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SYNTHESIS OF QUINOLINEALKYL-PHOSPHINE OXIDES AND –PHOSPHONATES FROM *N*-ARYLIMINES DERIVED FROM PHOSPHINE OXIDES AND PHOSPHONATES.[#]

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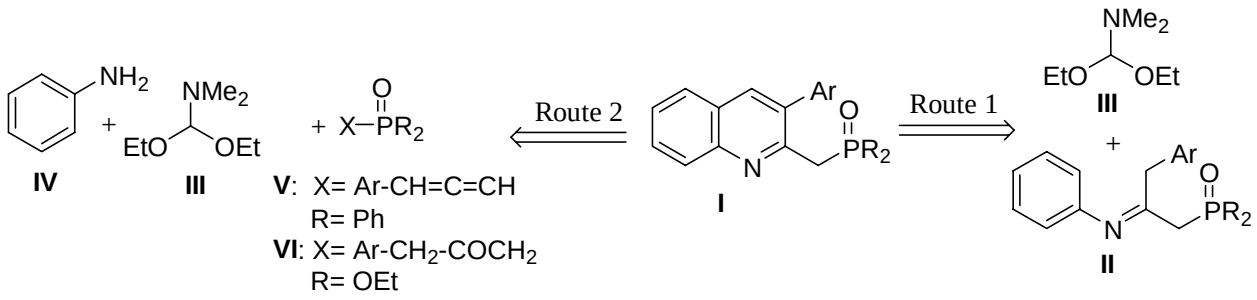
Abstract- Quinolinealkylphosphine oxides are obtained by thermal treatment of *N*-arylimines derived from phosphine oxides with *N*,*N*-dimethylformamide diethyl acetal (DMF-DEA). In a similar manner, quinolinealkylphosphonates are obtained by reaction of DMF-DEA with *N*-arylimines derived from phosphonates or from their precursors, arylamines and carbonyl derivatives.

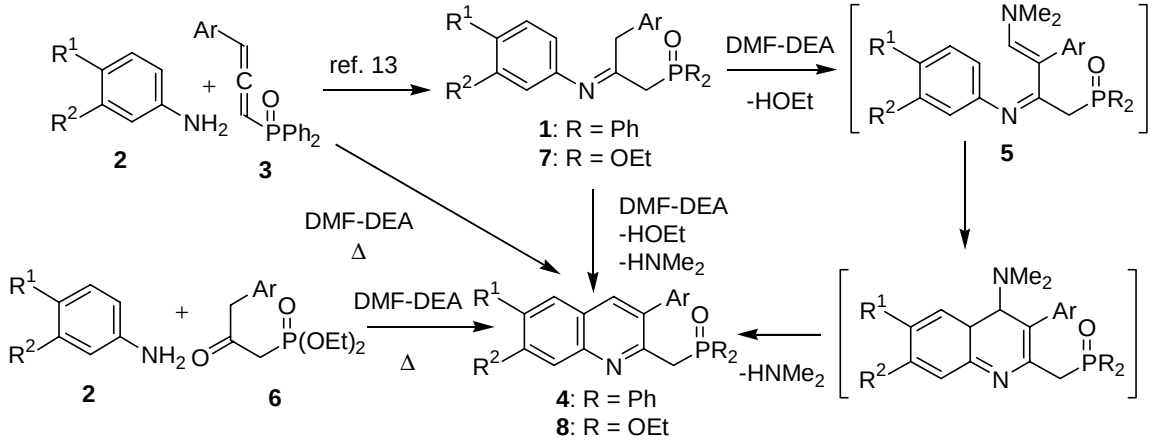
Quinolines are widely used intermediates for functional transformations.[1,2] Simple quinolines are common units in a wide variety of natural products possessing biological activity,[3] and they are constituents of alkaloids or antibiotics with remarkable cytotoxic and antitumor properties.[4] Furthermore, the presence of alkylphosphonates in position 2 of the ring increases the synthetic value of quinolines because these compounds can be used as metal complexes ligands[5] and as key phosphorus intermediates for olefination reactions.[6] We are interested in the design of new nitrogen heterocycles bearing a phosphine oxide or a phosphonate moiety. This substituent could regulate important biological functions and increase the biological activity of these compounds.[7] In this context, we have described the synthesis of three-,[8] five-[9] and six-membered phosphorus[10] substituted nitrogen heterocycles from functionalized enamines and imines as well as phosphorylated 4-aminoquinolines[11] and phosphorus-containing heterocycles.[12] Continuing with our interest in the chemistry of new phosphorus substituted compounds, we report here an easy and regioselective synthesis of quinolinealkylphosphine oxides (**I**, R=Ph) and -phosphonates (**I**, R=OEt) from *N*,*N*-dimethylformamide diethyl acetal (DMF-DEA, **III**) and phosphorylated *N*-arylimines (**II**) (Scheme 1, Route 1), or from their precursors (Scheme 1, Route 2) such as arylamines (**IV**) and phosphorylated allenes (**V**) or carbonyl derivatives (**VI**) and DMF-DEA (**III**).

[#] Dedicated to Professor Y. Kanoaka on the occasion of his 75th birthday



Scheme 1.

Required *N*-arylimines derived from phosphine oxides (**1**) were easily prepared by addition of aryl amines (**2**) to allenes (**3**).[13] Thermal treatment of 2-(*N*-*p*-tolylimino)-3-tolylpropylphosphine oxide (**1a**)[∀] (R^1 = CH_3, R^2 = H, Ar = *p*-$CH_3C_6H_4$) with DMF-DEA in toluene at 110ºC (48 h) gave quinolinealkylphosphine oxide (**4a**) (Scheme 1) in moderate yield (Table 1, Entry 1).[14,15] Compound (**4a**) was characterized on the basis of its spectroscopic data. Thus, the ^{31}P NMR spectrum of **4a** showed a resonance at δ_P = 31.6 and the ^{1}H NMR spectrum showed well resolved doublet for methylene protons at δ_H = 4.07 ($^2J_{PH}$ = 15.3 Hz), while ^{13}C NMR spectrum gave doublets at δ_C = 38.2 ($^1J_{PC}$ = 66.0 Hz) for the methylene carbon substituent as well as at δ_C = 150.8 ($^2J_{PC}$ = 8.6 Hz) C-2 of quinoline (**4a**). The formation of this heterocycle (**4a**) can be explained by a condensation reaction of imine (**1a**) with DMF-DEA followed by the loss of ethanol (Scheme 2) and subsequent 6π-azaelectrocyclization of this azadiene (**5a)** with the loss of dimethylamine, in a similar manner to that reported for azapolyenes.[11c,16]



Scheme 2.

With these results we tried to explore whether quinolinealkylphosphine oxides (**4**) could be directly obtained from the precursors of *N*-arylimines (**1**). From a preparative point of view, it is of interest that

[∀] This derivative was obtained as a mixture of imino- (85%) and the isomeric enamino-phosphine oxide (15%) and was used without separation.

the synthesis of quinolinealkylphosphine oxides (**4**) does not require the isolation and purification of the imines (**1**) and the former can be obtained in a regioselective fashion and in good yields in "*one pot*" reaction from arylamines (**2**) and arylallenes derived from phosphine oxides (**3**) by means of "*in situ*" formation of imines (**1**), followed by heating with DMF-DEA (Table 1, Entries 1-5).[17] The scope of the reaction was not limited to 2-aryl- (**4a-d**) (Ar = *p*-$CH_3C_6H_4$, Table 1, Entries 1-4) and 2-heteroaryl-quinolines (**4e**) (Ar = 2-Fur, Table 1, Entry 5), because quinolines (**4**) containing electron-donating substituents in the aromatic ring (Table 1, Entries 1, 2, 4), as well as containing an electron-withdrawing substituents (R^1 = Cl, R^2 = H) (Table 1, Entry 3) were also obtained.

Table 1. Quinolines (**4** and **8**) obtained.

Entry	Compd.	R	R^1	R^2	Ar	Yield (%)	mp (ºC)
1	**4a**	Ph	Me	H	Tol	48 (46)[a]	154 - 155
2	**4b**	Ph	MeO	H	Tol	55[a]	151 - 152
3	**4c**	Ph	Cl	H	Tol	71[a]	143 - 144
4	**4d**	Ph	OMe	OMe	Tol	64[a]	239 - 240
5	**4e**	Ph	-O-CH_2-O-		2-fur	61[a]	201 - 202
6	**8a**	OEt	Me	H	Ph	64[b]	Oil
7	**8b**	OEt	-O-CH_2-O-		Ph	63[b]	Oil

[a] Yield from allenyl-phosphine oxide in "*one pot*". [b] Yield from β-Ketophosphonate.

This methodology can also be extended to the synthesis of quinolines containing a phosphonate group in position 2. It is noteworthy that quinolinealkyl-phosphonates (**8**) can be directly obtained from arylamines (**2**) and carbonyl phosphonates (**6**)[18] by "*in situ*" formation of the imines derived from phosphonates (**7**),[11a] followed by heating with DMF-DEA (Scheme 2, Table 1, Entries 6, 7).[19] Similar "*one pot*" processes as well as reactions using very small amounts of solvents are acquiring important relevance in "Green Chemistry" for their applications in the pharmaceutical industry.[20]

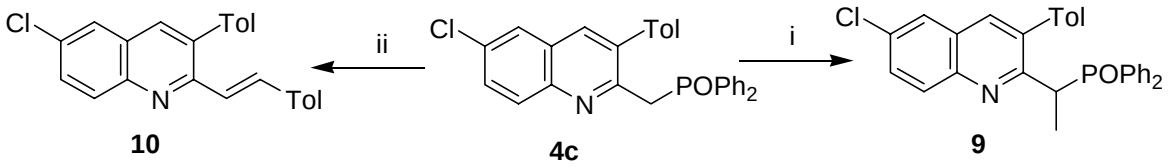
Table 2. Selected spectral data for quinolines (**4** and **8**).

	^{1}H NMR[a] δ (ppm)	^{13}C NMR[a] δ (ppm)	^{31}P NMR[a] δ (ppm)	MS[b] (*m/z*)
4a	7.72 (s, 1H), 7.66–7.59 (m, 4H), 7.54 (d, $^{3}J_{HH}$ = 8.6 Hz, 1H), 7.39–7.14 (m, 12H), 4.07 (d, $^{2}J_{PH}$ = 15.3 Hz, 2H) 2.41 (s, 3H), 2.13 (s, 3H).	150.8 (d, $^{2}J_{PC}$ = 8.6 Hz), 145.3, 137.3, 136.3, 136.2, 136.0, 137.3–128.0 (m), 131.4, 129.3 126.7, 126.1, 38.2 (d, $^{1}J_{PC}$ = 66.0 Hz), 21.5, 21.2.	31.6	447 (M^{+}, 8)
4b	7.78 (s, 1H), 7.73–7.65 (m, 4H), 7.61 (d, $^{3}J_{HH}$ = 9.2 Hz, 1H), 7.50–7.19 (m, 11H), 6.97 (s, 1H), 4.24 (d, $^{2}J_{PH}$ = 15.1 Hz, 2H) 3.88 (s, 3H), 2.41 (s,3 H).	157.6, 152.9, 148.8 (d, $^{2}J_{PC}$ = 8.6 Hz), 142.8, 137.1, 136.5, 136.4, 136.1, 135.4, 133.8–127.8 (m), 121.9, 121.5, 55.3, 37.7 (d, $^{1}J_{PC}$ = 66.0 Hz), 21.0.	31.6	463 (M^{+}, 100)
4c	7.69 (s, 1H), 7.61–7.55 (m, 4H), 7.52 (d, $^{3}J_{HH}$ = 8.8 Hz, 1H), 7.41–7.10 (m, 12H), 4.03 (d, $^{2}J_{PH}$ = 15.0 Hz, 2H) 2.30 (s, 3H).	153.0, 152.1 (d, $^{2}J_{PC}$ = 8.6 Hz), 144.7, 137.2, 137.0, 135.3, 132.1, 131.6, 133.5–127.8 (m), 127.0, 125.6, 122.0, 37.8 (d, $^{1}J_{PC}$ = 65.5 Hz), 20.9.	31.4.	467 (M^{+}, 44)
4d	7.72–6.94 (m, 17H), 4.11 (d, $^{2}J_{PH}$ = 15.0 Hz, 2H) 3.98 (s, 6H), 2.40 (s, 3H).	152.3, 149.8, 148.8 (d, , $^{2}J_{PC}$ = 8.6 Hz), 137.1, 136.5, 135.1, 131.5–128.0 (m), 122.1, 107.3, 104.6, 56.0, 55.9, 38.1 (d, $^{1}J_{PC}$ = 66.0 Hz), 21.1.	31.2	494 (M^{+}+1, 100).
4e	7.77–7.04 (m, 14H), 6.76 (d, $^{3}J_{HH}$ = 3.0 Hz, 1H), 6.42 (dd, $^{3}J_{HH}$ = 3.0 Hz, $^{3}J_{HH}$ = 2.0 Hz, 1H), 6.02 (s, 2H), 4.08 (d, $^{2}J_{PH}$ = 15.0 Hz, 2H).	150.9, 144.6, 134.2, 133.2, 133.7–125.1 (m), 111.2, 108.4, 114.0, 101.6, 38.5 (d, $^{2}J_{PC}$ = 8.6 Hz).	31.5	454 (M^{+}+1, 100).
8a	8.05 (d, $^{3}J_{HH}$ = 7.1 Hz, 1H), 7.85 (d, $^{3}J_{HH}$ = 7.1 Hz, 1H), 7.57–7.44 (m, 6H), 7.37 (s, 1H), 7.01 (s, 1H), 4.12–3.99 (m, 4H), 3.38 (d, $^{2}J_{PH}$ = 22.9 Hz, 2H), 2.28 (s, 3H), 1.31–1.25 (m, 6H).	148.7 (d, $^{2}J_{PC}$ = 10.0 Hz), 145.2, 139.9, 138.9, 137.1, 135.0, 132.3, 131.9, 128.5, 127.9, 126.5, 105.6, 101.9, 62.0, 59.9, 33.5 (d, $^{1}J_{PC}$ = 136.3 Hz), 16.3. 1.62.	25.6	369 (M^{+}+1, 100).
8b	7.80 (s, 1H), 7.51–7.46 (m, 5H), 7.34 (s, 1H), 7.00 (s, 1H),6.09 (s, 2H), 4.12–4.03 (m, 4H), 3.55 (d, $^{2}J_{PH}$ = 22.4 Hz, 2H), 1.28–1.22 (m, 6H).	150.7, 148.9 (d, $^{2}J_{PC}$ = 10.1 Hz), 147.8, 145.2, 139.4, 129.6, 128.3, 127.5, 105.0, 102.3, 101.5, 62.0, 61.9, 33.9 (d, $^{1}J_{PC}$ = 136.5 Hz), 34.8, 33.0.	25.7	400 (M^{+}+1, 100).

[a] Obtained on a Varian VXR 300 Spectrometer. [b] Obtained at 50–70 eV by electron impact (EIMS) on a Hewlett Packard 5973 spectrometer or by chemical ionization (CI) on a Hewlett Packard 1100MSD (fragmentor = 50).

Taking into account the interest of functionalized phosphorus derivatives[5, 21] in the carbon-carbon bond construction, the Cα-alkylation and the olefination reaction of quinolinealkyl-phosphine oxide were explored. Thus, when functionalized quinoline (**4c**) was treated with methyllithium followed by addition

of methyl iodide and aqueous work-up, C-methylated derivative (**9**)[22] was obtained (Scheme 3) in good yield (85%). Likewise, quinolinealkylphosphine oxide (**4c)** can be suitable to efficiently achieve the homologation of quinolines into their vinylogous compounds. Functionalized phosphine oxide (**4c**) was treated with methyllithium, followed by addition of *p*-methyl benzaldehyde leading to *E*-vinylquinoline (**10**) [22] with high *E*-stereoselectivity of the carbon-carbon double bond in good yield (86%), after aqueous work-up and flash-chromatography (Scheme 3).



Scheme 3: i) 1. MeLi, 2.MeI. ii) 1. MeLi, 2. *p*-MeC_6H_4-CHO.

In conclusion, the synthesis described in this paper provides an efficient and easy access to quinolines substituted with an alkylphosphine oxide or an alkylphosphonate group in position 2, making use of readily available starting materials. These quinolines can be prepared in a stepwise fashion or in a "*one pot*" reaction from arylamines, phosphorylated allenes or carbonyl compounds and *N*,*N*-dimethylformamide diethyl acetal. Phosphorylated quinolines can be used as starting substrates for carbon-carbon bond construction and for olefination processes. Functionalized quinolines are important synthons in organic synthesis and for the preparation of biologically active compounds with interest in medicinal chemistry.[1-4]

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14. All new compounds gave satisfactory spectral and elemental analyses. (**4a**). White solid. IR (KBr) ν: 2956, 1739, cm^{-1}. MS (m/z): 447 (M^+, 8) amu. Anal. Calcd for $C_{30}H_{26}NOP$: C. 80.52, H. 5.86, N. 3.13. Found: C. 80.45, H. 5.80, N. 3.16.
15. General Procedure for the preparation of quinoline (**4a**)from *N*-arylimine (**1a**). A solution of a mixture of diphenyl 3-*p*-tolyl-2-(*p*-tolylimino)propyldiphenylphosphine oxide (85%) and 2-(*p*-tolylamino)-3-*p*-tolyl-1-propenylphosphine oxide (15%) (2.19 g, 5 mmol) and 1.03 mL of DMF-DEA (6 mmol) in toluene (15 mL) was stirred under reflux until TLC indicated the disappearance of imine/enamine (48 h). The mixture was then concentrated under vacuum and the crude residue was purified by flash column chromatography eluting with AcOEt/hexanes (3:1).
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17. General Procedure for the preparation of quinolines (**4**) from *N*-arylamines (**2**) and allenes (**3**). A solution of allene (**3**) (5 mmol) and aromatic amine (**2**) (5 mmol) in $CHCl_3$ (15 mL) was stirred under reflux overnight. Solvent was evaporated under vacuum and diluted in toluene. DMF-DEA (1.03 mL, 6 mmol) was then added and the mixture was stirred under reflux until the completation of the reaction (2–3 d.). The mixture was then concentrated under vacuum and the crude residue was purified by flash column chromatography eluting with AcOEt/hexanes (3:1).
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19. General Procedure for the preparation of quinolines (**4**) from *N*-arylamines (**2**) and 2-oxoalkyl phosphonates (**6**). A solution of diethyl 2-oxo-3-phenylpropylphosphonate (**6**) (1.35 g, 5 mmol) and *N*-arylamine (**2**) (5 mmol) in toluene (15 mL) was stirred under reflux with a Dean–Stark. After 3 h. the reaction was cooled to rt and DMF-DEA (1.03 mL, 6 mmol) was then added. The mixture was stirred under reflux until the completation of the reaction (2–3 d). The mixture was then concentrated under vacuum and the crude residue was purified by flash column chromatography eluting with AcOEt/hexanes (2:1).
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22.**9**. White solid. mp 149 – 150 ºC. ^{1}H NMR δ: 7.97 (d, $^{3}J_{HH}$ = 9.0 Hz, 1H), 7.81–7.29 (m, 13H), 7.25 (d, $^{3}J_{HH}$ = 6.6 Hz, 2H), 6.95 (d, $^{3}J_{HH}$ = 6.6 Hz, 2H), 4.35 (m, 1H), 2.40 (s, 3H)1.71 (dd, $^{3}J_{HH}$ = 7.2 Hz, $^{3}J_{PH}$ = 16.5 Hz, 3H). ^{13}C NMR δ: 157.9, 145.3, 138.8–125.7 (m), 41.0 (d, $^{1}J_{PH}$ = 67.0), 25.0, 21.2, 15.8. ^{31}P NMR δ: 31.7. IR (KBr) ν: 2919, 1725, cm^{-1}. MS (*m/z*): 481 (M^{+}+1, 100) amu. *Anal.* Calcd for $C_{30}H_{25}NOClP$: C. 74.76, H. 5.23, N. 2.91. Found: C. 74.81, H. 5.20, N. 2.88. **10**. White solid. m.p. 80 – 81 ºC. ^{1}H NMR δ: 8.07 (d, $^{3}J_{HH}$ = 9.0 Hz, 1H), 7.98 (d, $^{3}J_{HH}$ = 15.6 Hz, 1H), 7.91 (s, 1H), 7.63 (dd $^{3}J_{HH}$ = 9.0 Hz, $^{4}J_{HH}$ = 2.3 Hz, 1H), 7.76 (d, $^{4}J_{HH}$ = 2.3 Hz, 1H), 7.42–7.13 (m, 9H), 2.40 (s, 3H), 2.27 (s, 3H). ^{13}C NMR δ: 154.1, 145.7, 138.6, 137.7, 135.9, 135.7, 135.6, 135.3, 134.1, 131.7, 130.6, 130.3, 129.7, 129.4, 129.2, 129.0, 128.8, 128.6, 127.4, 126.0, 124.6, 121.1, 21.4, 21.3. IR (KBr) ν: 2922. cm^{-1}. MS (*m/z*): 369 (M^{+}+1, 100) amu. *Anal*. Calcd for $C_{25}H_{20}NCl$: C. 81.18, H. 5.45, N. 3.79. Found: C. 81.24, H. 5.41, N. 3.82.