

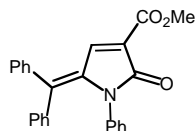
A HETEROCUMULENIC PAUSON–KHAND REACTION OF KETENIMINES:
A NEW SYNTHETIC METHOD FOR γ -EXO-METHYLENE- α,β -UNSATURATED
 γ -LACTAMS

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A mixture of the dicobaltoctacarbonyl (622 mg, 1.82 mmol) and methyl propiolate (153 mg, 1.82 mmol) in dichloromethane (10 mL) was stirred at room temperature for 2 hours. Removal of the solvent and column chromatography of the residue on silica gel (hexane/ethyl acetate (3:1)) afforded quantitatively the dicobalthexacarbonyl–methyl propiolate complex as an oil.

A mixture of the dicobalthexacarbonyl–methyl propiolate complex (112 mg, 0.303 mmol), *C,C,N*-triphenylketenimine (97.8 mg, 0.363 mmol) and DMSO (0.11 mL, 1.51 mmol) in toluene (5 mL) was heated at 115 °C for 2 hours. The reaction mixture was evaporated and the residue was chromatographed on silica gel eluting with hexane/ethyl acetate (3:1) to give the P–K product **4a** (57.8 mg, 50%).

Methyl 5-(diphenylmethylene)-2-oxo-1-phenyl-2,5-dihydro-1*H*-pyrrole-3-carboxylate (**4a**)



Yield 50%, Yellow solid, mp: 149.0-151.0 °C.

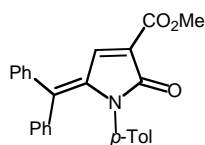
¹H-NMR (300 MHz, CDCl₃) δ : 7.82 (s, 1H), 7.24-7.47 (m, 5H), 6.83-7.01 (m, 10H), 3.89 (s, 3H).

¹³C-NMR (76 MHz, CDCl₃) δ : 166.8, 162.7, 146.4, 140.0, 137.5, 137.0, 135.8, 135.3, 132.0 (x2), 131.1 (x2), 129.5, 128.7, 128.4 (x2), 128.0 (x2), 127.3 (x2), 127.0 (x2), 126.3, 122.6, 52.2.

IR (KBr): 1754, 1686, 1560, 1346, 1190, 1064, 740, 688 cm⁻¹.

HRMS-ESI (m/z): [M]⁺ calcd for C₂₅H₁₉NO₃: 381.1365, found: 381.1358.

Methyl 5-(diphenylmethylene)-2-oxo-1-*p*-tolyl-2,5-dihydro-1*H*-pyrrole-3-carboxylate (**4b**)



Yield 45%, Yellow solid, mp: 190.4-193.1 °C.

¹H-NMR (500 MHz, CDCl₃) δ : 7.80 (s, 1H), 7.35-7.48 (m, 3H), 7.20-7.26 (m, 2H), 6.73-7.02

(m, 9H), 3.88 (s, 3H), 2.14 (s, 3H).

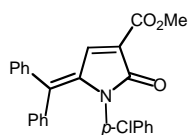
¹³C-NMR (126 MHz, CDCl₃) δ: 166.7, 162.8, 146.2, 140.1, 137.5, 136.7, 136.0, 135.9, 132.7, 132.0 (x2), 131.1 (x2), 129.4, 128.5 (x2), 128.4, 128.3 (x2), 127.2 (x2), 126.8 (x2), 123.2, 52.1, 20.8.

IR (KBr): 1751, 1697, 1573, 1511, 786, 701 cm⁻¹.

HRMS-ESI (m/z): [M]⁺ calcd for C₂₆H₂₁NO₃: 395.1521, found: 395.1539.

Methyl

1-(4-chlorophenyl)-5-(diphenylmethylene)-2-oxo-2,5-dihydro-1*H*-pyrrole-3-carboxylate (**4c**)



Yield 43%, Yellow solid, mp: 198.4-199.8 °C.

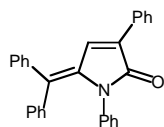
¹H-NMR (300 MHz, CDCl₃) δ: 7.83 (s, 1H), 6.84-7.49 (m, 14H), 3.88 (s, 3H).

¹³C-NMR (76 MHz, CDCl₃) δ: 166.5, 162.5, 146.4, 139.7, 137.4, 137.2, 135.4, 134.0, 132.0 (x2), 131.9, 131.1 (x2), 129.7, 129.0, 128.5 (x2), 128.1 (x2), 128.0 (x2), 127.6 (x2), 123.2, 52.2.

IR (KBr): 1751, 1689, 1565, 1488, 779, 694 cm⁻¹.

HRMS-ESI (m/z): [M]⁺ calcd for C₂₅H₁₈NO₃Cl: 415.0975, found: 415.0971.

5-(Diphenylmethylene)-1,3-diphenyl-1*H*-pyrrol-2(5*H*)-one (**4d**)



Yield 69%, Yellow solid, mp: 154.0-157.0 °C.

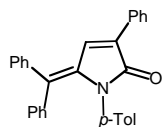
¹H-NMR (500 MHz, CDCl₃) δ: 7.96 (s, 1H), 7.29-7.45 (m, 10H), 6.85-7.05 (m, 10H).

¹³C-NMR (126 MHz, CDCl₃) δ: 170.4, 140.9, 138.4, 137.1, 136.1, 132.9, 131.9 (x2), 131.5, 131.2, 131.1 (x2), 130.6, 128.6, 128.5 (x2), 128.4, 128.2 (x2), 127.9 (x2), 127.7, 127.3 (x2), 127.2 (x4), 126.0.

IR (KBr): 1682, 1590, 1368, 1212, 1132, 740, 688 cm⁻¹.

HRMS-ESI (m/z): [M]⁺ calcd for C₂₉H₂₁NO: 399.1623, found: 399.1615.

5-(Diphenylmethylene)-1-*p*-tolyl-1*H*-pyrrol-2(5*H*)-one (**4e**)



Yield 45%, Yellow solid, mp: 172.3-181.0 °C.

¹H-NMR (500 MHz, CDCl₃) δ: 7.96 (s, 1H), 7.30-7.41 (m, 10H), 6.79-7.97 (m, 9H), 2.16 (s,

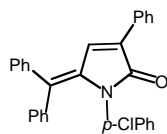
3H).

^{13}C -NMR (126 MHz, CDCl_3) δ : 170.4, 141.1, 138.5, 137.3, 135.8, 133.5, 132.7, 131.9 (x2), 131.6, 131.2, 131.1 (x2), 130.4, 128.6, 128.5, 128.4 (x2), 128.2 (x2), 127.9 (x2), 127.4, 127.3 (x2), 127.2 (x2), 127.1 (x2), 20.8.

IR (KBr): 1689, 1589, 1504, 1180, 779, 701 cm^{-1} .

HRMS-ESI (m/z): $[\text{M}]^+$ calcd for $\text{C}_{30}\text{H}_{23}\text{NO}$: 413.1780, found: 413.1782.

1-(4-Chlorophenyl)-5-(diphenylmethylene)-3-phenyl-1*H*-pyrrol-2(5*H*)-one (**4f**)



Yield 46%, Yellow solid, mp: 190.9-194.5 $^{\circ}\text{C}$.

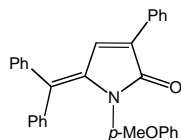
^1H -NMR (500 MHz, CDCl_3) δ : 7.95 (s, 1H), 7.30-7.44 (m, 10H), 6.86-7.05 (m, 9H).

^{13}C -NMR (126 MHz, CDCl_3) δ : 170.1, 143.7, 140.7, 138.3, 136.7, 134.7, 133.0, 131.8 (x2), 131.6, 131.3, 131.1 (x2), 130.8, 128.8, 128.6, 128.5 (x2), 128.4 (x2), 128.3 (x2), 128.0 (x2), 127.9, 127.5 (x2), 127.3 (x2).

IR (KBr): 1682, 1581, 1488, 1180, 779, 701 cm^{-1} .

HRMS-ESI (m/z): $[\text{M}]^+$ calcd for $\text{C}_{29}\text{H}_{20}\text{NOCl}$: 433.1233, found: 433.1235.

5-(Diphenylmethylene)-1-(4-methoxyphenyl)-3-phenyl-1*H*-pyrrol-2(5*H*)-one (**4g**)



Yield 77%, Orange solid, mp: 73.8-74.6 $^{\circ}\text{C}$.

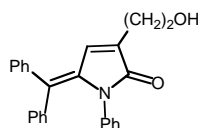
^1H -NMR (500 MHz, CDCl_3) δ : 7.96 (d, $J = 8.0$ Hz, 2H), 7.27-7.41 (m, 9H), 6.98 (dd, $J = 6.9$, 6.9 Hz, 1H), 6.89-6.94 (m, 4H), 6.86 (d, $J = 8.0$ Hz, 2H), 6.53 (d, $J = 8.5$ Hz, 2H), 3.66 (s, 3H).

^{13}C -NMR (126 MHz, CDCl_3) δ : 170.5, 157.6, 141.0, 138.3, 137.3, 132.5, 131.8 (x2), 131.5, 131.2, 131.1 (x2), 130.4, 129.1, 128.6, 128.5 (x2), 128.4 (x2), 128.3, 128.1 (x2), 127.6, 127.3 (x2), 127.2 (x2), 113.4 (x2), 55.4.

IR (KBr): 1689, 1604, 1373, 1241, 1133, 755, 694 cm^{-1} .

HRMS-ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{30}\text{H}_{23}\text{NNaO}_2$: 452.1621, found: 452.1641.

5-(Diphenylmethylene)-3-(2-hydroxyethyl)-1-phenyl-1*H*-pyrrol-2(5*H*)-one (**4h**)



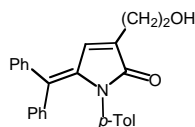
Yield 50%, Brown solid, mp: 118.0-119.1 $^{\circ}\text{C}$.

¹H-NMR (300 MHz, CDCl₃) δ: 7.36-7.38 (m, 3H), 7.24-7.26 (m, 2H), 6.82-7.02 (m, 11H), 3.84 (t, *J* = 5.4 Hz, 2H), 3.54 (br, 1H), 2.72 (t, *J* = 5.4 Hz, 2H).

¹³C-NMR (76 MHz, CDCl₃) δ: 172.8, 140.6, 138.0, 136.9, 135.9, 135.8, 133.1 (x2), 131.6, 130.9, 130.5 (x2), 128.4, 128.1 (x2), 127.9 (x2), 127.7 (x2), 127.2 (x2), 127.0, 126.1, 61.3, 30.2.
IR (KBr): 3471, 1681, 1596, 1496, 1203, 755, 694 cm⁻¹.

HRMS-ESI (m/z): [M]⁺ calcd for C₂₅H₂₁NO₂: 367.1572, found: 367.1575.

5-(Diphenylmethylene)-3-(2-hydroxyethyl)-1-*p*-tolyl-1*H*-pyrrol-2(5*H*)-one (**4i**)



Yield 46%, Brown solid, mp: 134.8-137.8 °C.

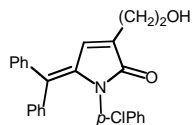
¹H-NMR (300 MHz, CDCl₃) δ: 7.35-7.37 (m, 3H), 7.22-7.25 (m, 2H), 6.75-6.97 (m, 10H), 3.83 (t, *J* = 5.1 Hz, 2H), 2.72 (t, *J* = 5.1 Hz, 2H), 3.59 (br, 1H), 2.14 (s, 3H).

¹³C-NMR (76 MHz, CDCl₃) δ: 172.9, 140.7, 138.1, 137.0, 135.9, 135.6, 133.2, 133.1 (x2), 131.6, 130.9, 130.2 (x2), 128.5, 128.3 (x2), 128.0 (x2), 127.4 (x2), 127.1 (x2), 126.9, 61.3, 30.2, 20.8.

IR (KBr): 3486, 1681, 1604, 1511, 1172, 763, 701 cm⁻¹.

HRMS-ESI (m/z): [M]⁺ calcd for C₂₆H₂₃NO₂: 381.1729, found: 381.1722.

1-(4-Chlorophenyl)-5-(diphenylmethylene)-3-(2-hydroxyethyl)-1*H*-pyrrol-2(5*H*)-one (**4j**)



Yield 53%, Brown solid, mp: 138.2-141.5 °C.

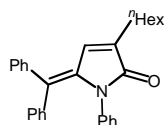
¹H-NMR (300 MHz, CDCl₃) δ: 7.36-7.39 (m, 3H), 7.23-7.25 (m, 2H), 6.81-7.00 (m, 10H), 3.84 (t, *J* = 5.3 Hz, 2H), 3.31 (br, 1H), 2.72 (t, *J* = 5.3 Hz, 2H).

¹³C-NMR (76 MHz, CDCl₃) δ: 172.5, 140.4, 137.9, 136.6, 136.0, 134.9, 134.5, 133.0, 131.7 (x2), 131.6, 130.9 (x2), 130.5, 128.5, 128.2 (x2), 128.0 (x2), 127.9 (x2), 127.4 (x2), 61.2, 30.0.

IR (KBr): 3478, 1681, 1596, 1488, 1172, 763, 701 cm⁻¹.

HRMS-ESI (m/z): [M]⁺ calcd for C₂₅H₂₀NO₂Cl: 401.1183, found: 401.1174.

5-(Diphenylmethylene)-3-hexyl-1-phenyl-1*H*-pyrrol-2(5*H*)-one (**4k**)



Yield 53%, Yellow solid, mp: 63.5-64.8 °C.

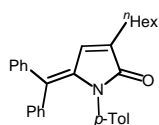
$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ : 6.80-7.79 (m, 16H), 2.41 (t, $J = 7.3$ Hz, 2H), 1.59 (m, 2H), 1.33 (m, 6H), 0.88 (t, $J = 6.7$ Hz, 3H).

$^{13}\text{C-NMR}$ (76 MHz, CDCl_3) δ : 172.0, 141.1, 138.6, 137.3, 136.3, 136.1, 133.6, 131.7 (x2), 131.0, 130.5, 128.3, 128.1 (x2), 127.8 (x2), 127.3 (x2), 127.2 (x2), 127.1 (x2), 125.8, 31.6, 29.1, 27.9, 25.7, 22.6, 14.1.

IR (KBr): 2915, 1689, 1589, 1488, 1203, 763, 694 cm^{-1} .

HRMS-ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{29}\text{H}_{29}\text{NNaO}$: 430.2141, found: 421.2130.

5-(Diphenylmethylene)-3-hexyl-1-*p*-tolyl-1*H*-pyrrol-2(5*H*)-one (**4l**)



Yield 47%, White solid, mp: 45.1-45.8 $^{\circ}\text{C}$.

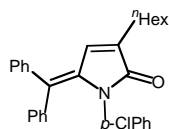
$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ : 6.80-7.79 (m, 16H), 2.41 (t, $J = 7.3$ Hz, 2H), 1.59 (m, 2H), 1.33 (m, 6H), 0.88 (t, $J = 6.7$ Hz, 3H).

$^{13}\text{C-NMR}$ (76 MHz, CDCl_3) δ : 172.1, 141.2, 138.5, 137.5, 136.1, 135.5, 133.6, 133.4, 132.4 (x2), 131.0 (x2), 128.4, 128.2, 128.1 (x2), 128.0 (x2), 127.9 (x2), 127.1 (x2), 126.9, 31.6, 29.1, 27.9, 25.7, 22.6, 20.9, 14.1.

IR (KBr): 2923, 1720, 1596, 1511, 748, 701 cm^{-1} .

HRMS-ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{30}\text{H}_{31}\text{NNaO}$: 444.2298, found: 444.2298.

1-(4-Chlorophenyl)-5-(diphenylmethylene)-3-hexyl-1*H*-pyrrol-2(5*H*)-one (**4m**)



Yield 43%, White solid, mp: 46.0-49.9 $^{\circ}\text{C}$.

$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ : 6.80-7.79 (m, 16H), 2.41 (t, $J = 7.3$ Hz, 2H), 1.59 (m, 2H), 1.33 (m, 6H), 0.88 (t, $J = 6.7$ Hz, 3H).

$^{13}\text{C-NMR}$ (76 MHz, CDCl_3) δ : 171.8, 140.7, 138.4, 136.9, 136.0, 134.9, 133.8, 132.4 (x2), 131.6, 131.3 (x2), 130.1, 128.6, 128.3, 128.1 (x2), 128.0 (x2), 127.6 (x2), 127.4 (x2), 31.5, 29.1, 27.8, 25.7, 22.5, 14.1.

IR (KBr): 2923, 1697, 1596, 1488, 1203, 763, 701 cm^{-1} .

HRMS-ESI (m/z): $[\text{M}]^+$ calcd for $\text{C}_{29}\text{H}_{28}\text{NNaOCl}$: 464.1752, found: 464.1762.