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Research Paper

An efficient synthesis of new (2-chloroqunoline-3-yl)methyl diethyl phosphate

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Abstract: A simple and high yielding method was developed for the synthesis of new (2-chloroquinoline-3-yl)methyl diethyl phosphate from (2-chloroquinoline-3-yl)methanol derivatives, obtained from 2-chloroquinoline-3-carbaldehydes, by using *O,O*-diethyl chlorophosphate in the presence of sodium hydroxide and methylene chloride as the solvent at room temperature. This method developed for the synthesis of (2-chloroquinoline-3-yl)methyl diethyl phosphate gave excellent yields.

Introduction

Quinolines [1] are an important class of heterocyclic compounds and have been screened for biological activities such as bactericidal, [2] antitumor, [3] anti-inflammatory, [4] antimalarial [5] activities. Quinolines such as 2-chloroquinoline-3-carbaldehyde occupy a prominent position as they are key intermediates for further annelation and for various functional group interconversions.[6] Quinolines have been associated with broad spectrum of biological activities [7].

It is also reported that organophosphates are potent pesticides which have wide variety of application.[8] Recently, some new vinyl phosphates have been reported as potent inhibitors of phosphatase [9] and phosphodiesterase.[10] There are only few reports on the synthesis and bioactivity of their analogues which have been found to have insecticidal [11] and antifungal [12] activities.

The syntheses of α-hydroxy phosphonates have received an increasing amount of attention due to significant biological interests. They showed potential biological activities, such as antiviral, antibacterial, anticancer, pesticides, renin inhibitors, HIV protease, and enzyme inhibitor properties [13]. Much of these activities has been attributed to the relatively inert nature of the C–P bond and to the physical and structural similarity of phosphonic and phosphinic acids to the biologically important

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phosphate ester and carboxylic acid functionality [14]. In addition, α -hydroxy phosphonates are useful precursors for the preparation of α -functionalized phosphonates, such as amino, keto, halo, and acetoxy phosphonates [15–19].

Phosphate esters have been recognized in a variety of biological molecules as diverse as nucleic acids, proteins, carbohydrates, lipids, coenzymes and steroids.[20] The methods that currently exists for the introduction of a phosphate group into a substrate molecule largely depends on the substrate itself.[21] Hwang et al. reported the compound phosphoric ester exhibit excellent insecticidal effect and bioactivity.[22] Daniel Demosay and coworkers showed that phosphate compounds used as insecticides, acaricides, nematicides and fungicides.[23]. A number of Lewis acids have been evaluated as catalysts by Jones et al. for the phosphoryl transfer, the most efficient being $TiCl_4$.[24] Sengupta and coworkers described the synthesis of organophosphorous derivates by reaction of *O,O*-diethyl chlorophosphate in the presence of pyridine.[25] Mark McLaughlin reported the benzilic phosphate preparation by the reaction of benzyl alcohol with *O,O*-diethyl chlorophosphate in the presence of DMAP and triethyl amine in THF.[26]

Result and Discussion

Studies on organophosphorous derivatives could constitute new and promising field of application. The present study, therefore, was undertaken to develop new (2-chloroquinoline-3-yl)methyl diethyl phosphate by using some bioactive quinoline moieties with organophosphorous reagents. Literature survey revealed that there found no such report for the synthesis of (2-chloroquinoline-3-yl)methyl diethyl phosphate compounds.

In continuation of our work related to phosphorus chemistry,[27] we were interested in the synthesis of new (2-chloroquinoline-3-yl)methyl diethyl phosphate. We have synthesized for the first time (2-chloroquinoline-3-yl)methyl diethyl phosphate containing highly bioactive quinoline moiety in two steps. In the first step, derivatives of (2-chloroquinoline-3-yl)methanol **(2a-h) (scheme 1, Table I)** were prepared at room temperature from derivatives of 2-chloroquinoline-3-carbaldehyde **(1a-h) (scheme 1)** and sodium borohydride in methanol in excellent yields and were characterized by mass spectra. In the next step, (2-chloroquinoline-3-yl)methyl diethyl phosphate **(3a-h) (scheme 1, Table II)** were then prepared in excellent yields by reacting derivatives of (2-chloroquinoline-3-yl)methanol **(2 a-h)** with *O,O*-diethyl chlorophosphate in the presence of sodium hydroxide using dichloromethane as the solvent at room temperature. After the completion of the reaction, water was added to the reaction mixture. Separate out dichloromethane layer, dried over sodium sulphate and concentrated under vacuum to get the desired crude product, which was purified by column chromatography. All the compounds synthesized were unequivocally characterized on the basis of analytical data.

Conclusion

In conclusion, a new methodology was developed for the synthesis of new (2-chloroquinoline-3-yl)methyl diethyl phosphate **(3a-h)** from of (2-chloroquinoline-3-yl)methanol derivatives **(2a-h)**, obtained from 2-chloroquinoline-3-carbaldehydes **(1a-h)** for the first time using *O,O*-diethyl chlorophosphate in the presence of sodium hydroxide. All the reactions were performed under mild reaction conditions, shorter reaction time and in quantitative

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yields (Table-II). The methodology developed will be of much use to combinatorial chemist.

Experimental section

2-Chloroquinoline-3-carbaldehydes were prepared in the laboratory by the reported method.[28] *O,O*-diethyl chlorophosphate, was procured from Aldrich. Dichloromethane, sodium borohydride, sodium hydroxide, and methanol were procured from S.D.Fine-chem. All physical constants were determined in open capillaries at atmospheric pressure. ^{1}H NMR spectra were recorded on Mercury Plus Varian in $CDCl_3$ at 400 MHz using TMS as an internal standard. IR spectra were recorded on a Perkin-Elmer FTIR. Mass spectra were recorded on Micromass Quatrro II using electrospray Ionization technique, showing (m+1) peak as a molecular ion peak. The test for the purity of products and the progress of the reactions were accomplished by TLC on Merck silica gel plates.

General Procedure:

(2-chloro-8-methylquinoline-3-yl)methanol (2d)

To the stirred solution of 2-chloro-8-methylquinoline-3-carbaldehyde (1.5 gm, 7.2 mmol) in 10 ml methanol was slowly added sodium borohydride (0.2 gm, 5.2 mmol) at room temperature. The progress of reaction was monitored on TLC (solvent system-Hexane: Ethyl acetate). After the completion of the reaction (10 min), the reaction mixture was concentrated under reduced pressure to obtain residue. To the residue was added ice cold water and the solid obtained was filtered and washed with water, dried in oven at 50 ^{0}C for 8.0 hr (1.44 gm).

(2-chloro-8-methylquinoline-3-yl)methyl diethyl phosphate (3d)

To the stirred solution of (2-chloro-8-methylquinoline-3-yl)methanol (1.0 gm, 4.8 mmol) and sodium hydroxide (0.5 gm, 12.5 mmol) in 10 ml dichloromethane was added *O,O*-diethyl chlorophosphate (1.65 gm, 9.6 mmol). The progress of the reaction was monitored on TLC using Hexane: Ethyl acetate (8:2) as the solvent system. After the completion of the reaction, water was added to the reaction mixture. Separate out dichloromethane layer, dried over sodium sulphate and concentrated under vacuum to get the desired crude product, which was purified by column chromatography.

2d) (2-chloro-8-methylquinoline-3-yl)methanol

ES-MS: m/z 207.8 (m+1) and 209.9 (m+3)

3d) (2-chloro-8-methylquinoline-3-yl)methyl diethyl phosphate

IR (KBr): 2935 cm^{-1} (-CH stretching); 1239 cm^{-1} (-P=O); 1056 cm^{-1} (-P-O-C).

^{1}H NMR ($CDCl_3$, δ ppm): 1.30 – 1.38 (m, 6H, (-O-CH_2-C$\underline{H}_3$)$_2$); 2.74 (s, 3H, Ar-C$\underline{H}_3$), 4.07 - 4.25 (m, 4H, (-O-C$\underline{H}_2$-CH_3)$_2$); 5.26 (d, 2H, -C$\underline{H}_2$-O-P, J = 8 Hz); 7.42 (t, 1H, Ar-$\underline{H}$, C_6, J = 8 Hz); 7.55 (d, 1H, Ar-$\underline{H}$, C_7, J = 8 Hz); 7.65 (d, 1H, Ar-$\underline{H}$, C_5, J = 8 Hz); 8.24 (s, 1H, Ar-$\underline{H}$, C_4).

ES-MS: m/z 344.1 (m+1) and 346.1 (m+3).

3a) (2-chloroquinoline-3-yl)methyl diethyl phosphate

IR (KBr): 2992 cm^{-1} (-CH stretching) ; 1234 cm^{-1} (-P=O) ; 1032 cm^{-1} (-P-O-C)

^{1}H NMR ($CDCl_3$, δ ppm): 1.28 – 1.35 (m, 6H, (-O-CH_2-C$\underline{H}_3$)$_2$); 4.01 - 4.17 (m, 4H, (-O-C$\underline{H}_2$-CH_3)$_2$); 5.29 (d, 2H, -C$\underline{H}_2$-O-P); 7.54 – 8.00 (m, 4H, Ar-$\underline{H}$, C_5, C_6, C_7, C_8); 8.45 (s, 1H, Ar-$\underline{H}$, C_4).

ES-MS: m/z 330.1 (m+1) and 332.1 (m+3).

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3b) (2-chloro-6-methylquinoline-3-yl)methyl diethyl phosphate

IR (KBr): 2981 cm^{-1} (-CH stretching) ; 1231 cm^{-1} (-P=O) ; 1028 cm^{-1} (-P-O-C)

^{1}H NMR ($CDCl_3$, δ ppm): 1.25 – 1.39 (m, 6H, (-O-CH_2-C$\underline{H}_3$)$_2$); 2.52 (s, 3H, Ar-C$\underline{H}_3$), 4.05 - 4.25 (m, 4H, (-O-C$\underline{H}_2$-CH_3)$_2$); 5.24 (d, 2H, -C$\underline{H}_2$-O-P); 7.54 – 7.59 (m, 2H, Ar-$\underline{H}$, C_5, C_7); 7.88 (d, 1H, Ar-$\underline{H}$, C_8); 8.20 (s, 1H, Ar-$\underline{H}$, C_4).

ES-MS: m/z 344.1 (m+1) and 346.1 (m+3).

3c) (2-chloro-7-methylquinoline-3-yl)methyl diethyl phosphate

IR (KBr): 2986 cm^{-1} (-CH stretching) ; 1223 cm^{-1} (-P=O) ; 1027 cm^{-1} (-P-O-C)

^{1}H NMR ($CDCl_3$, δ ppm): 1.31 1.39 (m, 6H, (-O-CH_2-C$\underline{H}_3$)$_2$); 2.58 (s, 3H, Ar-C$\underline{H}_3$), 4.02 - 4.21 (m, 4H, (-O-C$\underline{H}_2$-CH_3)$_2$); 5.27 (d, 2H, -C$\underline{H}_2$-O-P); 7.35 – 7.55 (m, 2H, Ar-$\underline{H}$, C_5, C_6); 7.84 (s, 1H, Ar-$\underline{H}$, C_8); 8.20 (s, 1H, Ar-$\underline{H}$, C_4).

ES-MS: m/z 344.1 (m+1) and 346.1 (m+3).

3e) (2-chloro-6-methoxyquinoline-3-yl)methyl diethyl phosphate

IR (KBr): 2983 cm^{-1} (-CH stretching) ; 1228 cm^{-1} (-P=O) ; 1022 cm^{-1} (-P-O-C)

^{1}H NMR ($CDCl_3$, δ ppm): 1.22 – 1.35 (m, 6H, (-O-CH_2-C$\underline{H}_3$)$_2$); 3.71 (s, 3H, Ar-OC$\underline{H}_3$), 4.08 - 4.27 (m, 4H, (-O-C$\underline{H}_2$-CH_3)$_2$); 5.24 (d, 2H, -C$\underline{H}_2$-O-P); 7.19 – 7.38 (m, 2H, Ar-$\underline{H}$, C_5, C_7); 7.70 (d, 1H, Ar-$\underline{H}$, C_8,); 8.22 (s, 1H, Ar-$\underline{H}$, C_4).

ES-MS: m/z 360.1 (m+1) and 362.1 (m+3).

3f) (2-chloro-7-methoxyquinoline-3-yl)methyl diethyl phosphate

IR (KBr): 2987 cm^{-1} (-CH stretching) ; 1234 cm^{-1} (-P=O) ; 1032 cm^{-1} (-P-O-C)

^{1}H NMR ($CDCl_3$, δ ppm): 1.24 1.40 (m, 6H, (-O-CH_2-C$\underline{H}_3$)$_2$); 3.75 (s, 3H, Ar-OC$\underline{H}_3$), 4.04 – 4.21 (m, 4H, (-O-C$\underline{H}_2$-CH_3)$_2$); 5.26 (d, 2H, -C$\underline{H}_2$-O-P); 7.15 – 7.29 (m, 2H, Ar-$\underline{H}$, C_6, C_8); 7.65 (d, 1H, Ar-$\underline{H}$, C_5); 8.18 (s, 1H, Ar-$\underline{H}$, C_4).

ES-MS: m/z 360.1 (m+1) and 362.1 (m+3).

3g) (2-chloro-6-ethoxyquinoline-3-yl)methyl diethyl phosphate

IR (KBr): 2985 cm^{-1} (-CH stretching) ; 1220 cm^{-1} (-P=O) ; 1026 cm^{-1} (-P-O-C)

^{1}H NMR ($CDCl_3$, δ ppm): 1.23 – 1.41 (m, 9H, (-O-CH_2-C$\underline{H}_3$)$_2$ and Ar-OCH_2C$\underline{H}_3$); 4.03 – 4.25 (m, 6H, (-O-C$\underline{H}_2$-CH_3)$_2$ and Ar-OC$\underline{H}_2$$CH_3$); 5.21 (d, 2H, -C$\underline{H}_2$-O-P); 7.03 (d, 1H, Ar-$\underline{H}$, C_5); 7.32 (dd, 1H, Ar-$\underline{H}$, C_7); 7.87 (d, 1H, Ar-$\underline{H}$, C_8, J = 8 Hz); 8.16 (s, 1H, Ar-$\underline{H}$, C_4).

ES-MS: m/z 374.1 (m+1) and 376.1 (m+3).

3h) (2-chloro-8-ethylquinoline-3-yl)methyl diethyl phosphate

IR (KBr): 2932 cm^{-1} (-CH stretching) ; 1236 cm^{-1} (-P=O) ; 1029 cm^{-1} (-P-O-C).

^{1}H NMR ($CDCl_3$, δ ppm): 1.30 – 1.37 (m, 9H, (-O-CH_2-C$\underline{H}_3$)$_2$ and Ar-CH_2-C$\underline{H}_3$), 3.21 (q, 2H, Ar-C$\underline{H}_2$-CH_3); 4.13 - 4.21 (m, 4H, (-O-C$\underline{H}_2$-CH_3)$_2$); 5.27 (d, 2H, -C$\underline{H}_2$-O-P); 7.47 – 7.66 (m, 3H, Ar-$\underline{H}$, C_5, C_6, C_7); 8.25 (s, 1H, Ar-$\underline{H}$, C_4).

ES-MS: m/z 358.2 (m+1) and 360.2 (m+3).

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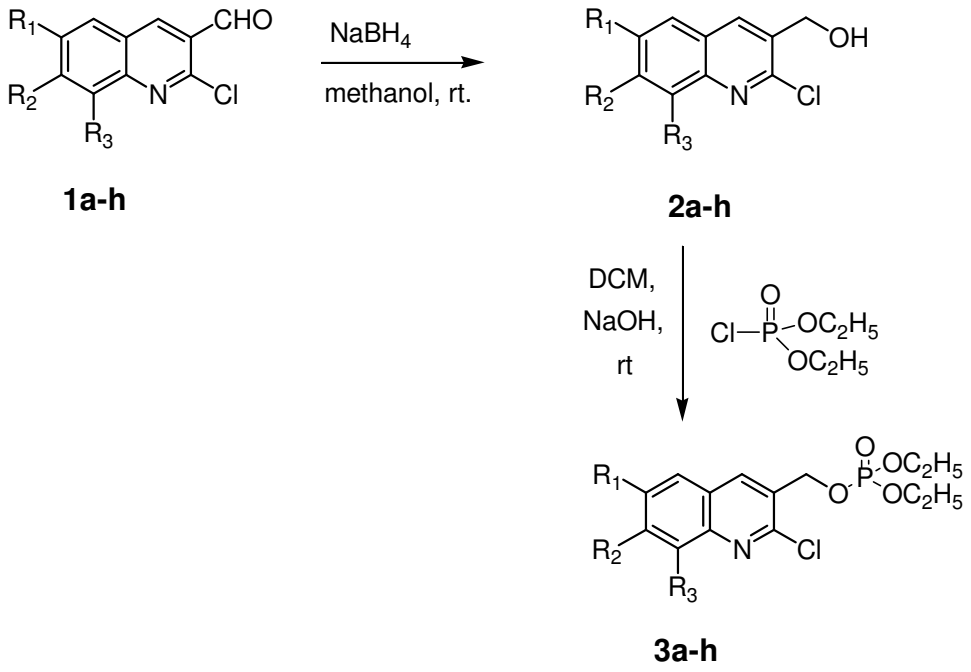
Scheme 1



1a-h **2a-h** **3a-h**

Table 1: Synthesis of (2-chloroquinoline-3-yl)methanol derivatives

Entry	R_1	R_2	R_3	Reaction Time (min)	Yield (%)	Melting Point (^{0}C)
2a	H	H	H	10	95	166-168
2b	CH_3	H	H	10	95	144-146
2c	H	CH_3	H	10	96	131-133
2d	H	H	CH_3	10	95	160-162
2e	OCH_3	H	H	10	97	129-131
2f	H	OCH_3	H	10	95	122-124
2g	OC_2H_5	H	H	10	97	120-122
2h	H	H	C_2H_5	10	94	130-132

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Table II: Sodium hydroxide facilitated synthesis of (2-chloroquinoline-3-yl)methyl diethyl phosphate

Entry	R_1	R_2	R_3	Reaction Time (min)	Yield (%)	Boiling Point (^{0}C)
3a	H	H	H	45	92	224-226
3b	CH_3	H	H	50	93	148-150
3c	H	CH_3	H	45	93	178-180
3d	H	H	CH_3	40	91	238-240
3e	OCH_3	H	H	55	90	210-212
3f	H	OCH_3	H	50	92	232-234
3g	OC_2H_5	H	H	50	94	190-192
3h	H	H	C_2H_5	45	91	228-230

- boiling points are measured at atmospheric pressure

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