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A SHORT AND VERSATILE SYNTHESIS OF 3-SUBSTITUTED 2-AMINOQUINOLINES

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Abstract:

A short and versatile synthesis of a series of 3-substituted -2-aminoquinolines was accomplished in good yields starting from 2-nitrobenzaldehide. Organic phosphonates were used as key synthetic intermediates and in some cases aminoacids as readily available starting materials. The finals two key steps of the sequence involving a reduction and ring closure that led to the 2-aminoquinoline skeleton were carried out in a "one pot" procedure using $SnCl_2.2H_2O$.

2-Aminoquinolines derivatives have attracted a high concern due their biological properties[1]. For instance simple molecules as 2-aminoquinoline has been isolated from a North American mushroom known for its antibacterial and antihelmintic activity[2]. Reports on the antihypertensive[3a], antiprotozoal[3b] and antidepressant[4] properties of 2-aminoquinolines analogs have been also documented. In most of the reported methods[5-8] for the synthesis of 2-aminoquinolines derivatives is common the use of strong basic solvents as well as severe thermal conditions .

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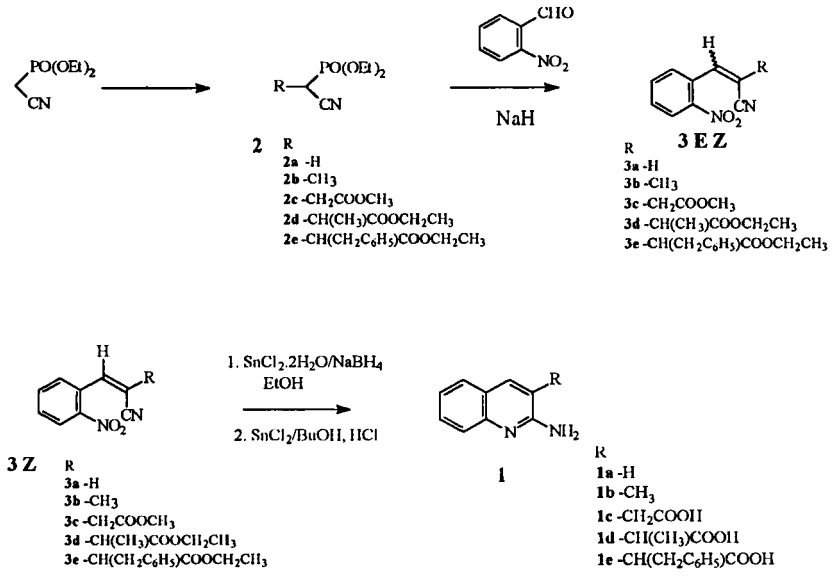
Some of the syntheses of 2-aminoquinolines derivatives, involve: nucleophilic substitution on the previously formed chloroquinoline under strong basic conditions[5], Frielander,s approach[6], reductive cyclizations[7] and basic condensations of aromatic ketones with N,N (dimethylamino) propionitrile [8]. In this paper we report a short and efficient synthesis of 3-substituted 2-aminoquinolines using as key step a "one pot" reductive cyclization procedure under mild acidic conditions. Our synthetic strategy, outlined in scheme 1, was based on the use of organic phosphonate as key intermediates prepared from readily available starting materials.

SCHEME 1



Diethylcyanomethylphosphonate was conveniently alkylated as a way to introduce a substituent in the 3 position for the future 2-aminoquinoline ring. In two case we used, as substituents in the 3 position, groups originated from α-bromoester which can be readily prepared from the corresponding aminoacids according to a previous reported procedure[9]

This could describe a symple to introduce a chiral center in this carbon . Horner-Wadsworth-Emmons reaction of phosphonates **2** with 2-nitrobenzalhedyde resulted in the expected E/Z olefin mixture **3** in good yields. A reductive cyclization of nitrocyano olefins **3** accompanied with ester hydrolisis, to the corresponding 3-substituted-2-aminoquinoline **1** was carried out in a "one pot" procedure in reasonable yields. The reduction of the nitro group was achieved using $NaBH_4$ and $SnCl_2.2H_2O$ in refluxing ethanol. After the reduction was completed the ethanol was evaporated and a higher boiling point solvent as butanol was added along with catalytic amounts of acid[10] to promote the cyclization This "one pot" step represents a direct way to selectively reduce a nitro group in the presence of other funtionalities and to promote the nucleophilic addition of the recently formed amino group to the cyano.The use of anhydrous instead of dihydrated stanous chloride resulted in poor yields of the 2-aminoquinoline derivatives. Apparently the presence of water in $SnCl_2$ is important for the appropiate complex configuration and geometry for ther reduction step[11]. The remaining **3E** olefin can be readily isomerized photochemically to the olefin **3Z** using a 100 watt hanovia lamp in methanol

In summary, this method ilustrates a short, versatile and attractive route to 3-susbstituted-2-aminoquinoline heterocycle moiety.

Experimental Section

General : Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. 1,2 Dimethoxyethane (glyme) was distilled from sodium-benzophenone immediately prior to use. All reactions involving carbanion formation were conducted under N_2 atmosphere. Evaporation of solvents was accomplished with a rotary evaporator. Melting points are uncorrected. Mass spectra were recorded on a HP800 spectrometer. ^1H and ^{13}C NMR spectra were determined in a JEOL Eclipse-270 MHz

spectrometer as $CDCl_3$ solutions, unless otherwise indicated. J values are in Hertz. Chemical shifts are expressed in ppm downfield from internal tetramethylsilane.

(R,S)-1-Methyl-1-cyano-diethylphosphonate (2b)

The diethylcyanomethylphosphonate (1.0g, 5.64 mmol) was added dropwise to a cooled (0 ^{0}C) suspension of (60%) NaH (0.226g, 5.64 mmol) in glyme (25 mL) . After stirring for 45 min, methyl iodide (0.8g, 5.64 mmol) was added dropwise. After 30 min at 0 ^{0}C, the mixture was subsequently stirred for 15 h at rt. under nitrogen atmosphere. Evaporation of the solvent gave a syrup that was dissolved in water (15 mL) .This aqueous solution was extracted with ethyl acetate. The organic extract was dried (Na_2SO_4), filtered, and evaporated to give a brown oil which was chromatographed using flash technique with silica gel and chloroform. This procedure gave the alkylated phosphonate **2b** in 76 % yield. NMR ^{1}H ($CDCl_3$) δ :1.32 (6H, t, J = 7.1 Hz), 1.57 (3H, d, J = 7.9 Hz), 4.10 (1H, m) , 4.22 (4H, q, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ : 12.6, 16.4(x2), 22.6-24.8 (d,J= 147 Hz), 64.0(x2), 117.2; IR: 3040; 2210; 1600, 1510; 1340; 965; 740; 695; 670 cm^{-1}; m/z = 192.

(R,S) Methyl-3-Cyano-3-(diethylphosphono) propanoate (2c)

Diethylcyanomethylphosphonate (1.0 g, 5.64 mmol) was added dropwise to a suspension of NaH (0.266 g, 5.64 mmol) in glyme (20 mL) at 0 ^{0} C. The mixture was stirred by 1 h at rt. and cooled again. Methylbromoacetate (0.86g, 5.64 mmol) was added and the resulting solution stirred under N_2 atmosphere for 16 h . The solvent was evaporated in vacuo and the residue chromatographed on silica gel and $CHCl_3$ to afford **2c** (0.98 g, 74% yield).

^{1}H NMR ($CDCl_3$) δ : 1.31 (6H, t, 7.1 Hz), 2,08- 3.07 (2H, m), 3.37 (1H, dq), 3.72 (3H, d), 4.20 (4 H, m); ^{13}C NMR ($CDCl_3$) δ : 16.4, 25.0-27.1, 32.5-35.2, 52.7, 65.2, 115.7, 168.8; IR: 3045, 2200, 1650, 965, 750 cm^{-1}; m/z = 249.

(R,S)-Ethyl-3-cyano-3-(diethylphosphono)-2-methyl propanoate (2d)

To a stirred suspension of (60%) NaH (1.2 g , 50.0 mmol) in glyme (40 mL) under N_2 atmosphere was added diethylcyanomethylphosphonate (5.1 g , 29 mmol) as above. After 1 h the solution was cooled and ethyl (R,S)-2-bromopropanoate (5.04 g, 28.0 mmol) dissolved in glyme (5 mL) added. After being warmed to rt., the mixture was stirred for 20 h . The solution was diluted with water (15 mL) and extracted with EtOAc (3 x 50 mL). The organic phase was dried over $MgSO_4$ and concentrated in vacuo , and the residue was purified by column chromatography (silica gel, EtOAc : $CHCl_3$ 6 : 4) to afford 5.40 g (64 %) of **2d** as a yellow oil.

^1H NMR ($CDCl_3$) δ : 1.17 -1.34(9H, m), 1.45 (3H, d), 2.98 - 3.04(1H, m), 3.63 -3.70(1H, m), 4.15 - 4.25(6H, m); ^{13}C NMR ($CDCl_3$) δ: 14.1, 16.3, 16.4, 18.3, 31.4 - 31.9(d, J = 34.5 Hz), 33.5 - 34.0(d, J = 34.5 Hz), 37.3, 58.4, 61.9, 64.3, 114.4, 172.6; IR: 3000; 2250; 1730; 1450; 1150; 950; 720 cm^{-1}; m/z = 277

(R,S)-Ethyl-3-cyano-3-(diethylphosphono)-2-benzyl propanoate (2e)

Diethylcyanomethylphosphonate (1.72g, 9.8 mmol) dissolved in 2 mL of glyme was added to a suspension of (60 %) NaH (0.43g, 11.0 mmol) in glyme (50 mL), and the mixture was stirred from 0 ^0C to rt. After 1h the solution was cooled and ethyl (R,S)-2-bromo-3-phenyl propanoate (2.5g, 9.8 mmol) dissolved in glyme (5 mL) was added . The solution was stirred at rt., for 20h and then treated with H_2O (10 mL) and extracted with EtOAc (3 x 50 mL) The organic layer was dried with $MgSO_4$, evaporated in vacuo and chromatographed (silica gel EtOAc : $CHCl_3$ 6 : 4) to give **2e** as an orange oil (2.97 g 78 % yield).

^1H NMR ($CDCl_3$) δ : 1.27 - 1.34(9H, m), 2.97 - 3.21(2H, m), 4.10 - 4.20(6H, m), 7.23 - 7.40(5H, m); ^{13}C NMR ($CDCl_3$) δ: 16.1, 16.2, 16.3, 37.2, 44.0, 61.5, 63.8, 64.2, 114.8,

127.1, 127.4, 128.5, 129.0, 129.1, 136.5, 171.3; IR:3000, 2900, 2240, 1730, 1620, 1400, 1150, 1070 cm^{-1}; m/z =353.

1-Cyano-2-(-2'-nitrophenyl)ethene (3a) General Procedure

Diethylcyanomethylphosphonate (2.05 g, 12.0 mmol) dissolved in 3 mL of glyme was added dropwise over 30 min to a stirred suspension of (60%) NaH (0.51 g, 13 mmol) in 20 mL of glyme at 0 C. The mixture was allowed to warm up to rt, stirred for 1h, and then cooled again to 0 C. A solution of (1.80g, 12 mmol) of 2-nitrobenzaldehyde in glyme (5 mL) was added dropwise in 15 min. The solution was stirred for another 45 min at 0 °C and 30 min at rt. The mixture was quenched by addition of 5% $NaHSO_3$ (20 mL) and extracted with EtOAc (3 x 20 mL) . The combined organic extracts were dried with $MgSO_4$ and evaporated under vacuo. A 2:1 **Z,E** olefin mixture was obtained in 92 % yield after column chromatography with silica gel eluting with a 4:5:1mixture of $CHCl_3$ heptan ether

3a-Z: White solid mp = 82 - 83 °C; ^1H NMR ($CDCl_3$) δ : 5.70 (1H, d, J = 11.6 Hz), 7.62 (1H, dd, J= 6.4, 7.8 Hz), 7.71 (1H, d, J = 11.6 Hz), 7.76 (1H, dd, J = 6.9 Hz), 7.84 (1H, d, J = 6.4 Hz), 8.20 (1H, d, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ: 100.2, 115.9, 125.3, 129.6, 130.7 (x2), 131.1, 134.4, 146.7; m/z = 174.

3a-E: Yellow solid mp =90-91 C; ^1H NMR ($CDCl_3$) δ :5.84 (1H, J=16.3 Hz), 7.58 (1H, dd, J = 7.9, 1.5 Hz), 7.68 (1H, d, J= 7.9 Hz), 7.92 (1H, d, J=16.3 Hz), 8.09 (1H, dd, J= 7.9, 1.5 Hz); ^{13}C NMR ($CDCl_3$) δ: 101.6, 117.0, 125.7, 128.5, 131.1, 131.4(x2), 134.1, 147.2; m/z = 174.

(R,S)-2-Cyano-3-(2'-nitrophenyl) propene (3b)

Th reaction of **2b** and 2-nitrobenzaldehide was carried out according to the previuos procedure. Flash chromatography of the reaction crude on silica gel eluting with 5:4:1 chloroform:heptane:ether gave 70% of the **E/Z** olefin mixture.

^{1}H NMR ($CDCl_3$) δ : 2.20(3H, d, J = 1.4 Hz), 7.42 (1H, d, J = 1.2 Hz), 7.53 -7.76(3H, m), 8.13-8.20 (1H, dd, J = 0.9 Hz, 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ: 21.6, 114.4, 118.1, 125.1, 130.1, 130.3, 131.1, 132.1, 141.2, 147.2.; m/z = 188.

2-Cyano-3-(-2'-nitrophenyl)-2-methyl propenoate (3c)

The reaction of **2c** and 2-nitrobenzaldehyde was carried out exactly as described for the olefin **3a**. A mixture of **Z/E** olefins was obtained in 76% yield.

^{1}H NMR ($CDCl_3$) δ : 3.50(3H, s), 3.72-3.78 (2H, s), 7.57-7.73 (2H, m), 7.94 (1H, m), 8.20 (1H, d, J=8.1 Hz), 8.72 (1H, s); ^{13}C NMR ($CDCl_3$) δ: 23.6, 35.5, 52.4, 108.6, 116.9, 125.2, 127.9, 130.9, 131.2, 134.2, 144.6, 169.8; Anal. calc. for $C_{12}H_{10}N_2O_4$: C, 58.53; H, 4.06; N, 11.38. Found: C, 58.75; H, 4.21; N, 11.30.

(R,S)-2-Methy-3-cyano-4-(2'-nitrophenyl)-3-ethyl butenoate (3d)

The corresponding phosphonate **2d** was prepared as above to give **3d** in 69 % yield as an **E/Z** olefin mixture.

^{1}H NMR ($CDCl_3$) δ : 1.28(3H, t, J = 7.1 Hz), 1.39 (3H, d, J = 6.9 Hz), 3.34 (1H, q, J = 7.1 Hz), 4.19 (2H, q, J = 6.9 Hz), 7.38 (1H, d, J = 7.4 Hz), 7.57-7.76 (3H, m), 7.74-7.78 (2H, m), 8.22 (1H, d, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ: 14.0, 16.0, 39.9, 61.9, 116.6, 117.2, 125.5, 129.1, 130.5, 130.7, 134.2, 142.8, 147.0, 171.0; Anal. calc. for $C_{14}H_{14}N_2O_4$: C, 61.31; H, 5.11; N, 10.22. Found: C, 61.36; H, 5.30; N, 10.20.

(R,S)-2-Benzyl-3-cyano-4-(2'-nitrophenyl)-3-ethyl butenoate (3e)

Prepared by the specified general procedure in 76% overall yield

^{1} H NMR ($CDCl_3$) δ : 1.26(3H, t, J = 7.1 Hz), 3.03(1H, d, J = 2.9Hz), 3.20(1H, m), 3.36(1H, m), 4.20(1H, m), 6.60(1H, m), 7.03(1H, m), 7.19-7.40(4H, m), 7.49-7.56 (2H, m), 7.63 (1H, brs), 8.08-8.15 (1H, m);^{13}C NMR ($CDCl_3$) δ: 14.2, 36.1, 47.7, 61.9, 114.3,

117.2, 125.2, 127.2, 128.2, 128.7, 128.8, 129.0, 130.3, 130.6, 133.8, 136.9, 134.2, 145.1, 146.6, 170.3; Anal. cal. for $C_{20}H_{18}N_2O_4$: C, 68.57; H, 5.14; N, 8.00. Found: C, 68.60; H, 5.25; N, 7.93.

2-Aminoquinoline (1a) General Procedure

A E/Z mixture of **3a** (0.206 g , 1.22 mmol) and $SnCl_2.2\ H_2O$ (1.564 g, 6.96 mmol) suspended in ethanol (30 mL) in a Morton flask was stirred and refluxed for 30 min. After cooling the mixture to rt , a suspension of $NaBH_4$ (0.11g, 2.92 mmol) in ethanol (30 mL) was poured into slowly. When the addition was complete heating was continued until TLC indicated complete consumption of the starting material. The solvent was evaporated to dryness and the residue was suspended in n-butanol (30 mL). Concentrated HCl (0.5 mL) was added and this solution refluxed for 6h. The solvent was evaporated and the residue was treated with saturated $NaHCO_3$ (20 mL). The aqueous solution was extracted with EtOAc (5x25 mL). The organic phase was dried with Na_2SO_4 and evaporated in vacuo to afford a crude which was purified by flash chromatography with silica gel eluting with 8:2 $CHCl_3$:MeOH to give a white solid (63%) mp : 127-129 °C (lit[2] 128-130 °C)

^1H NMR ($CDCl_3$) δ :5.02 (2H, brs), 6.68 (1H, d, J = 8.9 Hz), 7.23 (1H, ddd, J = 8.0, 6.4, 1.2 Hz), 7.52 (1H, ddd, J= 8.4, 6.9, 1.5 Hz), 7.58 (1H, d, 8.4 Hz), 7.64 (1H, d, J= 8.4 Hz), 7.83 (1H, d, J = 8.9 Hz); ^{13}C NMR ($CDCl_3$) δ: 111.8, 122.7, 123.6, 125.8, 127.6, 129.8, 138.2, 147.6,157.2; IR: 3450; 3360; 3230; 3000; 1450; 1250 cm^{-1}; m/z 144

3-Methyl-2-aminoquinoline (1b)

1b was prepared according to the previous procedure to give a brown oil. Purification by flash chromatography on silica gel with $CHCl_3$/MeOH 9:1 gave **1b** in 58% yield as a light yellow oil that crystallized on standing mp : 155-156 °C (lit[5] 157-159 °C)

^{1}H NMR ($CDCl_3$) δ : 2.36(3H, s), 5.14(1H, brs), 6.24(1H, brs), 7.24-7.29 (1H, m), 7.49-7.57 (2H, m), 7.66-7.73 (2H, m); ^{13}C NMR ($CDCl_3$) δ : 18.5, 120.1, 122.6, 123.3, 123.6, 127.0, 129.9, 138.2, 142.4, 156.0; IR : 3360, 3344, 1670, 1625, 1561, 1497, 1430, 1008; m/z = 158

3-(Methyl carboxyl)-2-aminoquinoline (1c)

Yield 51% , mp = 215 - 216 °C

^{1}H NMR ($CDCl_3$) δ : 3.14(2H, s), 7.07(1H, d, J=8.1 Hz), 7.23(1H, ddd, J = 8.0, 7.1, 1.2 Hz), 7.45(1H, ddd, J= 8.1, 6.8, 1.7 Hz), 7.36(1H, d, J=8.0 Hz), 7.47 (1H, s) 8.35(1H, brs); ^{13}C NMR ($CDCl_3$) δ: 37.0, 106.3, 118.5, 122.0, 124.8, 125.8, 131.2, 131.5, 136.3, 143.8, 169.5 ; IR: 3744, 2352, 1670, 1644 cm^{-1}; Anal calc. for $C_{11}H_{10}N_2O_2$: C, 65.34; H, 4.95; N, 13.86. Found: C, 65.22; H, 4.86; N, 13.97.

3-(-2'-Propyl carboxyl)-2-aminoquinoline (1d)

Yield 53 % , mp = 248 - 249 °C

^{1}H NMR ($CDCl_3$) δ :1.54(3H, d, J= 7.1 Hz), 2.75(1H, dq, J = 7.1, 1.5 Hz), 7.12 (1H, d, J= 8 Hz) 7.23 (1H, ddd, J= 8.0, 7.4, 1.2 Hz), 7.45 (1H, ddd, J= 8.1, 7.3, 1.4 Hz), 7.37 (1H, d, 8.0 Hz), 7.48 (1H,d, J= 1.5 Hz); ^{13}C NMR ($CDCl_3$) δ: 12.4, 37.2, 112.8, 116.2, 122.0, 124.7, 126.2, 130.8, 131.5, 136.5, 142.9, 171.9 ; IR: 3468; 3314; 3177; 3077; 3056; 3000; 1709; 1613; 1403; 758 cm^{-1}; Anal. calc. for $C_{12}H_{12}N_2O_2$: C, 66.67; H, 5.55; N, 12.96. Found: C, 66.41; H, 5.42; N, 13.16.

3-(3'-Phenyl-2-carboxypropyl)-2-aminoquinoline (1e)

Yield 40%, mp = 212 - 214 °C

^{1}H NMR ($CDCl_3$) δ : 3.02 (1H, t, J= 7.2 Hz), 3.17 (1H, dd, J=14.1, 7.0 Hz), 3.49(1H, dd, J

= 14.1, 7.5 Hz), 7.09 (1H, d, J = 8.1 Hz), 7.15-7.48 (5H, m), 7.24 (1H, m), 7.38 (1H, d , 8.1 Hz), 7.47 (1H, ddd, J = 8.1, 6.7, 1.5 Hz), 7.49 (1H, s), 9.05 (1H, bs); ^{13}C NMR ($CDCl_3$) δ : 32.9, 45.4, 111.4, 117.2, 122.1, 124.8, 126.0, 126.8, 128.6(x2), 129.3(x2), 130.9, 131.6, 136.4, 137.8, 143.4, 170.1; IR: 3451; 3322; 3089; 3032; 2967; 2870; 1725; 1632; 1500; 1290; 775; 662 cm^{-1}; Anal. calc. for $C_{18}H_{16}N_2O_2$: C, 73.97, H, 5.48, N, 9.59. Found: C, 74.14; H, 5.57; N, 9.43.

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