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The Vilsmeier cyclization of 2′-azido and 2′-aminochalcones—a mild one pot synthesis of 2-aryl-4-chloroquinoline and its *N*-formyl-1,2-dihydro derivatives

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Abstract—The Vilsmeier cyclization of 2′-aminochalcones provides a mild one pot synthesis of 2-aryl-4-chloro-*N*-formyl-1,2-dihydroquinolines. The scope of the reaction has been extended for the synthesis of quinolines themselves, by replacing 2′-aminochalcones with 2′-azidochalcones as the starting material. The yields are reasonably good and a plausible mechanism for the formation of the products in each case has been discussed. © 2001 Elsevier Science Ltd. All rights reserved.

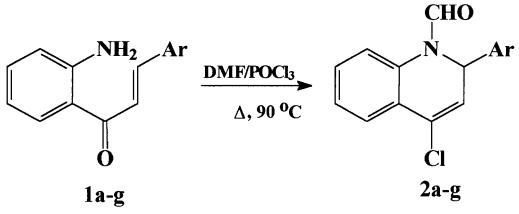
Quinolines and their derivatives occur in numerous natural products.[1] Many quinolines display interesting physiological activities and have found attractive applications as pharmaceuticals and as general synthetic blocks.[2] Many syntheses have been developed for quinolines,[3] but due to their great importance, the development of novel synthetic methods remains an active research area. Convenient synthesis of 2′-aminochalcone and its amide derivatives and the ready cyclization of these compounds to 2′-aryl-1,2,3,4-tetrahydro-4-quinolone has been explored widely.[4] However, until now, the cyclization of 2′-aminochalcones under Vilsmeier conditions has remained an uncharted territory.

Vilsmeier–Haack–Arnold reactions that were initially used for the formylation of activated aromatic substrates[5] and carbonyl compounds[6] have now evolved into a powerful synthetic tool for the construction of many heterocyclic compounds such as quinolines, indoles, quinazolines, pyridines,[7] etc. Although various substituted quinolines have been synthesized by both normal[8] and reverse Vilsmeier approaches,[9] the synthesis of quinoline derivatives from 2′-aminochalcones using the Vilsmeier reagent has not been reported so far. This led us to conduct a systematic investigation of the feasibility of cyclization of 2′-aminochalcones under Vilsmeier conditions.

In this paper, we report a novel and mild method towards the synthesis of 2-aryl-4-chloro-*N*-formyl-1,2-dihydroquinolines and 2-aryl-4-chloroquinolines from 2′-aminochalcones and 2′-azidochalcones respectively.

1. Results and discussion

The prerequisite 2′-aminochalcones were prepared from *o*-aminoacetophenone and the corresponding benzaldehydes following the reported procedure.[4b] Initially, the reactions were carried out at room temperature in anticipation of the formation of 2-aryl-*N*-formyl-1,2-dihydroquinolones. We envisaged the amino group to undergo formylation, followed by ring closure to yield an *N*-formyl



1a-g 2a-g

Scheme 1.

Table 1. Reaction products of 2′-aminochalcones with the Vilsmeier reagent

Entry	Product[a]	Ar	Yield (%)[b]
1	**2a**[c]	Ph	76
2	**2b**	*p*-ClC_6H_4	80
3	**2c**	*p*-$CH_3C_6H_4$	78
4	**2d**	*p*-$OCH_3C_6H_4$	68
5	**2e**	*o*-ClC_6H_4	75
6	**2f**	*o*-$CH_3C_6H_4$	82
7	**2g**	*m*-ClC_6H_4	85

[a] All products were characterized using ^1H and ^{13}C NMR, IR, mass spectra and CHN analysis.
[b] Isolated yield.
[c] Dense oil.

Keywords: quinolines; aminochalcones; Vilsmeier reaction; azides.
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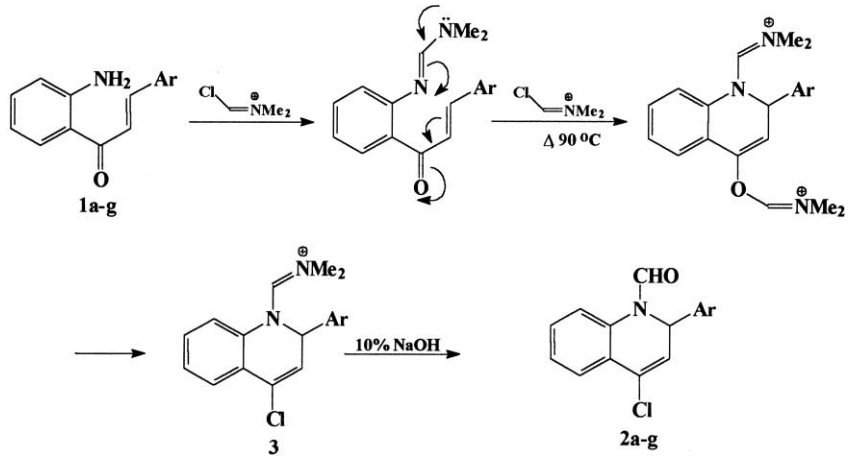


Scheme 2.

quinoline derivative. However, these reactions resulted only in the formation of the corresponding uncyclized products, *N*-formyl-2′-aminochalcones. Prolonged reaction time or variation in the DMF/$POCl_3$ ratio could not impart any change in the formation of products.

Gratifyingly, when the reaction temperature was raised to 90°C, the desired cyclization proceeded smoothly to give 2-aryl-4-chloro-*N*-formyl-1,2-dihydroquinolines **2a–g** in good yields (Scheme 1, Table 1).

1,2-Dihydroquinolines are important target molecules, mainly due to their synthetic utility as precursors for a variety of biologically active compounds.[10] Literature also reveals a number of patent applications concerning their industrial uses.[11] To the best of our knowledge this is the first report on the one-pot synthesis of *N*-formyl-1,2-dihydroquinolines.[12] Also, it is worth emphasizing the difficulty in preparing 1,2-dihydroquinolines by traditional methods, which mainly depend upon the addition of nucleophiles to *N*-alkylquinolinium salts,[13] and suffer from the simultaneous production of 1,4-dihydro derivatives.

The reaction seems to proceed through *N*-formylation followed by ring closure to give the intermediate **3**, which on hydrolysis furnishes the corresponding dihydroquinoline as represented in Scheme 2.

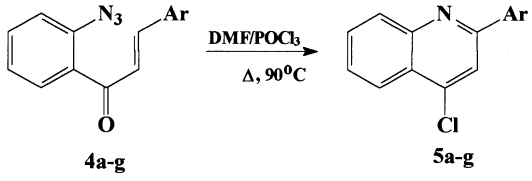
The mild reaction conditions employed and the ready availability of the starting materials enticed us to adapt this useful methodology for the synthesis of quinolines themselves.

We selected 2′-azidochalcone as a suitable starting material since the in situ elimination of nitrogen in the course of the reaction could provide the desired 2-aryl-4-chloroquinolines. We were also encouraged by recent reports on the cyclization of the azido moiety with iminium salts generated in-situ under Vilsmeier conditions.[14] Application of azides in organic synthesis has attracted considerable attention in recent years, owing to their versatility for synthetic manipulations.[15] In addition, a wide array of synthetic methods are available for the introduction of the azido moiety into organic substrates. The prerequisite 2′-azidochalcones **4a–f** necessary for the study, were prepared from the corresponding 2′-aminochalcones, by diazotization followed by treatment with NaN_3.

When various substituted 2′-azidochalcones were treated with the Vilsmeier reagent, a smooth conversion of the starting material to 2-aryl-4-chloroquinolines **5a–f** was observed in moderate yields at 90°C (Scheme 3, Table 2). Attempts to accomplish the cyclization at lower temperatures, using excess of reagents or by prolonging the reaction time were not rewarded with favorable results.

The reaction may be proceeding through initial cyclization followed by reductive elimination of nitrogen as proposed in Scheme 4.

In conclusion, we have unraveled a new, efficient and one pot synthesis of *N*-formyl-4-aryl-1,2-dihydroquinolines and 2-aryl-4-chloroquinolines from the corresponding 2′-aminochalcones and 2′-azidochalcones, respectively.

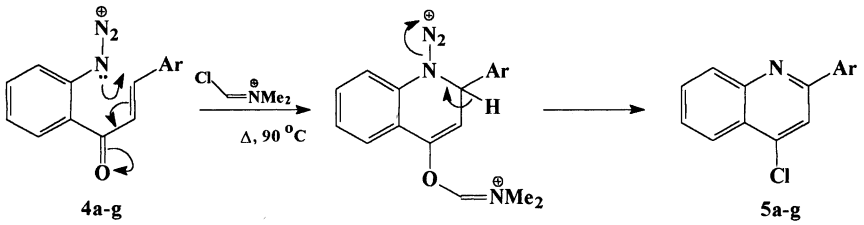


Scheme 3.

Table 2. Reaction products of 2′-azidochalcones with Vilsmeier reagent

Entry	Product[a]	Ar	Yield (%)[b]
1	**5a**	*p*-ClC_6H_4	72
2	**5b**	*p*-$CH_3C_6H_4$	71
3	**5c**	*p*-CH_3OC6H4	62
4	**5d**	*o*-ClC_6H_4	51
5	**5e**	*o*-$CH_3C_6H_4$	63
6	**5f**	*m*-ClC_6H_4	68

[a] All products were characterized using ^1H and ^{13}C NMR, IR, mass spectra and CHN analysis.
[b] Isolated yield.



Scheme 4.

2. Experimental

Mass spectra were recorded on Varian VG 70-70H mass spectrometer. Melting points were measured in capillary tubes and are uncorrected. Analytical thin layer chromatography was performed on precoated sheets of silica gel G of 0.25 mm thickness containing PF 254 indicator (Merck, Darmstadt). Column chromatography was performed with silica gel (60–120 mesh; SD Fine, Boisar). IR spectra were recorded as solids in KBr pellets on Nicolet Impact-400 spectrometer. NMR spectra were obtained on a Bruker spectrometer. ^{1}H NMR spectra were recorded at 300 MHz in $CDCl_3$ and the chemical shifts are given in δ relative to the internal standard TMS. ^{13}C NMR spectra were recorded at 75 MHz in $CDCl_3$ and the chemical shift was given in δ relative to the solvent (77.0). DMF was vacuum distilled from calcium hydride and dried over 4 Å molecular sieves.

2.1. General procedure for the preparation of 2-aryl-4-chloro-*N*-formyl-1,2-dihydro quinolines (2a–g)

To an ice-cold magnetically stirred solution of **1a–g** (5 mmol) in DMF (10 mL), $POCl_3$ (2.8 mL, 30 mmol) was added dropwise. The reaction mixture was allowed to attain room temperature and was heated over a water bath for 3 h, after which it was poured into crushed ice, neutralized with 10% NaOH solution and extracted with ethyl acetate. The organic layer was washed with water, dried over anhydrous Na_2SO_4, filtered and the solvent evaporated. The crude reaction product was purified by column chromatography using 5% ethyl acetate in petroleum ether as eluent.

2.1.1. 4-Chloro-1-formyl-2-phenyl-2*H*-quinoline (2a). 1.02 g of dense oil (76%); IR (KBr) 1923, 1665, 769 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.69 (dd, 1H, J=1.5, 2.1 Hz), 7.30–7.21 (m, 7H), 7.03 (dd, 1H, J=1.5, 2.1 Hz), 6.41 (d, 1H, J=6.3 Hz), 6.33 (d, 1H, J=6.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.4, 137.8, 134.7, 130.0, 128.9, 128.7, 128.5, 128.3, 127.2, 125.6, 124.9, 124.4, 117.9, 52.6; MS *m/z* 270 (M^+), 272 (M+2); Anal. Calcd for $C_{16}H_{12}ClNO$; C, 71.24; H, 4.48; N, 5.19; Found C, 71.29; H, 4.52; N, 5.21.

2.1.2. 4-Chloro-1-formyl-2-(4-chloro)phenyl-2*H*-quinoline (2b). 1.2 g of colorless crystals (80%); mp 119–110°C; IR (KBr) 1666, 1598, 823, 760 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.70 (d, 1H, J=7.0 Hz), 7.32–7.19 (m, 6H), 7.03 (d, 1H, J=7.5 Hz), 6.37 (d, 1H, J=6.3 Hz), 6.29 (d, 1H, J=6.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.1, 136.1, 134.2, 134.1, 130.1, 128.9, 128.7, 128.6, 128.5, 128.4, 125.6, 124.1, 117.8, 51.7; MS *m/z* 304 (M^+), 306 (M+2), 308 (M+4); Anal. Calcd for $C_{16}H_{11}Cl_2NO$; C, 63.17; H, 3.64; N, 4.60; Found C, 63.13; H, 3.62; N, 4.52.

2.1.3. 4-Chloro-1-formyl-2-(4-methyl)phenyl-2*H*-quinoline (2c). 1.1 g of colorless crystals (78%); mp 118–119°C; IR (KBr) 1668, 910, 750 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.71–7.68 (m, 1H), 7.31–7.22 (m, 3H), 7.15 (d, 2H, J=8.1 Hz), 7.04 (d, 2H, J=8.1 Hz,), 6.38 (d, 1H, J=6.3 Hz), 6.32 (d, 1H, J=6.3 Hz), 2.25 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.4, 138.2, 134.9, 134.7, 130.0, 129.6, 129.4, 128.4, 127.4, 125.7, 125.2, 124.6, 118.0, 52.5, 21.1; MS *m/z* 283 (M^+), 285 (M+2); Anal. Calcd for $C_{17}H_{14}ClNO$; C, 71.96; H, 4.97; N, 4.94; Found C, 72.18; H, 4.82; N, 4.94.

2.1.4. 4-Chloro-1-formyl-2-(4-methoxy)phenyl-2*H*-quinoline (2d). 1.02 g of oil which solidified on storage (68%); mp 68–69°C IR (KBr) 1660, 831 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, 1H, J=6.6 Hz), 7.25–7.22 (m, 3H), 7.17 (d, 2H, J=8.7 Hz), 6.99 (d, 1H, J=7.5 Hz), 6.73 (d, 2H, J=8.7 Hz), 6.34 (d, 1H, J=6.3 Hz), 6.27 (d, 1H, J=6.3 Hz), 3.68 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.3, 159.5, 134.5, 129.8, 129.2, 128.5, 125.9, 125.5, 125.4, 125.2, 124.4, 117.9, 114.2, 55.1, 52.1; MS *m/z* 300 (M^+). Anal. Calcd for $C_{17}H_{14}ClNO_2$; C, 68.12; H, 4.7; N, 4.67; Found C, 68.20; H, 4.79; N, 4.71.

2.1.5. 4-Chloro-1-formyl-2-(2-chloro)phenyl-2*H*-quinoline (2e). 1.14 g of colorless crystals (75%); mp 125–126°C; IR (KBr) 1666, 831, 756 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.67 (d, 1H, J=7.5 Hz), 7.43–7.24 (m, 4H), 7.18–7.08 (m, 1H), 7.04 (s, 1H), 7.02 (s, 1H), 6.69 (d, 1H, J=6.0 Hz), 6.47 (d, 1H, J=6.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.5, 137.2, 135.8, 130.9, 130.4, 129.9, 129.3, 127.9, 126.8, 126.1, 125.8, 125.7, 123.9, 123.8, 117.2, 51.5; MS *m/z* 304 (M^+), 306 (M+2), 308 (M+4); Anal. Calcd for $C_{16}H_{11}Cl_2NO$; C, 63.18; H, 3.64; N, 4.60; Found C, 63.10; H, 3.67; N, 4.42.

2.1.6. 4-Chloro-1-formyl-2-(2-methyl)phenyl-2*H*-quinoline (2f). 1.16 g of colorless crystals (82%); mp 130–131°C; IR (KBr) 1678, 759 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.69 (m, 1H,), 7.37–7.24 (m, 5H), 7.14–7.09 (m, 3H), 7.00–6.75 (m, 2H), 6.52 (d, 1H, J=6.3 Hz), 6.26 (d, 1H, J=6.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.72, 136.9, 135.6, 134.8, 130.9, 130.2, 128.3, 127.5, 126.7, 126.4 (2), 125.7, 125.6, 124.5, 117.9, 50.9, 19.6; MS *m/z* 283 (M^+). 285 (M+2); Anal. Calcd for $C_{17}H_{14}ClNO$; C, 71.95; H, 4.97; N, 4.93; Found C, 71.89; H, 4.91; N, 4.87.

2.1.7. 4-Chloro-1-formyl-2-(3-chloro)phenyl-2*H*-quinoline (2g). 1.29 g of colorless crystals (85%); mp 77–78°C; IR (KBr) 1676, 823, 769 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.65–7.62 (m, 1H), 7.27–7.17 (m, 3H), 7.16–7.07 (m, 3H), 7.00 (d, 1H, J=9 Hz), 6.32 (d, 1H, J=6.6 Hz), 6.24 (d, 1H, J=6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.0, 140.4, 135.1, 134.9, 130.8, 130.5, 129.7, 129.0, 127.9, 126.4, 126.3, 125.9, 124.7, 124.4, 118.5, 52.3; MS m/z 304 (M^+) 306 (M+2); Anal. Calcd for $C_{16}H_{11}Cl_2NO$; C, 63.18; H, 3.64; N, 4.60; Found C, 63.22; H, 3.65; N, 4.58.

2.2. General procedure for the preparation of 2-aryl-4-chloroquinolines (5a–g)

To an ice-cold magnetically stirred solution of 2′-azidochalcones **4a–g** (5 mmol) in DMF (10 mL), $POCl_3$ (2.8 mL, 30 mmol) was added dropwise. The reaction mixture was allowed to attain room temperature and was heated over a water bath for 3 h, after which it was poured into crushed ice, neutralized with 10% NaOH solution and extracted with ethyl acetate. The organic layer was washed with water, dried over anhydrous Na_2SO_4, filtered and the solvent evaporated. The crude reaction product was purified by column chromatography using 5% ethly acetate in petroleum ether as eluent.

2.2.1. 4-Chloro-2-(4-chloro)phenyl quinoline (5a). 0.98 g of crystalline solid (72%); mp 99–100°C; IR (KBr) 2927, 1584, 831, 753 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, 1H, J=8.4 Hz), 8.13 (d, 1H, J=8.1 Hz), 8.10 (d, 2H, J=8.1 Hz), 7.90 (s, 1H), 7.76 (t, 1H, J=7.5 Hz), 7.60 (t, 1H, J=7.5 Hz), 7.47 (d, 2H, J=8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.9, 149.0, 143.4, 136.9, 136.1, 130.8, 130.1, 129.1, 128.7, 127.5, 125.4, 124.0, 118.6.; MS m/z 273 (M^+), 275 (M+2), 277 (M+4); Anal. Calcd for $C_{15}H_9Cl_2N$; C, 65.72; H, 3.31; N, 5.11; Found C, 65.62; H, 3.23; N, 4.99.

2.2.2. 4-Chloro-2-(4-methyl)phenyl quinoline (5b). 0.89 g of crystalline solid (71%); mp 78–79°C; (79–80°C).[16]

2.2.3. 4-Chloro-2-(4-methoxy)phenyl quinoline (5c). 0.83 g of crystalline solid (62%); mp 77–78°C; IR (KBr) 2897, 1154, 831, 753 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.15–8.05 (m, 4H), 7.86 (s, 1H) 7.70 (t, 1H, J=7.5 Hz), 7.52 (t, 1H, J=7.5 Hz), 6.99 (d, 2H, J=8.7 Hz), 3.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.1, 156.6, 148.9, 142.8, 131.0, 130.3, 129.7, 128.7, 126.7, 124.9, 123.8, 118.4, 114.2, 55.3; MS m/z 269 (M^+), 271 (M+2); Anal. Calcd for $C_{16}H_{12}ClNO$; C, 71.25; H, 4.48; N, 5.19; Found C, 71.15; H, 4.57; N, 4.95.

2.2.4. 4-Chloro-2-(2-chloro)phenyl quinoline (5d). 0.69 g of crystalline solid (51%); mp 132–133°C; IR (KBr) 3010, 1592, 835, 763 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, 1H, J=6.6 Hz), 8.16 (d, 1H, J=6.0 Hz) 7.84 (s, 1H), 7.79 (t, 1H, J=4.0 Hz), 7.69–7.65 (m, 2H), 7.53–7.44 (m, 1H), 7.41–7.37 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.1, 148.8, 142.1, 138.6, 132.3, 131.6, 130.5, 130.2, 130.1, 130.0, 127.7, 127.2, 125.3, 124.0, 122.8; MS m/z 273 (M^+), 275 (M+4), 277 (M+4); Anal. Calcd for $C_{15}H_9Cl_2N$; C, 65.72; H, 3.31; N, 5.11; Found C, 65.63; H, 3.28; N, 5.26.

2.2.5. 4-Chloro-2-(2-methyl)phenyl quinoline (5e). 0.79 g of crystalline solid (63%); mp 67–68°C; (67–68°C).[16]

2.2.6. 4-Chloro-2-(3-chloro)phenyl quinoline (5f). 0.92 g of crystalline solid (68%); mp 58–59°C; IR (KBr) 2957, 1110, 843, 735 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.20–8.13 (m, 3H), 7.97 (t, 1H, J=1.5 Hz), 7.89 (s, 1H), 7.76 (t, 1H, J=8.2 Hz), 7.62 (t, 1H, J=7.5 Hz), 7.42 (d, 2H, J=5.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.5, 149.0, 143.4, 140.3, 135.1, 130.7, 130.0, 129.9, 129.8, 129.7, 127.6, 127.5, 125.5, 124.0, 118.7; MS m/z 273 (M^+), 275 (M+2), 277 (M+4); Anal. Calcd for $C_{15}H_9Cl_2N$; C, 65.72; H, 3.31; N, 5.11; Found C, 65.68; H, 3.28; N, 5.22.

Acknowledgements

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