; H, 6.93; N, 3.85. Found: C, 62.54; H 6.90; N, 3.72. Mp 82-84 ºC.

X-ray structure (CCDC 1420767)
GC–MS spectrum of 5
$^1$H NMR spectra in CDCl$_3$ of 5
HMBC spectrum in CDCl$_3$ of 5