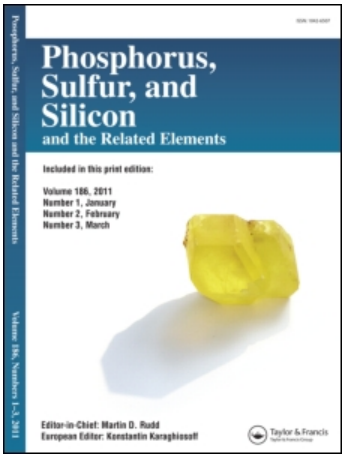

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Chemistry of Substituted Quinolinones. v. Synthesis and Use of Quinolinylphosphazenes in Amination of 8-Methylquinoline

M. M. Ismail[a]; M. Abass[a]; M. M. Hassan[a]
[a] Department of Chemistry, Faculty of Education, Ain Shams University, Roxy Cairo, Egypt

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CHEMISTRY OF SUBSTITUTED QUINOLINONES. V. SYNTHESIS AND USE OF QUINOLINYLPHOSPHAZENES IN AMINATION OF 8-METHYLQUINOLINE

M.M. ISMAIL, M. ABASS* and M.M. HASSAN

Department of Chemistry, Faculty of Education, Ain Shams University, Roxy, Cairo 11711, Egypt

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2,4-Dihalo-8-methylquinolines **2,3** have been prepared and subjected to azidation and hydrazination reactions showing interesting regioselective properties to give compounds **4–10**. The targeted aminoquiolines **13, 14, 15, 17, 19, 22** and **23** were obtained via hydrolysis of their corresponding phosphazenes **11, 12, 16, 18, 20** and **21**, respectively. These phosphazenes have been preliminary obtained by condensation of azido and/or tetrazoloquinolines **4, 5, 6, 10, 18** and **22**, with triphenylphosphine in either boiling benzene or 1,2-dichlorobenzene.

Keywords: haloquinolines; hydrazinoquinolines; azidoquinolines; tetrazoloquinolines; phosphazenes; aminoquinolines

INTRODUCTION

In continuation to our current research work on substituted quinolines and quinolin-2-ones [1–3], this article deals with study of synthesis and nucleophilic substitution of 2,4-dihalo-8-methylquinolines. Direct nucleophilic amination of haloquinolines is mostly not efficient in production of aminoquinolines.

Herein the known *Staudinger* method was used for reduction of azido and/or tetrazoloquinolines, which were obtained from haloquinolines, to the desired aminoquinolines [4–7].

* To whom correspondence should be addressed. Email: mohamedabass@hotmail.com

RESULTS AND DISCUSSION

4-Hydroxy-8-methyl-1,2-dihydroquinolin-2-one (**1**) [3] was subjected to chlorination reaction using a mixture of phosphorus oxychloride and phosphorus pentachloride at the molar ratio (3:2). Using of phosphorus oxychloride gave a very low yield of 2,4-dichloro-8-methylquinoline (**2**), while phosphorus pentachloride only yielded a tary product that needs several crystallizations to obtain a much lesser yield of dichloroquinoline **2**. On the other hand phosphorus pentabromide was used to obtain 2,4-dibromo-8-methylquinoline (**3**). The yield herein is also low and trials to enhance this yield, by increasing time of reaction or amount of brominating agent or addition of phosphorus oxybromide or phosphorus tribromide, were unsuccessful and mostly effected production of several by-products. The azidation reaction of both dihaloquinolines **2** and **3** was investigated to check their behaviour towards nucleophilic substitution at both α- and γ-positions. Thus, when compounds **2** and/or **3** were reacted with sodium azide at the molar ratio (1:1), in DMF or N-methylpyrrolidone (NMP), only 4-azido-2-halo-8-methylquinolines **4,5** were afforded while the expected 5-chloro-9-methyl[1,2,3,4]tetrazolo-[1,5-*a*]quinoline (**6**) had not been achieved at these conditions. This result is consistent with the literature in which kinetic studies indicate that γ-chloro atom of dichloquinolines is about two times more reactive towards nucleophiles and predominately an addition-elimination process occurred [8,9]. This led us to try the latter reaction in different conditions. Thus it was found that addition of an acid as a catalyst led to the tetrazoloquinoline **6**. This reaction was found catalyzable by methane sulphonic acid or trichloroacetic acid, or trifluoroacetic acid in either ethanol or dioxane. The best yield was obtained on using toluene-4-sulphonic acid in absolute ethanol.

Hydrazination of compound **2** showed the same interesting regioselective property that was observed in azidation. Reaction of the dichloroquinoline **2** with hydrazine hydrate furnished only 2-chloro-4-hydrazino-8-methylquinoline (**7**). It is clear that there is a possibility in this reaction to form the isomeric 2-hydrazinoquinoline derivative **8**. Since IR and ^{1}H NMR spectra of the product of this reaction may not be satisfactory for the elucidation of which isomer was actually obtained, two reactions were carried out with compound **7**. Treatment of which with nitrous acid led to the formation of 4-azido-2-chloro-8-methylquinoline (**4**), that was previously obtained and characterized. Also, treating compound **7** with sodium azide in the presence

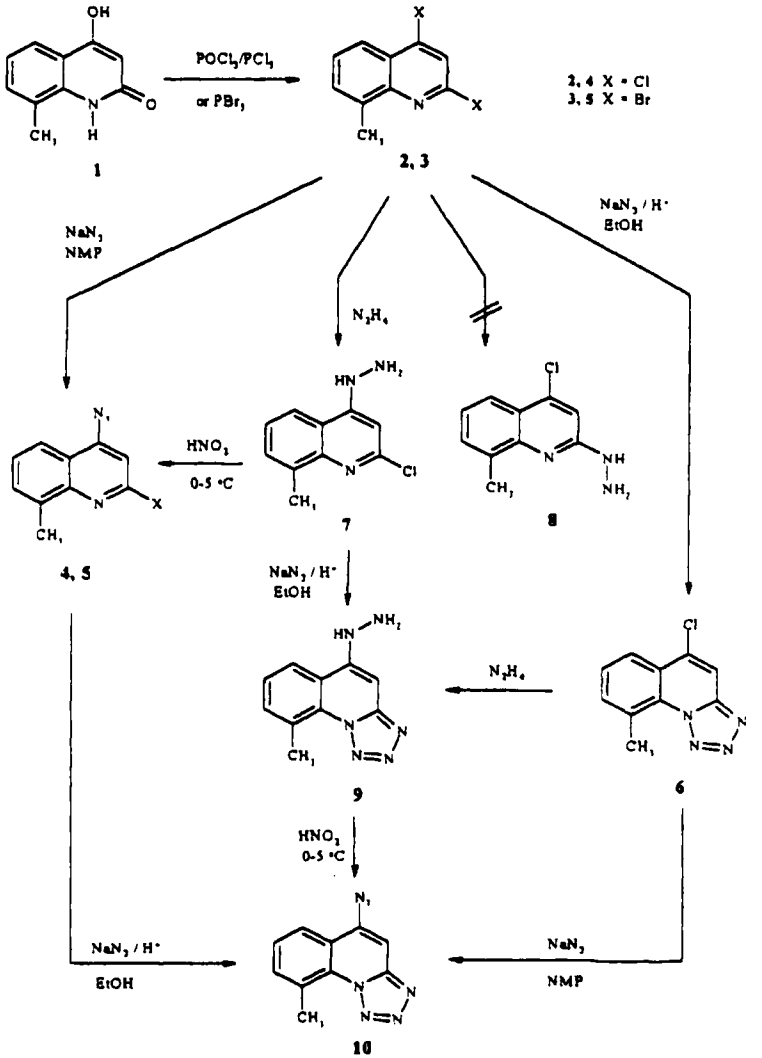
of toluene-4-sulphonic acid gave the same product obtained by reaction of 5-chlorotetrazoloquinoline **6** with hydrazine hydrate which its structure was indicated and characterized as 5-hydrazino-9-methyl[1,2,3,4]tetrazolo [1,5-*a*]quinoline (**9**).

5-Azido-9-methyl[1,2,3,4]tetrazolo[1,5-*a*]quinoline (**10**) was achieved through different pathways. Treating compound **2** with high excess of sodium azide and refluxing for a long time did not produce compound **10** in good yield or satisfactory purity. Compound **4** was the main product beside other different by-products. It is thought that step-wise treatment of the dihaloquinolines **2, 3** with sodium azide might furnish the desired product. Compounds **4** and/or **5** were treated with sodium azide in the presence of an acid catalyst and compound **6** was treated with sodium azide, in boiling DMF, to give the target compound **10**. Moreover when, hydrazinotetrazoloquinoline **9** was reacted with nitrous acid at 0–5 °C, the azidotetrazoloquinoline **10** was also obtained (Scheme 1).

The eighty years-old *Staudinger* method for reduction of azides into their corresponding amines was utilized to obtain the desired aminoquinolines [4,5,7,10]. The method includes reaction of various azides with triphenylphosphine to give the phosphazene derivatives followed by hydrolysis with aqueous hydrochloric acid leading to the aminoquinoline derivatives. Thus, azides **4** and/or **5** were reacted with triphenylphosphine in boiling benzene to give the 4-quinolinylphosphazenes **11** and **12**. Hydrolysis of the latter phosphazenes by dilute hydrochloric acid gave a mixture of 4-amino-2-halo-8-methylquinolines **13** or **14** and 4-amino-8-methyl-1,2-dihydroquinolin-2-one (**15**).

On carrying out condensation reaction of tetrazoloquinoline **6** with triphenylphosphine, in boiling benzene, the reactants were completely recovered unchanged. This reaction was found successful on using a much higher boiling point solvent such as DMSO or 1,2-dichlorobenzene. The latter solvent led to a much better yield of 4-chloro-2-quinolinylphosphazene **16**. Hydrolysis of phosphazene **16** furnished 2-amino-4- chloro-8-methylquinoline (**17**). Reacting compound **16** with sodium azide in DMF resulted in 4-azido-2-quinolinylphosphazene **18** which upon hydrolysis gave 2-amino-4-azido-8-methylquinoline (**19**) that was also afforded from azidation of compound **17**.

The difference in activity of both isomers **4** and **6** towards condensation with triphenylphosphine prompted our interest to study the behavior of azidotetrazoloquinoline **10** towards the same reagent. So that when compound **10** was subjected to react with an equimolar amount of triphenyl-



SCHEME I

phosphine, in boiling benzene, the tetrazoloquinolylphosphazene **20** was achieved and hydrolyzed to give the aminotetrazoloquinoline **22**.

TABLE I Analytical Data of the New Compounds

Cpd. No	Yield (%)	M.P. (°C) Crystaln. Solvent	Mol. Form. Mol. Wt.	Elemental Analysis Calcd. /Found (%)		
				C	H	N
2	46	81–82 MeOH	$C_{10}H_7Cl_2N$ 212.08	56.64 56.70	3.33 3.39	6.60 6.60
3	23	62–64 EtOH	$C_{10}H_7Br_2N$ 300.98	39.91 39.88	2.34 2.31	4.65 4.70
4	50[a], 66	92 MeOH	$C_{10}H_7ClN_4$ 218.65	54.93 54.90	3.23 3.24	25.62 25.61
5	78	155–156 EtOH	$C_{10}H_7BrN_4$ 263.10	45.65 45.60	2.68 2.68	21.30 21.31
6	55	175 Pet. Ether	$C_{10}H_7ClN_4$ 218.65	54.93 54.88	3.23 3.20	25.62 25.64
7	61	192–194 Benzene	$C_{10}H_{10}Cl\,N_3$ 207.66	57.84 57.84	4.85 4.81	20.26 20.22
9	35	210 DMF/H_2O	$C_{10}H_{10}N_6$ 214.23	56.07 56.09	4.71 4.69	38.25 38.22
10	75[a], 70[b], 64[c]	208 THF	$C_{10}H_7N_7$ 225.21	53.33 53.30	313 310	43.53 43.61
11	80	196–197 EtOH	$C_{28}H_{22}ClN_2P$ 452.93	74.25 74.24	4.90 4.91	6.19 6.20
12	85	245–246 EtOH	$C_{28}H_{22}BrN_2P$ 497.38	67.61 67.59	4.46 4.40	5.63 5.60
13	65	170 DMF	$C_{10}H_9ClN_2$ 192.65	62.35 62.30	4.71 4.70	14.54 14.58
14	42	> 300 DMF	$C_{10}H_9BrN_2$ 237.10	50.66 50.58	3.83 3.82	11.82 11.78
15	32	> 300 DMF	$C_{10}H_{10}N_2O$ 174.20	68.95 69.00	5.79 5.74	16.08 16.00
16	70	224 EtOEt	$C_{28}H_{22}ClN_4$ 452.92	74.25 74.23	4.90 4.90	6.19 6.20
17	70	> 300 DMF	$C_{10}H_9ClN_2$ 192.65	62.35 62.33	4.71 4.70	14.54 14.55
18	80	145–147 DMF/H_2O	$C_{28}H_{22}N_5P$ 459.49	73.19 73.20	4.83 4.81	15.24 15.32
19	60[a], 74[b]	220–222 DMF	$C_{10}H_9N_5$ 199.22	60.29 60.31	4.55 4.52	35.16 35.24

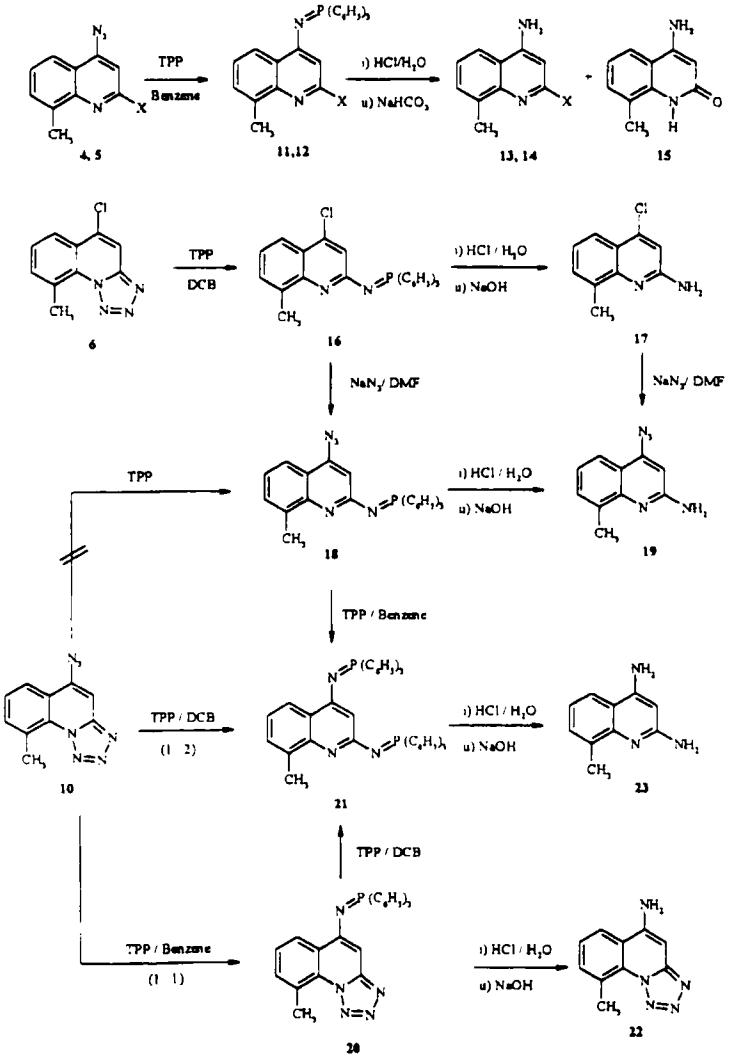
Cpd. No	*Yield (%)*	*M.P. (°C) Crystaln. Solvent*	*Mol. Form. Mol. Wt.*	*Elemental Analysis Calcd. /Found (%)*		
				C	*H*	*N*
20	65	168–170 Acetone	$C_{28}H_{22}N_5P$ 459.49	73.19 73.25	4.83 4.81	15.24 15.30
21	75[a], 81[b], 85[c]	136 Benzene	$C_{46}H_{37}N_3P_2$ 693.77	79.64 79.71	5.37 5.32	6.06 6.10
22	70	> 300 DMF	$C_{10}H_9N_5$ 199.22	60.29 60.32	4.55 4.52	35.16 35.21
23	70	> 300 DMF	$C_{10}H_{11}N_3$ 173.22	69.34 69.42	6.40 6.30	24.26 24.32

a., b., and c. are Yields (%) of methods [a], [b], and [c] respectively.

Use of excess reagent did not reveal any variation of the product. This may be attributed due to thermal stability of tetrazole ring compared by azide group. In the meantime, replacement of benzene as the reaction solvent by 1,2-dichlorobenzene showed interesting results where the excess reagent led to another product that was characterized as the diphosphazene **21**. It was very important to verify if both phosphazenes **18** and **20** could be converted to the diphosphazene **21** by the action of triphenylphosphine. This was investigated and also it was found that solvent of these reactions plays a role. Thus, compound **18** underwent smooth condensation with triphenylphosphine in dry benzene, while compound **20** needed 1,2-dichlorobenzene to furnish the diphosphazene **21**. Finally the targeted 2,4-diamino-8-methylquinoline (**23**) was obtained by hydrolysis of the diphosphazene **21**, using dilute hydrochloric acid (Scheme 2).

EXPERIMENTAL

Melting points were measured on a Gallen-Kemp MFB-595 in open capillary tubes and are incorrected. IR spectra were recorded on Perkin-Elmer 598 and FT-IR 1650 instruments (ν, cm^{-1}). ^{1}H-NMR spectra were measured on Jeol FX90-NMR or Varian EM-390 NMR (90 MHz) spectrometers (δ, ppm) using DMSO-d_6 or $CDCl_3$ as solvents and TMS as internal standard. Elemental microanalyses were performed on a Perkin-Elmer



SCHEME 2

CHN-2400 analyzer. Compound **1** was prepared according to literature [3]. Analytical and spectral data are listed in Tables I and II, respectively.

TABLE II Spectral Data of the New Compounds

Cpd. No	*IR, ν (cm^{-1})*	*^{1}H NMR, δ (ppm)*
2	1615 (C=N), 760 (C-Cl)	7.85–7.20 (m, 3H, arom), 6.30 (s, 1H, 3-H), 2.60 (s, 3H, CH_3)
3	1610, (C=N), 760, 645 (C-Br)	8.05–7.15 (m, 3H, arom), 5.85 (s, 1H, 3-H), 2.55 (s, 3H, CH_3)
4	2120 (N_3), 1608 (C=N), 762 (C-Cl)	7.85–7.10 (m, 3H, arom), 6.85 (s, 1H, 3-H), 2.60 (s, 3H, CH_3)
5	2115 (N_3), 1610 (C=N), 670 (C-Br)	7.67–7.14 (m, 3H, arom), 6.86 (s, 1H, 3-H), 2.50 (s, 3H, CH_3)
6	1605, (C=N), 1100, 1080, 1040 (tetrazole)	7.86–7.56 (m, 3H, arom), 6.92 (s, 1H, 3-H), 2.32 (s, 3H, CH_3)
7	3450, 3340, 3270 (NH_2, NH), 1630 (C=N) and 745 (C-Cl)	8.20 (bs, 1H, N-H), 7.95–7.15 (m, 3H, arom), 6.10 (s, 1H, 3-H), 4.40 (bs, 2H, NH_2), 2.55 (s, 3H, CH_3)
9	3370, 3280 (NH_2, NH), 1610 (C=N), 1100–1060 (tetrazole)	8.30 (bs, 1H, N-H), 7.96–7.15 (m, 3H, arom), 6.30 (s, 1H, 3-H), 4.30 (bs, 2H, NH_2), 2.90 (s, 3H, CH_3)
10	2120 (N_3), 1605 (C=N), 1100, 1080, 1040 (tetrazole)	7.95–7.15 (m, 3H, arom), 6.80 (s, 1H, 3-H), 2.80 (s, 3H, CH_3)
11	1630 (C=N), 1430 (P=N), 720 (C-Cl)	8.05–7.10 (m, 18H, arom), 5.90 (s, 1H, 3-H), 2.40 (s, 3H, CH_3)
12	3060, 1615 (C=N), 1440 (P=N), 670 (C-Br)	8.05–7.10 (m, 18H, arom), 6.95 (s, 1H, 3-H), 2.55 (s, 3H, CH_3)
13	3490, 3400–3220 (NH_2), 1625 (C=N), 745, 690 (C-Cl)	7.85–7.15 (m, 3H, arom), 6.30 (bs, 2H, NH_2), 5.85 (s, 1H, 3-H), 2.45 (s, 3H, CH_3)
14	3430, 3320 (NH_2), 1620 (C=N), 660 (C-Br)	7.95–7.15 (m, 3H, arom), 6.25 (bs, 2H, NH_2), 5.95 (s, 1H, 3-H), 2.30 (s, 3H, CH_3)
15	3430, 3388, 3200 (NH_2, NH), 1660 (C=O)	10.20 (bs, 1H, CONH), 8.10–7.00 (m, 3H, arom), 6.20 (bs, 2H, NH_2), 5.80 (s, 1H, 3-H), 2.30 (s, 3H, CH_3)
16	1610 (C=N), 1445 (P=N), 720 (C-Cl)	8.04–7.47 (m, 17H, arom), 7.09 (s, 1H, 3-H), 6.91 (d, 1H, 7-H), 2.53 (s, 3H, CH_3)

Cpd. No	*IR, ν (cm^{-1})*	*^1H NMR, δ (ppm)*
17	3480, 3330, 3200 (NH_2), 1625 (C=N), 740 (C-Cl)	8.15 (d, 1H, 5-H), 7.55–7.40 (m, 2H, 6-H + 7- H), 6.69 (s, 1H, 3-H), 4.61 (b, 2H, NH_2), 2.79 (s, 3H, CH_3)
18	2130 (N_3), 1620 (C=N), 1480, 1445 (P=N)	8.06–7.10 (m, 17H, arom), 6.71 (d, 1H, 7-H), 6.35 (s, 1H, 3-H), 2.53 (s, 3H, CH_3)
19	3400, 3340 (NH_2), 2120 (N_3), 1620 (C=N)	8.05–7.15 (m, 3H, arom), 6.35 (bs, 2H, NH_2), 5.90 (s, 1H, 3-H), 2.35 (s, 3H, CH_3)
20	1608 (C=N), 1485, 1440 (P=N), 1100,1020 (tetrazole)	7.95–7.15 (m, 18H, arom), 6.35 (s, 1H, 3-H), 2.80 (s, 3H, CH_3)
21	1610 (C=N), 1480, 1440, 1400 (P=N)	8.05–7.05 (m, 33H, arom), 6.15 (s, 1H, 3-H), 2.40 (s, 3H, CH_3)
22	3460, 3220 (NH_2), 1620 (C=N), 1100, 1070 (tetrazole)	7.90–7.10 (m, 3H, arom), 6 55 (s, 1H, 3-H), 6.30 (bs, 2H, NH_2), 2.80 (s, 3H, CH_3)
23	3460, 3380 (NH_2), 1620, 1600 (C=N and C=C)	7.95–7.10 (m, 3H, arom), 6.40–6.20 (b, 4H, 2 × NH_2), 5.85 (s, 1H, 3-H), 2.30 (s, 3H, CH_3)

2,4-Dichlro-8-methylquinoline (2)

A mixture of hydroxyquinolone **1** (0.1 mol), phosphorus oxychloride (0.3 mol) and phosphorus pentachloride (0.2 mol) was heated under reflux for 4 h, then left to cool to room temperature and poured into ice cold water. The white precipitate that formed was filtered off, washed with water, and crystallised

2,4-Dibrmo-8-methylquinoline (3)

A mixture of hydroxyquinolone **1** (0.01 mol) and phosphorus pentabromide (0.03 mol) was heated under reflux for 1 h, then left to cool poured into ice cold water. The solid deposits were collected by filtration and crystallised

4-Azido-2-chloro-8-methylquinoline (4)

[a] To a solution of dichloroquinoline **2** (0.01 mol) in NMP (50 ml), sodium azide (0.01) was added, then the mixture was warmed to 80–90°C for 2 h. Afterwards, the mixture was diluted with cold water (50 ml) to give a white precipitate, which was filtered off and crystallized.
[b] To a solution of compound **7** (0.01 mol) in hydrochloric acid (10 ml, 1 M), sodium nitrite solution (10 ml, 1 M) was added drop-wise with continuous stirring in an ice-bath at 0–5 °C. After completion of addition, the mixture was stirred for further 30 min, then filtered and the solid residue that obtained was recrystallized.

4-Azido-2-bromo-8-methylquinoline (5)

A solution of dibromoquinoline **3** (0.01 mol) in DMF (30 ml) was treated with sodium azide (0.01) and refluxed for 1 h. Then, the mixture was poured into ice-cold water and the precipitate so formed was collected by filtration and crystallized.

5-Chlor-9-methyl[1,2,3,4]tetrazolo[1,5-a]quinoline (6)

A mixture of dichloroquinoline **2** (0.01 mol), sodium azide (0.01 mol) and toluene-4-sulphonic acid (0.03 mol) in ethanol (30 ml) was heated under

reflux on a boiling water-bath for 5 h. Afterwards, the mixture was poured into crushed ice and the precipitate so formed was filtered off and crystallized.

2-Chloro-4-hydrazino-8-methylquinoline (7)

To a sodium of dichloroquinoline **2** (0.01 mol), in ethanol (25 ml), hydrazine hydrate (0.03 mol) was added and the mixture was heated under reflux for 6 h. Then the reaction mixture was poured into crushed ice and the obtained precipitate was filtered off and crystallized.

5-Hydrazino-9-methyl[1,2,3,4]tetrazolo[1,5-a]quinoline (9)

[a] A mixture of chlorotetrazoloquinoline **6** (0.01 mol) and hydrazine hydrate (0.01 mol) in ethanol (25 ml) was refluxed for 1 h. The reaction mixture was then cooled and poured into ice-cold water. The solid so formed was collected by filtration and crystallized.

[b] A mixture of the compound **7** (0.01 mol), sodium azide (0.015 mol) and toluene-4-sulphonic acid (0.005 mol), in ethanol (30 ml), was refluxed on a boiling water-bath for 4 h. Then, the mixture was diluted with water (30 ml) and neutralized with sodium bicarbonate. The precipitate so obtained was filtered off and crystallized

5-Azido-9-methyl[1,2,3,4]tetrazolo[1,5-a]quinoline (10)

[a] A mixture of either the 4-azido-2-haloquinoline **4** or **5** (0.01 mol) with sodium azide (0.015 mol) and toluene-4-sulphonic acid (0.005 mol), in ethanol (30 ml), was refluxed for 5 h. Then the mixture was diluted with cold water to give solid precipitate that was filtered off and crystallized.

[b] To a solution of compound **6** (0.01 mol) in DMF (20 ml), sodium azide (0.01 mol) was added, then the mixture was refluxed for 8 h and poured into cold water. The deposits were filtered off and crystallized.

[c] To a solution of compound **9** (0.01 mol) in hydrochloric acid (10 ml, 2 M), sodium nitrite (10 ml, 1 M) was added dropwise with continuous stirring in an ice bath at 0–5 °C. After completion of addition, the mixture was stirred for further 30 min, then filtered and the solid residue that obtained was recrystallized.

2-Halo-8-methyl-4-(triphenylphosphoranylideneamino) quinolines 11 and 12

A mixture of azidoquinolines **4** and/or **5** (0.01 mol), triphenylphosphine (0.011 mol) and benzene (25 ml) was refluxed for 3 h. Then the excess solvent was evaporated in vacuum and the solid deposits so obtained was triturated with petroleum ether (40–60 °C), filtered off and crystallized.

Hydrolysis of Phosphazenes 11 and 12

The phosphazenes **11** and/or **12** (0.01 mol) were treated with hydrochloric acid (50 ml, 6 M) and refluxed for 3 h. then left to cool and filtered. The clear filtrate was neutralized using aqueous sodium bicarbonate solution. The precipitate so formed was collected by filtration and crystallized from DMF (35 ml) to give the aminoquinolone **15**. Concentration of the crystallization mother liquor to half of its initial volume (~ 15 ml) furnished aminoquinolines **13** and/or **14**, respectively.

4-Chlor-8-methyl-2-(triphenylphosphoranylideneamino) quinoline (16)

A mixture of tetrazoloquinoline **6** (0.01 mol), triphenylphosphine (0.01 mol) and 1,2-dichlorobenzene (30 ml) was heated under reflux for 6 h. The solvent was evaporated in vacuum and the residue was triturated with diethyl ether (20 ml). The solid so obtained was filtered off, washed with excess diethyl ether (100 ml) and crystallized.

2-Amino-4-chloro-8-methylquinoline (17)

A similar procedure for hydrolysis of phosphazene **11** was followed for hydrolysis of phosphazene **16** using dilute hydrochloric acid. The acid solution that obtained was neutralized with aqueous sodium hydroxide to give the aminoquinoline **17**.

4-Azido-8-methyl-2-(triphenylphosphoryanylideneamino)quinoline (18)

Using the same procedure for obtaining compound **5**, compound **18** was prepared from compound **16** and sodium azide in DMF.

2-Amino-4-azido-8-methylquinoline (19)

[a] A similar procedure for hydrolysis of phosphazene **16** was applied to phosphazene **18** to give the aminoquinoline **19**.
[b] From compound **17** and sodium azide in DMF, using the same procedure for obtaining compound **5**, the compound **19** was prepared.

9-Methyl-5-(triphenylphosphoranylideneamino)[1,2,3,4]tetrazolo-[1,5-a]quinoline (20)

A similar procedure to that followed to prepare compound **11** was used starting with azidotetrazoloquinoline **10** and triphenylphosphine in boiling benzene.

2,4-Di(triphenylphosphoranylideneamino)-8-methylquinoline (21)

[a] A mixture of azidotetrazoloquinoline **10** (0.01 mol), triphenylphosphine (0.022 mol) and 1,2-dichlorobenzene (50 ml) was heated under reflux for 4 h. Then, the solvent was removed under vacuum and the residue so obtained was crystallized.
[b] Similar to phosphazene **16**, compound **21** was afforded from tetrazoloquinoline **20** and triphenylphosphine in 1,2-dichlorobenzene.
[c] Similar to phosphazene **11**, compound **21** was also obtained from azidoquinoline **18** and triphenylphosphine in benzene.

5-Amino-9-methyl[1,2,3,4] tetrazolo[1,5-a]quinoline (22)

The phosphazene **20** was treated with hydrochloric acid, following the same method described for hydrolysis of compound **16**.

2,4-Diamino-8-methylquinoline (23)

Compound **21** (0.01 mol) was treated with hydrochloric acid (50 ml, 6 M) using the method described for compound **11** to give compound **23**.

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