bromide (645 mg, 2 mmol) were dissolved in DMF (20 mL) and initially electrolyzed at an external voltage of 50 V. When the reaction temperature reached 60 °C, the voltage was reduced to about 30 V in order to maintain the temperature in the range of 50–60 °C. At the end of the electrolysis the temperature dropped below 50 °C. At this point, the loss of weight of the zinc anode amounted to about 1.3 g (20 g atom). The reaction mixture was poured onto a mixture of 5% aqueous HCl (100 mL) and ice (50 g) and extracted with EtOAc (5 × 40 mL). The extract was dried ($MgSO_4$) and concentrated under reduced pressure. The oily residue was purified by flash chromatography on silica gel 60 using hexane/EtOAc/HOAc (66:33:0.5) as the eluent. According to this procedure the following half esters have been obtained.

1-Ethyl 2,2-dimethyl-3-oxohexanedioate (6a): yield 2.11 g (65%); colorless crystals; mp 40–42 °C (*n*-pentane); ^{1}H NMR δ 1.18 (3 H, t, *J* = 7 Hz), 1.30 (6 H, s), 2.45–2.82 (4 H, m), 4.12 (2 H, q, *J* = 7 Hz), 10.35 (1 H, s); ^{13}C NMR δ 14.0, 22.0, 28.0, 32.6, 55.3, 61.5, 173.6, 178.3, 206.5. Anal. Calcd for $C_{10}H_{16}O_5$: C, 55.55; H, 7.46. Found: C, 55.68; H, 7.61.

1-Ethyl (±)-2-methyl-3-oxohexanedioate (6b): yield 1.70 g (56%); colorless oil; ^{1}H NMR δ 1.18 (3 H, t, *J* = 7 Hz), 1.31 (3 H, d, *J* = 7 Hz), 2.51–2.59 (4 H, m), 3.52 (1 H, q, *J* = 7 Hz), 4.15 (2 H, q, *J* = 7 Hz), 9.11 (1 H, s); ^{13}C NMR δ 12.7, 14.0, 27.9, 35.9, 61.1, 61.6, 170.6, 178.0, 204.5. Anal. Calcd for $C_9H_{14}O_5$: C, 53.46; H, 6.98. Found: C, 53.62; H, 7.12.

1-Ethyl (±)-2-ethyl-3-oxohexanedioate (6c): yield 2.17 g (67%); colorless crystals; mp 42–44 °C (pentane); ^{1}H NMR δ 0.86 (3 H, t, *J* = 7 Hz), 1.20 (3 H, t, *J* = 7 Hz), 1.83 (2 H, m), 2.41–2.96 (4 H, m), 3.34 (1 H, t, *J* = 7 Hz), 4.15 (2 H, q, *J* = 7 Hz), 10.61 (1 H, s); ^{13}C NMR δ 11.8, 14.1, 21.6, 27.7, 36.1, 60.6, 61.4, 169.6, 178.4, 203.4. Anal. Calcd for $C_{10}H_{16}O_5$: C, 55.55; H, 7.46. Found: C, 55.31; H, 7.59.

1-Ethyl (±)-3-oxo-2-propylhexanedioate (6d): yield 2.52 g (73%); colorless oil; ^{1}H NMR δ 0.85 (3 H, t, *J* = 7 Hz), 1.19 (3 H, t, *J* = 7 Hz), 1.24 (2 H, m), 1.76 (2 H, t, *J* = 7 Hz), 2.45–2.91 (4 H, m), 3.42 (1 H, t, *J* = 7 Hz), 4.14 (2 H, q, *J* = 7 Hz), 10.85 (1 H, s); ^{13}C NMR δ 13.8, 14.1, 20.6, 27.8, 29.0, 36.1, 58.9, 61.5, 169.9, 178.2, 203.6. Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88. Found: C, 57.67; H, 8.01.

1-Ethyl (±)-2-butyl-3-oxohexanedioate (6e): yield 1.83 g (50%); colorless oil; ^{1}H NMR δ 0.84 (3 H, t, *J* = 7 Hz), 1.17 (3 H, t, *J* = 7 Hz), 1.09–1.35 (4 H, m), 1.83 (2 H, m), 2.46–2.89 (4 H, m), 3.39 (1 H, t, *J* = 7 Hz), 4.14 (2 H, q, *J* = 7 Hz), 10.64 (1 H, s); ^{13}C NMR δ 13.8, 14.1, 22.4, 27.8, 28.0, 29.5, 36.1, 59.1, 61.4, 169.8, 178.4, 203.6. Anal. Calcd for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25. Found: C, 59.29; H, 8.56.

1-Ethyl (±)-2-hexyl-3-oxohexanedioate (6f): yield 2.49 g (61%); colorless oil; ^{1}H NMR δ 0.90 (3 H, t, *J* = 7 Hz), 1.11–1.39 (8 H, m), 1.21 (3 H, t, *J* = 7 Hz), 1.80 (2 H, m), 2.41–2.91 (4 H, m), 3.38 (1 H, t, *J* = 7 Hz), 4.14 (2 H, q, *J* = 7 Hz), 10.35 (1 H, s); ^{13}C NMR δ 14.0, 14.1, 22.5, 27.3, 27.8, 28.3, 29.0, 31.5, 36.1, 59.2, 61.4, 169.8, 178.3, 203.5. Anal. Calcd for $C_{14}H_{24}O_5$: C, 61.74; H, 8.88. Found: C, 61.73; H, 9.07.

1-Ethyl 2,2-dimethyl-3-oxoheptanedioate (7a): yield 2.24 g (65%); colorless liquid; ^{1}H NMR δ 1.04–1.35 (9 H, m), 1.70–2.61 (6 H, m), 4.13 (2 H, q, *J* = 7 Hz), 10.83 (1 H, s); ^{13}C NMR δ 14.0, 18.9, 21.9, 32.8, 36.8, 55.5, 61.5, 173.7, 179.0, 207.4. Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88. Found: C, 57.06; H, 7.79.

1-Ethyl (±)-2-methyl-3-oxoheptanedioate (7b): yield 1.55 g (48%); colorless liquid; ^{1}H NMR δ 1.00–1.44 (6 H, m), 1.72–2.85 (6 H, m), 3.48 (1 H, q, *J* = 7 Hz), 4.13 (2 H, q, *J* = 7 Hz), 10.25 (1 H, s); ^{13}C NMR δ 12.7, 14.1, 18.5, 33.0, 40.2, 52.9, 61.6, 171.0, 179.1, 205.7. Anal. Calcd for $C_{10}H_{16}O_5$: C, 55.55; H, 7.46. Found: C, 55.71; H, 7.63.

1-Ethyl (±)-2-ethyl-3-oxoheptanedioate (7c): yield 1.55 g (45%); colorless liquid; ^{1}H NMR δ 0.80 (3 H, t, *J* = 7 Hz), 1.22 (3 H, t, *J* = 7 Hz), 1.61–2.76 (8 H, m), 3.28 (1 H, t, *J* = 7 Hz), 4.13 (2 H, q, *J* = 7 Hz), 11.30 (1 H, s); ^{13}C NMR δ 11.9, 14.1, 18.5, 21.6, 32.8, 40.7, 60.6, 61.4, 169.9, 178.9, 204.9. Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88. Found: C, 57.11; H, 7.65.

1-Ethyl (±)-3-oxo-2-propylheptanedioate (7d): yield 1.83 g (50%); colorless liquid; ^{1}H NMR δ 0.86 (3 H, t, *J* = 7 Hz), 1.20 (3 H, t, *J* = 7 Hz), 1.62–2.08 (4 H, m, *J* = 7 Hz), 2.12–2.80 (6 H, m, *J* = 7 Hz), 3.40 (1 H, t, *J* = 7 Hz), 4.15 (2 H, q, *J* = 7 Hz), 10.82 (1 H, s); ^{13}C NMR δ 13.8, 14.1, 18.4, 20.7, 30.2, 32.8, 40.5, 58.9, 61.3, 169.9, 179.0, 204.7. Anal. Calcd for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25. Found: C, 59.17; H, 8.20.

1-Ethyl (±)-2-butyl-3-oxoheptanedioate (7e): yield 2.01 g (52%); colorless liquid; ^{1}H NMR δ 0.85 (3 H, t, *J* = 7 Hz), 1.08–1.49 (7 H, m), 1.66–1.98 (4 H, m), 2.13–2.71 (4 H, m), 3.36 (1 H, t, *J* = 7 Hz), 4.13 (2 H, q, *J* = 7 Hz); ^{13}C NMR δ 13.8, 14.1, 18.4, 22.5, 28.0, 29.6, 32.8, 40.6, 59.3, 61.5, 170.2, 179.4, 205.1. Anal. Calcd for $C_{13}H_{22}O_5$: C, 60.45; H, 8.59. Found: C, 59.97; H, 8.64.

1-Ethyl (±)-2-hexyl-3-oxoheptanedioate (7f): yield 2.23 g (52%); colorless liquid; ^{1}H NMR δ 0.82 (3 H, t, *J* = 7 Hz), 1.18 (3 H, t, *J* = 7 Hz), 1.48–2.64 (16 H, m), 3.18 (1 H, t, *J* = 7 Hz), 4.08 (2 H, q, *J* = 7 Hz); ^{13}C NMR δ 14.1, 18.5, 20.7, 22.6, 27.5, 28.3, 29.1, 31.6, 32.8, 40.6, 59.1, 61.4, 170.0, 178.7, 204.8. Anal. Calcd for $C_{15}H_{26}O_5$: C, 62.91; H, 9.15. Found: C, 62.91; H, 9.37.

Typical Procedure for the Synthesis of a 4-Oxoalkanoic Acid (on a Larger Scale). 4-Oxohexanoic Acid.[14] The bromo ester **3b** (36.20 g, 0.2 mol), succinic anhydride (1, 15.01 g, 0.15 mol), and tetrabutylammonium bromide (1.61 g, 0.005 mol) were dissolved in DMF (50 mL) and electrolyzed at an external voltage of 50 V. When the reaction temperature reached 60 °C the external voltage was reduced to about 30 V to maintain the temperature between 50 and 60 °C. The electrolysis was stopped as the temperature dropped below 50 °C. The loss of weight of the zinc anode amounted to 13.6 g (0.21 mol). The reaction mixture was poured onto ice (300 g) and 10% aqueous HCl (200 mL) and then extracted with EtOAc (6 × 100 mL). The extract was concentrated under reduced pressure. The residue was refluxed with concentrated HCl (60 mL) and water (60 mL) for 1.5 h. Then the solvent was distilled off. Traces of water were azeotropically removed with toluene. The residue was purified by distillation yielding 4-oxohexanoic acid (10.7 g, 55%) as a colorless crystalline solid: bp 147–150 °C (11 Torr); mp 36–38 °C (lit.[16] mp 37–38 °C).

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Registry No. 1, 108-30-5; 2, 108-55-4; **3a**, 600-00-0; (±)-**3b**, 41978-69-2; (±)-**3c**, 66025-42-1; (±)-**3d**, 79584-43-3; (±)-**3e**, 63927-44-6; (±)-**3f**, 138286-76-7; **6a**, 69527-64-6; (±)-**6b**, 141090-15-5; (±)-**6c**, 141090-16-6; (±)-**6d**, 141090-17-7; (±)-**6e**, 141090-18-8; (±)-**6f**, 141090-19-9; **7a**, 69527-63-5; (±)-**7b**, 141090-20-2; (±)-**7c**, 141090-21-3; (±)-**7d**, 141090-22-4; (±)-**7e**, 141090-23-5; (±)-**7f**, 141090-24-6; Zn, 7440-66-6; $CH_3CH_2C(O)(CH_2)_2CO_2H$, 1117-74-4.

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Synthesis of 1-Propyl-3-(3-hydroxyphenyl)piperidine by Regiocontrolled Palladium-Catalyzed Arylation

Kristina Nilsson and Anders Hallberg*

Department of Organic Pharmaceutical Chemistry, Uppsala Biomedical Center, Uppsala University, Box 574, S-751 23 Uppsala, Sweden

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Dopamine autoreceptor agonists reduce the dopaminergic neurotransmission and are theoretical alternatives to the postsynaptic dopamine D2 antagonists, commonly used in the pharmacotherapy of schizophrenia.[1] Preclamol, (−)-3-PPP, the first example of a dopamine autoreceptor agonist,[2] suppresses neuroleptic induced abnormal

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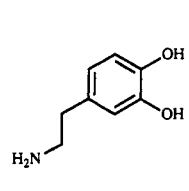
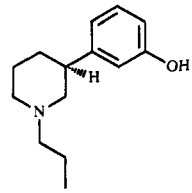
0022-3263/92/1957-4015$03.00/0

movements in monkeys without inducing parkinsonism.[3] The drug is now in clinical trials.



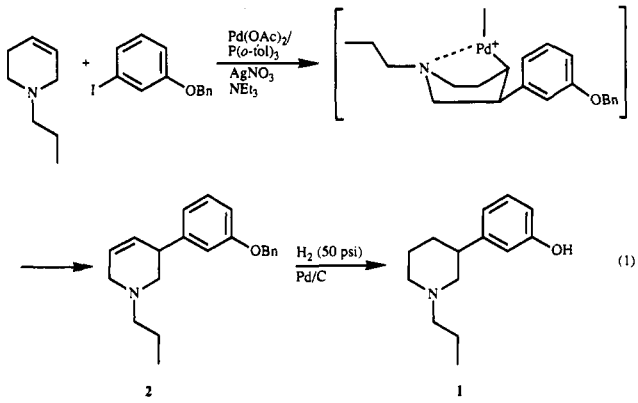
Dopamine



Preclamol [(-)-3-PPP]

We report herein a synthesis of 3-PPP (1) based on a highly regioselective Heck reaction[4] catalyzed by palladium.

Arylation of 1-propyl-1,2,3,6-tetrahydropyridine with 3-(benzyloxy)iodobenzene in the presence of silver nitrate[5] in acetonitrile, gave 1-propyl-3-(3-(benzyloxy)phenyl)-1,2,3,6-tetrahydropyridine (2). Palladium acetate/tri-o-tolylphosphine was used as catalyst with triethylamine as base. After hydrogenation of 2, racemic 3-PPP (1) was isolated in 40% yield, based on the aryl iodide (eq 1).

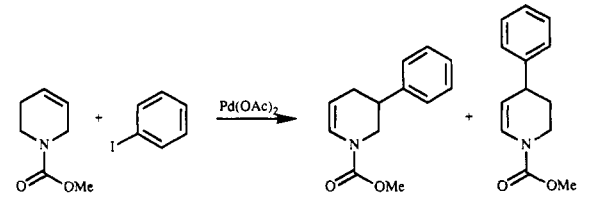


(1)

(Benzyloxy)benzene (GC 22%) was also formed in addition to 2 (GC 73%) in the coupling reaction. A saturated isomer of 2 was detected by GC/MS analysis and found to be less than 5% of the mixture. Subjecting 3-hydroxyiodobenzene to the same reaction conditions provided a low isolated yield of coupled product (28%) and a considerable amount of 3,3'-dihydroxybiphenyl.

Palladium-catalyzed arylation of aminoalkyl vinyl ethers can be achieved with high regioselectivity via nitrogen-chelation control.[6] We assume, in analogy, that the high preference for 3-arylation (3-aryl/4-aryl > 14) in the reaction with the cyclic allylamine is due to the formation of a stabilized 5-membered σ-palladium adduct.[7] Irreversible elimination of an HPd-species forms an intermediate π-complex that finally provides 2. In the absence of silver additives the yield of 2 is low, with high molecular weight compounds being formed. Silver salts suppress double-bond migration,[5c-i] and consequently the formation of reactive enamines is avoided.

We previously reported that α-arylation was achieved exclusively with cyclic enamides.[8] Arylation of an allylic carbamate,[9] in the absence or in the presence of silver nitrate, resulted in low regioselectivity (eq 2), suggesting that the amine nitrogen is important for the high selectivity observed with 1-propyl-1,2,3,6-tetrahydropyridine.



(2)

3 : 2

We believe that the regioselective arylation method presented here may also be useful for the preparation of other 3-aryl-substituted cyclic allylamines. Although this method requires silver additives, the simplicity of the experimental procedure merits attention.

Experimental Section

General. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 300 and 75.4 MHz, respectively, with a Varian XL 300 spectrometer. Chemical shifts are reported as δ values (ppm) relative to internal tetramethylsilane. Low- and high-resolution mass spectra were obtained on Finnigan 4021 (Data System Incos 2100) and JEOL JMS-X102 mass spectrometers, operating at an ionization potential of 70 eV. Quantitative gas chromatographic analyses were carried out on a Varian 3300 instrument equipped with a (2-m × 2-mm) glass column of 5% OV 17 on Chromosorb W. A Varian 3700 instrument was used for capillary gas chromatography on a DB 1701 (30-m × 0.32-mm) column. GC yields were determined using 2,3-dimethylnaphthalene as internal standard. HPLC separations were performed with a LDC Consta Metric III system equipped with a RI detector (LKB 2142 refractive index detector). For flash chromatography TLC silica gel 60 H (15 μm, E. Merck, No. 11695) was used. Elemental analyses were obtained from Mikro Kemi AB, Uppsala, Sweden. The coupling experiments were carried out in a 50-mL, heavy-walled and thin-necked Pyrex tube, sealed with a screw-cap fitted with a Teflon gasket.

Materials. Triethylamine was distilled from potassium hydroxide; other commercially available chemicals were used without further purification. Solvents for reactions and flash chromatography were distilled and stored over appropriate molecular sieves. 1-Propyl-1,2,3,6-tetrahydropyridine was prepared following a literature procedure.[10]

Procedure for the Arylation of 1-Propyl-1,2,3,6-tetra-

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hydropyridine. Each of the reactants was dissolved or dispersed in acetonitrile (a total of 10 mL) and was added to the reaction vessel in the following order: palladium acetate (0.11 g, 0.50 mmol) in 1 mL of acetonitrile, tri-*o*-tolylphosphine (0.61 g, 2.0 mmol) in 1 mL of acetonitrile, 3-(benzyloxy)iodobenzene or 3-hydroxyiodobenzene (10 mmol) in 4 mL of acetonitrile, silver nitrate (1.7 g, 10 mmol) in 2 mL of acetonitrile, triethylamine (2.0 g, 20 mmol) in 1 mL of acetonitrile, and 1-propyl-1,2,3,6-tetrahydropyridine (5.0 g, 40 mmol) in 1 mL of acetonitrile. The reaction mixture was magnetically stirred and heated at 100 °C for 4 h. The reaction was allowed to cool and thereafter dispersed in diethyl ether. The tarry mixture was filtered by suction, and the ethereal solution was extracted with 0.5 M HCl. The combined water phases were neutralized (2 M NaOH) and extracted with diethyl ether. The organic portions were dried (Na_2SO_4) and evaporated thoroughly. The excess of 1-propyl-1,2,3,6-tetrahydropyridine was removed by Kugelrohr distillation (40 °C (1.3 mmHg)). The residual oil was submitted to flash chromatography. Dichloromethane/methanol (95/5) was used as eluent for purification of **2** and dichloromethane/methanol (90/10) for purification of 1-propyl-3-(3-hydroxyphenyl)-1,2,3,6-tetrahydropyridine. The crude product was dissolved in dichloromethane and evaporated on coarse gel before application to the column. A 2-fold excess of 1-propyl-1,2,3,6-tetrahydropyridine resulted in lower yields.

1-Propyl-3-(3-(benzyloxy)phenyl)-1,2,3,6-tetrahydropyridine (2): yellow oil 1.37 g (43%); ^{1}H NMR δ 0.90 (t, 3 H, $NCH_2CH_2CH_3$, J = 7.3 Hz), 1.55 (sext, 2 H, $NCH_2CH_2CH_3$), 2.24 (dd, 1 H, NCH_2CHAr, J = 11.2 and 8.9 Hz), 2.38 (m, 2 H, $NCH_2CH_2CH_3$), 2.85 (m, 1 H, NCH_2CH=), 3.00 (dd, 1 H, NCH_2CHAr, J = 11.2 and 5.4 Hz), 3.23 (m, 1 H, NCH_2CH=), 3.62 (m, 1 H, CHAr), 5.05 (s, 2 H), 5.77 (m 1 H, NCH_2CH=CH), 5.86 (m, 1 H, NCH_2CH=), 6.80–7.28 (m, 4 H), 7.30–7.48 (m, 5 H); MS m/z (relative intensity) 307 (M^+, 27), 278 (16), 236 (29), 210 (12), 145 (41), 122 (10), 117 (21), 91 (100), 80 (18), 77 (10); HRMS (m/z) for $C_{21}H_{25}NO$ calcd 307.1936, found 307.1927.

Anal. Calcd for $C_{21}H_{25}NO$: C, 82.04; H, 8.20; N, 4.56. Found: C, 81.9; H, 8.4; N, 4.5.

GC yields before workup were 73% of **2**, <5% of a saturated isomer of **2**, and 22% of (benzyloxy)benzene.

1-Propyl-3-(3-hydroxyphenyl)-1,2,3,6-tetrahydropyridine: yellow oil 0.61 g (28%); mp (oxalate) 189–190 °C (methanol/diethyl ether); ^{1}H NMR (liberated amine) δ 0.89 (t, 3 H, $NCH_2CH_2CH_3$, J = 7.3 Hz), 1.58 (sext, 2 H, $NCH_2CH_2CH_3$), 2.27 (dd, 1 H, NCH_2CHAr, J = 11.4 and 9.9 Hz), 2.44 (m, 2 H, $NCH_2CH_2CH_3$), 2.88 (m, 1 H, NCH_2CH=), 3.10 (dd, 1 H, NCH_2CHAr, J = 11.4 and 5.6 Hz), 3.34 (br d, 1 H, NCH_2CH=, J = 17.3 Hz), 3.66 (m, 1 H, CHAr), 5.75–5.90 (m, 2 H, CH=), 6.64–7.20 (m, 4 H), 7.63 (v br s, 1 H, OH); MS m/z (relative intensity) 217 (M^+, 27), 188 (17), 146 (100), 131 (23), 117 (16), 72 (33).

Anal. Calcd for $C_{30}H_{40}N_2O_6$ (oxalate): C, 68.68; H, 7.68; N, 5.34. Found: C, 68.3; H, 7.8; N, 5.3.

1-Propyl-3-(3-hydroxyphenyl)piperidine (1). A mixture of **2** (0.41 g, 1.3 mmol), 5% Pd/C (0.28 g, 0.13 mmol Pd), and absolute ethanol (25 mL) was placed in a Parr shaking apparatus. The reaction was pressurized with H_2 to 50 psi and shaken vigorously at room temperature for 10 h. The catalyst was removed by filtration through Celite, and the solvent was evaporated. The reaction yielded 0.26 g (93%: total yield, 40% based on 3-(benzyloxy)iodobenzene) of the title compound **1** (100% pure according to GC analysis). Compound **1** exhibited spectroscopic data in agreement with the literature.[11]

1-(Methoxycarbonyl)-1,2,3,6-tetrahydropyridine. To a solution of 1,2,3,6-tetrahydropyridine (Aldrich; 25 g, 0.30 mmol), triethylamine (84 mL, 0.60 mmol), and dichloromethane (300 mL) was added methyl chloroformate (24 mL, 0.31 mmol) dropwise with stirring. After 3 h, the reaction was evaporated to dryness and the resulting semisolid mass was extracted with diethyl ether. The solvent was removed, and the crude product was distilled to give 1-(methoxycarbonyl)-1,2,3,6-tetrahydropyridine (36 g, 86%) as a colorless liquid, which exhibited ^{1}H NMR data in agreement with the literature.[12]

(11) Loozen, H. J. J.; Brands, F. T. L. *Rec. Trav. Chim. Pays-Bas* **1981**, *100*, 333.
(12) Avasthi, K.; Knaus, E. E. *Can. J. Pharm. Sci.* **1981**, *16*, 52.

Phenylation of 1-(Methoxycarbonyl)-1,2,3,6-tetrahydropyridine. A mixture of palladium acetate (0.11 g, 0.50 mmol), triethylamine (2.0 g, 20 mmol), iodobenzene (2.0 g, 10 mmol), 1-(methoxycarbonyl)-1,2,3,6-tetrahydropyridine (5.6 g, 40 mmol), and DMSO (8 mL) was stirred until homogenous and heated at 100 °C for 4 h. The cooled reaction mixture was diluted with diethyl ether, filtered, and washed with water. The aqueous layer was extracted with diethyl ether, and the combined organic phases were washed once with water, dried ($MgSO_4$), and evaporated. The excess of 1-(methoxycarbonyl)-1,2,3,6-tetrahydropyridine was thereupon removed by distillation (82–84 °C (9mmHg)). The resulting material was subjected to flash chromatography using pentane/diethyl ether (3/1) as eluent. The crude product was dissolved in diethyl ether and evaporated on coarse gel before application to the column. A yield of 1.56 g (72%) of a mixture of two regioisomers, in a ratio of 3:2, was obtained. The two isomers were separated by HPLC (a nucleosil silica gel column, 500 × 10 i.d., and eluation with heptane/ethyl acetate (95/5)).

Reactions in the presence of tri-*o*-tolylphosphine and silver nitrate resulted in a similar regioisomeric ratio but in a slower conversion. Structural assignment of the two isomers was confirmed by COSY, DEPT, and ^{13}C–^{1}H HETCOR experiments.

1-(Methoxycarbonyl)-3-phenyl-1,2,3,4-tetrahydropyridine: colorless crystals; mp 47–49 °C; ^{1}H NMR δ 2.30 (m, 2 H, $=CCH_2CHPh$), 2.99 (m, 1 H, CHPh), 3.16–3.32 (m, 1 H, NCH_2), 3.74, 3.78 (s, 3 H, CO_2CH_3), 4.10, 4.25 (br d, 1 H, NCH_2, J = 12.0 Hz), 5.01, 5.10 (m, 1 H, NCH=C*H*), 6.85, 6.99 (d, 1 H, N*CH*=CH, J = 8.1 Hz), 7.19–7.39 (m, 5 H); ^{13}C NMR δ 29.28 (CH_2), 38.52 (CH), 47.60, 47.93 (CH_2), 52.96 (CH_3), 106.10, 106.30 (CH), 124.87, 125.32 (CH), 126.88, 127.18, 127.34, 128.47 (CH), 142.91 (C), 153.76 (C); MS m/z (relative intensity) 217 (M^+, 20), 104 (100), 91 (15).

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.7; H, 6.8; N, 6.5.

1-(Methoxycarbonyl)-4-phenyl-1,2,3,4-tetrahydropyridine: colorless oil; ^{1}H NMR δ 1.82 (m, 1 H, NCH_2CH_2CHPh), 2.14 (m, 1 H, NCH_2CH_2CHPh), 3.51 (m, 1 H, CHPh), 3.55–3.76 (m, 2 H, NCH_2), 3.79 (s, 3 H, CO_2CH_3), 4.93, 5.03 (m, 1 H, NCH=C*H*), 6.96, 7.10 (d, 1 H, N*CH*=CH, J = 8.2 Hz), 7.19–7.36 (m, 5 H); ^{13}C NMR δ 31.07 (CH_2), 38.11 (CH), 40.36 (CH_2), 53.04 (CH_3), 108.88, 109.08 (CH), 125.62, 125.99 (CH), 127.65, 128.31, 128.46, 128.56 (CH); MS m/z (relative intensity) 217 (M^+, 49), 202 (100), 158 (19), 140 (20), 130 (25), 115 (38), 103 (15), 91 (34), 77 (18); HRMS (m/z) for $C_{13}H_{15}NO_2$ calcd 217.1103, found 217.1104.

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 70.6; H, 6.9; N, 6.5.

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Registry No. **1**, 83228-38-0; **2**, 141090-48-4; 3-(benzyloxy)iodobenzene, 107623-21-2; 3-hydroxyiodobenzene, 626-02-8; 1-propyl-1,2,3,6-tetrahydropyridine, 53385-78-7; 1-propyl-3-(3-hydroxyphenyl)-1,2,3,6-tetrahydropyridine, 141090-47-3; 1,2,3,6-tetrahydropyridine, 694-05-3; methyl chloroformate, 79-22-1; 1-(methoxycarbonyl)-1,2,3,6-tetrahydropyridine, 75250-59-8; 1-(methoxycarbonyl)-3-phenyl-1,2,3,4-tetrahydropyridine, 141090-49-5; 1-(methoxycarbonyl)-4-phenyl-1,2,3,4-tetrahydropyridine, 141090-50-8.

(*E*)-β,γ-Unsaturated Esters from 9-Alkenyl-9-BBN and Ethyl (Dimethylsulfuranylidene)acetate

Min-Zhi Deng,* Nan-Sheng Li, and Yao-Zeng Huang*

Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai 200032, China

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Introduction

β,γ-Unsaturated esters and lactones, which are important functionalities in naturally occurring compounds,[1] can

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