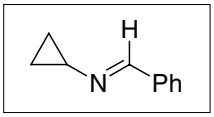
N-Cyclopropylimine-1-pyrroline rearrangement. A novel photochemical reaction.

Pedro J. Campos,* Alberto Soldevilla, Diego Sampedro and Miguel A. Rodríguez*

SUPPORTING INFORMATION

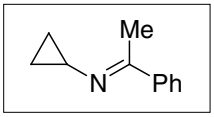
Characterization data of isolated new compounds:

•*E*-Benzylidenecyclopropylamine (4a)



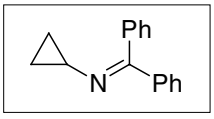
^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.88 (m, 2H), 0.98 (m, 2H), 3.00 (m, 1H), 7.37 (m, 3H), 7.65 (m, 2H), 8.42 (s, 1H).
^{13}C-NMR (75 MHz, $CDCl_3$): δ 8.8, 41.9, 127.5, 128.5, 130.0, 136.5, 158.4.
IR (neat): ν (cm^{-1}) 1635 (m) (C=N).
GC-MS: 145(M, 52), 144(78), 117(100), 104(22), 90(93).
MS-ES(+): 146 (M+1).
Anal. Calcd. for $C_{10}H_{11}N$: C, 82.72; H, 7.64; N, 9.65. Found: C, 82.83; H, 7.30; N, 9.87

•*E*-Cyclopropyl-(1-phenylethylidene)-amine (4b)



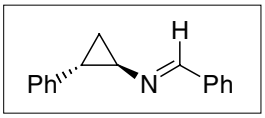
^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.98 (m, 4H), 2.40 (s 3H), 3.16 (m, 1H), 7.2-7.4 (m, 3H), 7.7-7.8 (m, 2H).
^{13}C-NMR (75 MHz, $CDCl_3$): δ 9.2, 34.2, 15.8, 126.4, 128.3, 129.1, 141.3, 163.4.
IR (neat): ν (cm^{-1}) 1628 (m) (C=N).
GC-MS: 159(M, 51), 144(73), 130(73), 117(30), 104(100), 91(48), 77(42).
MS-ES(+): 160 (M+1).
Anal. Calcd. for $C_{11}H_{12}N$: C, 82.97; H, 8.23; N, 8.80. Found: C, 82.91; H, 8.30; N, 8.79

•Benzhydrylidenecyclopropylamine (4c)



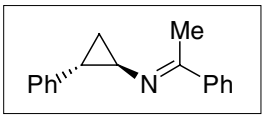
^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.77 (m, 2H), 1.03 (m, 2H), 2.88 (m, 1H), 7.2-7.5 (m, 10H).
^{13}C-NMR (75 MHz, $CDCl_3$): δ 9.9, 35.8, 127.7, 127.8, 128.0, 128.2, 128.3, 129.2, 136.9, 139.8, 165.9.
GC-MS: 221(M, 14), 144(10), 165(100), 55(25).
MS-ES(+): 222 (M+1).
Anal. Calcd. for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33. Found: C, 86.75; H, 6.99; N, 6.26

• ***trans-E*-Benzylidene-(2-phenylcyclopropyl)-amine (4d)**



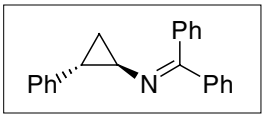
^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.46 (m, 1H), 1.66 (m, 1H), 2.52 (m, 1H), 3.16 (m, 1H), 7.1-7.4 (m, 8H), 7.68 (m, 2H), 8.38 (s, 1H).
^{13}C-NMR (75 MHz, $CDCl_3$): δ 18.5, 26.8, 53.2, 125.8, 126.0, 127.7, 128.4, 128.6, 130.3, 136.3, 141.3, 159.1.
IR (neat): ν (cm^{-1}) 1632 (m) (C=N).
GC-MS: 221(M, 19), 118(10), 117(100), 115(11), 90(46).
MS-ES(+): 222 (M+1).
Anal. Calcd. for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33. Found: C, 86.99; H, 6.75; N, 6.26

• ***trans-E*-(2-Phenylcyclopropyl)-(1-phenylethylidene)-amine (4e)**



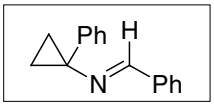
^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.48 (m, 1H), 1.62 (m, 1H), 2.32 (s, 3H), 2.46 (m, 1H), 3.26 (m, 1H), 7.1-7.4 (m, 8H), 7.76 (m, 2H).
^{13}C-NMR (75 MHz, $CDCl_3$): δ 16.1, 18.9, 27.2, 45.7, 125.7, 126.4, 126.7, 128.0, 128.2, 129.3, 141.0, 141.8, 164.2.
IR (neat): ν (cm^{-1}) 1685 (m) (C=N).
GC-MS: 235(M, 18), 220(5), 131(88), 130(93), 104(100), 78(39).
MS-ES(+): 236 (M+1).
Anal. Calcd. for $C_{17}H_{17}N$: C, 86.77; H, 7.28; N, 5.95. Found: C, 86.85; H, 7.35; N, 5.80

• ***trans*-Benzhydrylene-(2-phenylcyclopropyl)-amine (4f)**



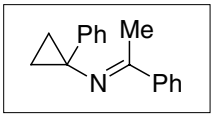
^{1}H-RMN (300 MHz, $CDCl_3$): δ 1.35 (m, 1H), 1.62 (m, 1H), 2.66 (m, 1H), 3.14 (m, 1H), 7.0-7.7 (m, 15H).
^{13}C-RMN (75 MHz, $CDCl_3$): δ 14.2, 37.3, 39.5, 127.3, 127.6, 127.7, 127.9, 128.1, 128.4, 128.6, 128.9, 129.2, 135.3, 136.5, 139.1, 165.8.
IR (neat): ν (cm^{-1}) 1660 (m) (C=N).
GC-MS: 297(M, 22), 220(23), 165(100), 143(9).
MS-ES(+): 298 (M+1).
Anal. Calcd. for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71. Found: C, 88.98; H, 6.57; N, 4.45

• ***E*-Benzylidene-(1-phenylcyclopropyl)-amine (4g)**



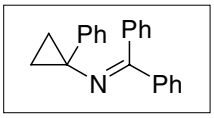
^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.32 (m, 2H), 1.50 (m, 2H), 7.3-7.4 (m, 8H), 7.62 (m, 2H), 7.76 (s, 1H).
^{13}C-NMR (75 MHz, $CDCl_3$): δ 16.8, 50.5, 127.4, 127.7, 128.4, 128.5, 130.0, 130.2, 136.6, 140.6, 157.7.
IR (neat): ν (cm^{-1}) 1637 (m) (C=N).
GC-MS: 221(M, 72), 220(32), 193(100), 165(37), 117(36), 89(75).
MS-ES(+): 222 (M+1).
Anal. Calcd. for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33. Found: C, 86.74; H, 6.82; N, 6.44

• ***E*-(2-Phenylcyclopropyl)-(1-phenylethylidene)-amine (4h)**



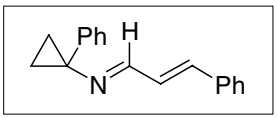
^{1}H-NMR(300 MHz, $CDCl_3$): δ 1.28 (m, 2H), 1.42 (m, 2H), 2.22 (s, 3H), 7.1-7.4 (m, 10H).
^{13}C-NMR (75 MHz, $CDCl_3$): δ 18.7, 44.5, 19.2, 126.4, 126.8, 127.2, 128.2, 130.0, 130.2, 140.2, 143.6, 173.1.
IR (neat): ν (cm^{-1}) 1687 (m) (C=N).
GC-MS: 235(M, 14), 234(30), 220(86), 206(74), 166(30), 115(31), 104(100), 78(62).
MS-ES(+): 236 (M+1).
Anal. Calcd. for $C_{17}H_{17}N$: C, 86.77; H, 7.28; N, 5.95. Found: C, 86.57; H, 7.39; N, 6.04

• **Benzhydrylene-(1-phenylcyclopropyl)-amine (4i)**



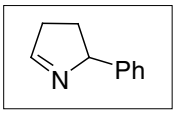
^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.13 (m, 4H), 6.9-7.8 (m, 15H).
^{13}C-NMR (75 MHz, $CDCl_3$): δ 19.6, 46.1, 125.3, 127.6, 127.9, 128.2, 128.5, 128.6, 130.0, 132.4, 132.8, 138.2, 140.6, 145.3, 172.0.
IR (neat): ν (cm^{-1}) 1660 (m) (C=N).
GC-MS: 297(M, 38), 296(17), 269(60), 193(12), 165(100), 115(32), 91(14), 77(15).
MS-ES(+): 298 (M+1).
Anal. Calcd. for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71. Found: C, 89.01; H, 6.41; N, 4.55

• ***E*-(*E*-3-Phenylallylidene)-(1-phenylcyclopropyl)-amine (4j)**



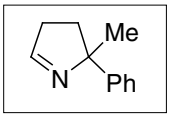
^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.32 (m, 2H), 1.44 (m 2H), 6.70 (d, *J*= 15Hz, 1H), 6.92 (dd, *J* = 15, 9Hz, 1H), 7.2-7.4 (m, 10H), 7.50 (d, *J*= 9Hz, 1H).
^{13}C-NMR (75 MHz, $CDCl_3$): δ 16.8, 50.8, 127.0, 127.5, 128.5, 128.6, 128.7, 128.7, 130.6, 136.0, 140.2, 159.7.
IR (neat): ν (cm^{-1}) 1631 (m) (C=N), 1682 (m) (alkene).
GC-MS: 247(M, 98), 219(14), 170(7), 143(14), 128(27), 119(76), 115(100), 104(28), 91(19), 77(25).
MS-ES(+): 248 (M+1).
Anal. Calcd. for $C_{18}H_{17}N$: C, 87.41; H, 6.93; N, 5.66. Found: C, 87.62; H, 6.73; N, 5.65

• **5-Phenyl-1-pyrroline (5a)**



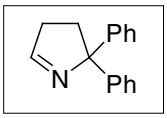
^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.68 (m, 1H), 2.38 (m, 1H), 2.62 (m, 1H), 2.72 (m,1H), 5.10 (m, 1H), 7.2-7.4 (m, 5H), 7.80 (s, 1H)
^{13}C-NMR (75 MHz, $CDCl_3$): δ 30.3, 37.4, 75.9, 126.4, 126.8, 128.5, 144.0, 167.6.
IR (neat): ν (cm^{-1}) 1634 (m) (C=N).
GC-MS: 145(M, 85), 144(50), 117(100), 104(16), 90(42).
MS-ES(+): 146 (M+1).
Anal. Calcd. for $C_{10}H_{11}N$: C, 82.72; H, 7.64; N, 9.65. Found: C, 82.89; H, 7.41; N, 9.70

•5-Methyl-5-phenyl-1-pyrroline (5b)



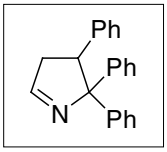
^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.52 (s, 3H), 2.06 (m, 2H), 2.64 (m, 2H), 7.2-7.4 (m, 5H), 7.68 (s, 1H).
^{13}C-NMR (75 MHz, $CDCl_3$): δ 29.7, 36.8, 78.4, 35.9, 125.2, 126.2, 128.1, 148.6, 164.8.
IR (neat): ν (cm^{-1}) 1625 (m) (C=N).
GC-MS: 159(M, 60), 144(80), 131(67), 130(77), 117(25), 104(100), 91(31), 77(35).
MS-ES(+): 160 (M+1).
Anal. Calcd. for $C_{11}H_{13}N$: C, 82.97; H, 8.23; N, 8.80. Found: C, 82.82; H, 8.12; N, 9.06

•5,5-Diphenyl-1-pyrroline (5c)



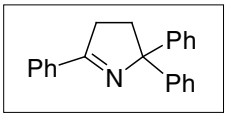
^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.56 (t, 2H), 2.68 (t, 2H), 7.2-7.6 (m, 10H), 7.90 (s, 1H).
^{13}C-NMR (75 MHz, $CDCl_3$): δ 36.0, 37.3, 89.1, 125.9, 126.1, 126.4, 127.4, 127.7, 128.1, 137.1, 147.1, 166.3.
GC-MS: 221(M, 5), 144(16), 165(100), 55(25).
MS-ES(+): 222 (M+1).
Anal. Calcd. for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33. Found: C, 86.92; H, 6.49; N, 6.59

•4,5,5-Triphenyl-1-pyrroline (5f)



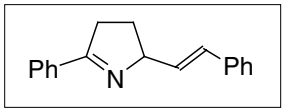
^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.91 (m, 1H), 3.20 (m, 1H), 4.31 (m, 1H), 6.8-7.6 (m, 15H), 7.92 (m, 1H).
^{13}C-NMR (75 MHz, $CDCl_3$): δ 46.8, 51.4, 93.9, 125.8, 125.9, 126.1, 126.3, 126.4, 127.1, 127.3, 127.7, 128.1, 141.4, 142.7, 146.9, 165.9.
GC-MS: 297(M, 15), 220(18), 165(100), 143(16).
MS-ES(+): 298 (M+1).
Anal. Calcd. for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71. Found: C, 89.12; H, 6.21; N, 4.67

•2,5,5-Triphenyl-1-pyrroline (5i)



^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.75 (t, 2H), 3.07 (t, 2H), 7.2-8.0 (m, 15H).
^{13}C-NMR (75 MHz, $CDCl_3$): δ 35.4, 37.6, 83.8, 126.3, 126.6, 127.9, 128.1, 128.2, 128.3, 130.0, 130.5, 132.4, 134.6, 137.5, 147.7, 172.4.
GC-MS: 297(M, 27), 296(25), 269(27), 220(15), 193(100), 165(50), 115(43), 91(19), 77(16).
MS-ES(+): 298 (M+1).
Anal. Calcd. for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71. Found: C, 89.03; H, 6.52; N, 4.45

• ***E*-5-Styryl-2-phenyl-1-pyrroline (5j)**



^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.88 (m, 1H), 2.38 (m, 1H), 2.98 (m, 1H), 3.10 (m,1H), 4.92 (m, 1H), 6.34 (dd, *J*= 15, 9Hz, 1H), 6.64 (d, *J*= 15Hz, 1H), 7.2-7.5 (m, 8H), 7.92 (m, 2H)
^{13}C-NMR (75 MHz, $CDCl_3$): δ 29.7, 35.1, 74.3, 126.3, 127.2, 127.8, 127.9, 128.4, 129.9, 130.5, 131.8, 134.4, 137.2, 173.4.
IR (neat): ν (cm^{-1}) 1613 (m) (C=N), 1682 (d) (alkene).
GC-MS: 247(M, 75), 207(33), 156(100), 119(61), 115(92), 104(27), 91(22), 77(27).
MS-ES(+): 248 (M+1).
Anal. Calcd. for $C_{18}H_{17}N$: C, 87.41; H, 6.93; N, 5.66. Found: C, 87.62; H, 7.08; N, 5.30

Representative UV-vis spectra of imines **4**: