SOME UNUSUAL REACTIONS OF 3-PHENYLAMINOISOXAZOL-5(2H)- ONES

J. Khalafy[1] and R.H. Prager[2]

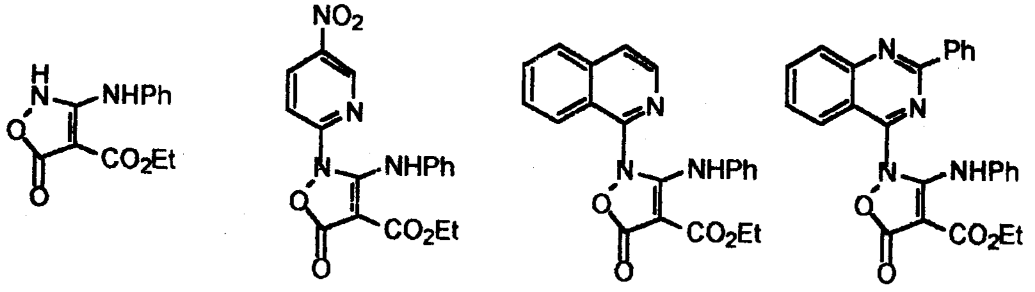
[1]*Chemistry Department, Urmia University, Urmia 57154, Islamic Republic of Iran*
[2]*Chemistry Department, Flinders University of South Australia, GPO Box 2100, Adelaide, 5001 Australia*

Abstract

3-Phenylaminoisoxazol-5(2H)-ones, substituted on nitrogen with an isoquinoline or quinazoline group, react with tertiary amine bases to give imidazo annelated compounds. When the N-substituent is a nitropyridine, 2-aminoindole derivatives are formed instead. Evidence is presented that the reactions proceed by initial addition of the tertiary amine to C-4.

Introduction

In previous studies we have shown that the products obtained from isoxazol-5(2H)-ones on photolysis [1-5] or pyrolysis [6,7] depend markedly on the nature of the substituent on the ring, particularly at C-4, but to a lesser extent on those at C-3 [8,9]. As part of that study, we prepared some derivatives of ethyl 3-phenylamino-5-oxo-2,5-dihydroisoxazole-4-carboxylate **1**, which were subjected to photolysis and pyrolysis. In this paper, we report the study of the base-induced rearrangement of the N-substituted derivatives of **1**, namely **2-4**.

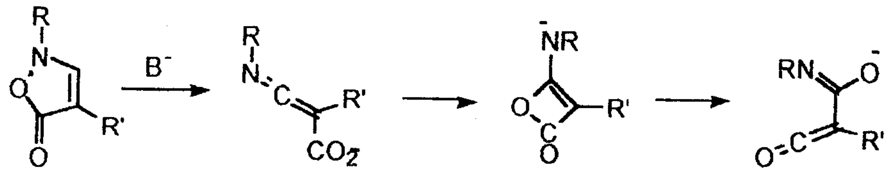


1 2 3 4

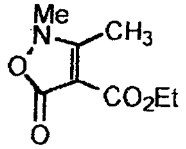
Figure 1

Keywords: Imidazoisoquinoline, Imidazoquinazoline, 2-aminoindole, Base induced rearrangement

The reaction of isoxazol-5(2H)-ones, unsubstituted at C-3, with base is well known [10-14], and the various intermediates (Scheme 1) have been trapped to prepare a large number of heterocyclic systems [15-21]. However, the reaction of 3-substituted compounds with base is not so well known, and the only reported reactions appear to be those due to Doleschall [22], who alkylated the anion of ethyl 2,3-dimethyl-2,5-dihydro-5-oxoisoxazole-4-carboxylate, **5**, in order to obtain γ-alkylated acetoacetates. We were interested in the possibility that 3-phenylaminoisoxazolones, like **2-4**, might be induced to react with bases to form ketenes, which could be intramolecularly trapped by the azene to give, eg **6**, (Scheme 2). Accordingly, in this paper we report the reactions of **2-4** with bases, and related reactions.



Scheme 1



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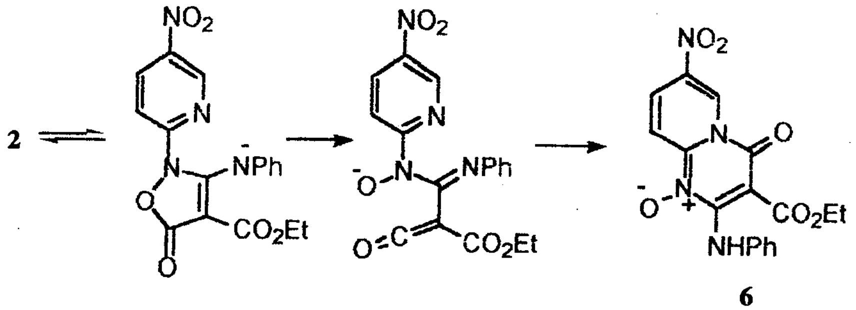
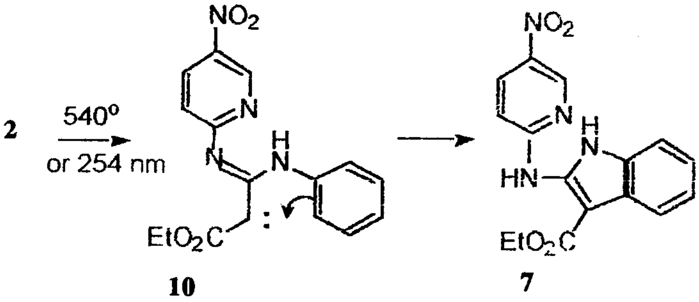


Scheme 2

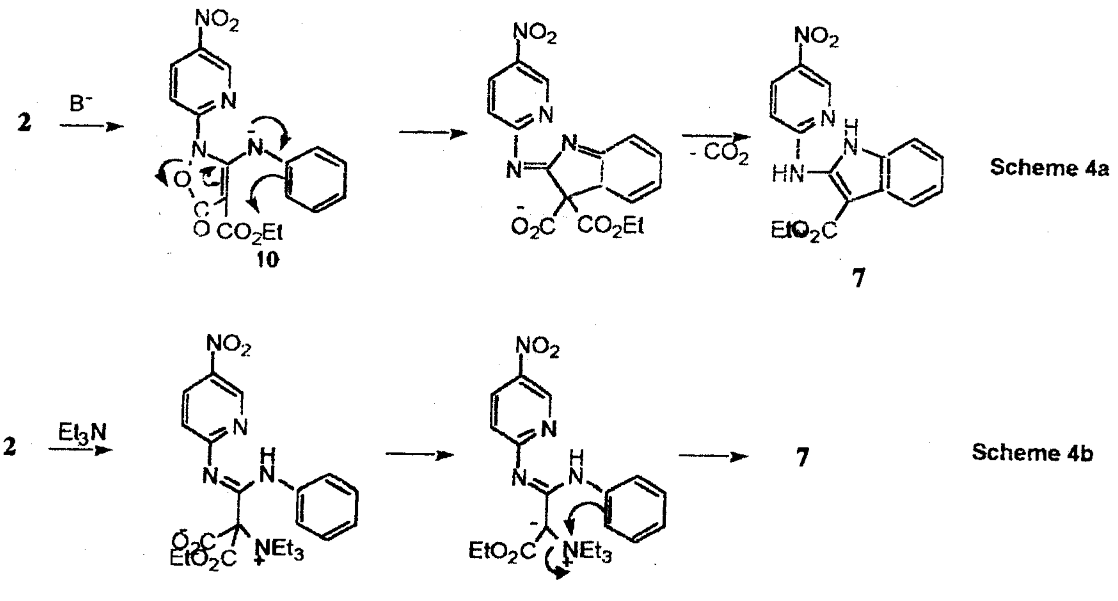


Scheme 3

Discussion

We have previously reported the synthesis of isoxazolones **2** and **3** [9] from the reaction of **1** with the corresponding chloro azines. Similarly, **1** reacted with 4-chloro-2-phenylquinazoline to give **4**, although, as expected, the reaction was more facile than those leading to **2** and **3**. Each of the compounds **2-4** was found to react with base. While the use of potassium t-butoxide in tetrahydrofuran gave a complex mixture, the use of triethylamine in ethanol gave a clean reaction leading to a single product (71-78%) in each case. The products obtained, **7-9**, were quite different in character to those akin to **6**, and have all resulted from the loss of CO_2, and are formally the same as those derivable from the carbene which arises from pyrolytic reactions (see further). However, when the compounds **2-4** were heated overnight at 80°C in the absence of base, no reaction occurred; the requirement for base is thus clearly indicated.

The nitropyridine **2** gave the indole **7** after 1 hour at 80°C in refluxing ethanol containing triethylamine. This product had previously been obtained [9] from **2** by flash vacuum pyrolysis (49%) or photolysis (89%), reactions in which the carbene **10** is implicated (Scheme 3). It is inconceivable that a carbene would be formed so readily



Scheme 4

at 80°C, or that it would not be consumed by the ethanolic solvent, so we considered two possible pathways (Schemes 4a, 4b).

Scheme 4a is not consistent with the products **8** and **9** obtained from **3** and **4**, respectively. Both **3** and **4** required considerabnly longer (20 hours at 80°C rather than 1hour at 80°C) to go to completion, and the sole product was the imidazoisoquinoline and imidazoquinazoline, respectively.

Compound **8** is also the sole product from the carbene **11**, when generated from **3** by flash vacuum pyrolysis, but photolysis of **3** apparently leads to an excited state of **11** which additionally gives the indole **12** [9]. Likewise, **4** gives **9** from the carbene **13** on flash vacuum pyrolysis (poor yield), and gives a complex mixture on photolysis. Scheme 4b, therefore, appears to best explain the formation of **7**, and an adaptation (Scheme 5) rationalises the formation of **8** and **9**; presumably the higher

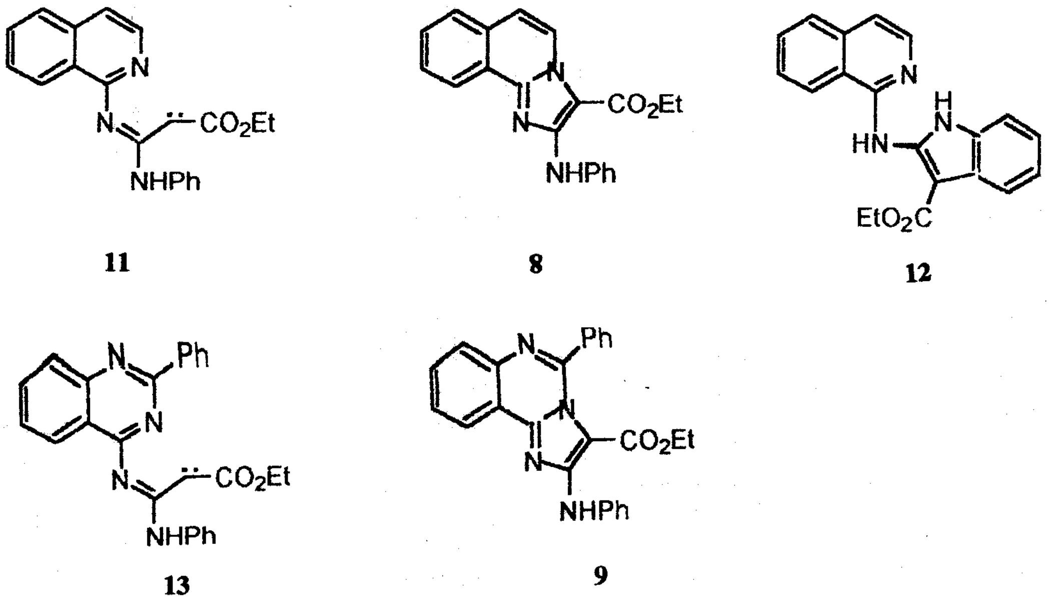
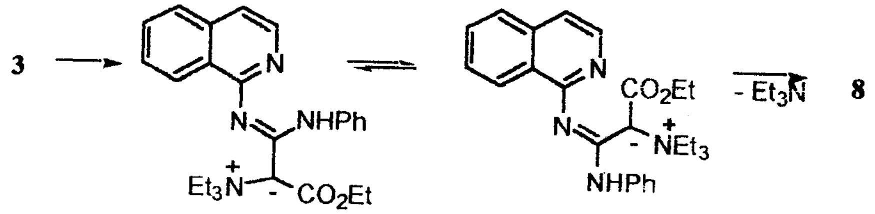
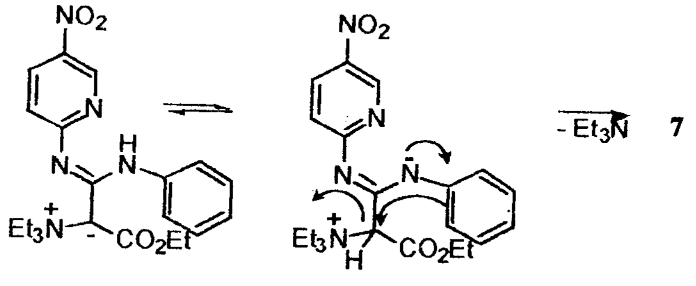


Figure 2



Scheme 5



Scheme 6

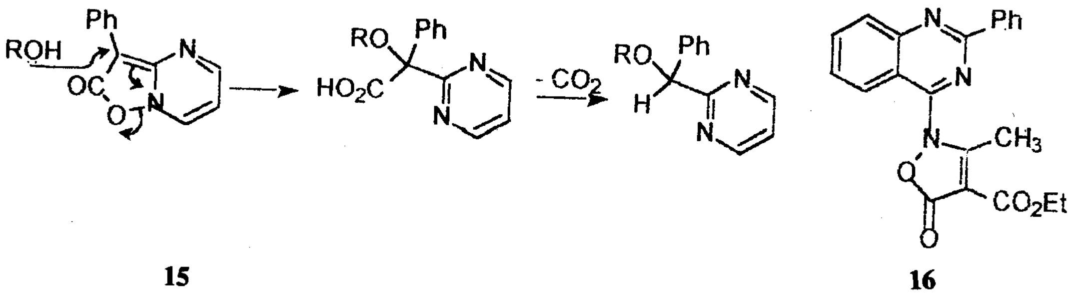
nucleophilicity of the isoquinoline and quinazoline drive the reaction in favour of the imidazole product. It is possible that the speed of indole formation in the case of 7 is due to the greater acidity of the arylamino group in the crucial intermediate 14 (Scheme 6).

The addition of a nucleophile to C-4 of the isoxazolone has not been noted by us previously, but has been invoked by Zvilichovsky [23] to rationalise the replacement of a carboxy group by an alkoxide in the isoxazolo [2,3-a] pyrimidine 15 (Scheme 7). However, the crucial role of the phenylamino group in this reaction is still not understood, as exposure of the quinazoline 16 to triethylamine in refluxing ethanol led only to the recovery of unreacted starting material. Reaction under more strongly basic conditions, sodium ethoxide in ethanol, gave only 4-ethoxy-2-phenylquinazoline. Direct nucleophilic substitutions of an isoxazolone group from a quinazoline have been noted previously [24].

Finally, Scheme 5 would suggest that larger bases would slow down the rate of reaction if they were required to act as nucleophiles, but have little effect if they reacted with the solvent, ethanol, to produce the required nucleophile. The reaction of the quinazoline 4 with diisopropylethylamine in refluxing ethanol gave the imidazoquinazoline 9 at a rate considerably slower than with triethylamine, consistent with the amine acting as a nucleophile. When 2-propanol was used as solvent instead of ethanol at 80°C, imidazoquinazoline 9 was obtained in 90% yield; the improvement is believed to be due to the lower solubility of product 9 in 2-propanol, allowing precipitation as the reaction progressed. Reaction in dichloroethane at 80°C proceeded at a rate comparable to that in ethanol (75% yield).

Experimental Section

Freshly distilled solvents were used throughout, and



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Scheme 7

anhydrous solvents were dried according to Perrin [25]. Melting points were determined on a Reichert hot stage microscope and are uncorrected. ^1H (300 MHz) and ^{13}C (75.5 MHz) n.m.r measurements were determined on a Gemini Varian 300 nuclear magnetic resonance spectrometer in deuterochloroform ($CDCl_3$) with tetramethylsilane (TMS) as an internal standard. Infrared spectra were recorded on a Perkin Elmer 1600 FT-infrared spectrophotometer, using fused sodium chloride cells. Solids were measured as nujol mulls and liquids as films. Mass spectra and high resolution mass spectra were recorded on a Kratos MS25RF spectrometer. Microanalyses were performed by the Australian Microanalytical Service, Melbourne and the Chemical & Micro Analytical Services Pty. Ltd, Essendon North.

Ethyl 5-oxo-3-phenylamino-2,5-dihydroisoxazole-4-carboxylate, 1

The isoxazolone was prepared by the method of Worral [26], mp 166-167°C (67%). (Found M+ 248.0798. Calc. for $C_{12}H_{12}N_2O_4$, 248.0797). 1H NMR ($CDCl_3$/CF_3CO_2H) δ 1.28 (t, J 7Hz, 3H), 4.25 (q, J 7Hz, 2H), 7.23 (m, 3H), 7.35 (m, 2H), 9.23 (bs, 2H), ^{13}C NMR ($CDCl_3$/CF_3CO_2H) δ 13.7, 60,9, 75.8, 122.5, 127.2, 129.9, 134.8, 162.8, 164.1, 169.8. IR: ν_{max} 3355, 1746, 1616, 1596, 1552, 1463, 1418, 1326, 1244, 1179, 1105, 1024, 983 cm^{-1}. MS: m/z 248 (M^+), 204, 176, 175, 131, 120, 119, 93, 77, 51, 45, 44.

Ethyl 2-(5-nitropyridin-2-yl)-5-oxo-3-phenylamino-2,5-dihydroisoxazole-4-carboxylate, 2

Isoxazole 1 (496 mg, 2 mmol) and 2-chloro-5-nitropyridine (317 mg, 2 mmol) were heated neat under nitrogen in an oil bath at 140°C for 2 hours. The product was passed through a short plug of silica in dichloromethane, and the residue was recrystallised from ethanol as yellow needles (535 mg, 72%), mp 170-171°C, (Found C, 55.3, H, 3.6, N, 15.3%, M^+ 370.0920. Calc. for $C_{17}H_{14}N_4O_6$ requires C, 55.1, H, 3.8, N, 15.1%, M^+ 370.0913). ^1H NMR ($CDCl_3$)δ 1.25 (t, J 7Hz, 3H), 4.22 (q, J 7 Hz, 2H), 7.12-7.18(m, 3H), 7.27(t, J 7.3Hz, 2H) 7.55 (d, J 9 Hz, 1H), 8.55 (dd, J9, 2.6 Hz, 1H), 8.88 (d, J 2.6 Hz, 1H), 10.40 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 14.1, 60.9, 78.8, 114.9, 122.1, 126.5, 129.4, 134.4, 137.7, 141.5, 143.5, 153.9, 160.3, 163.2, 163.8. IR: ν_{max} 3200, 1783, 1672, 1598, 1587, 1553, 1526, 1498, 1456, 1407, 1341, 1211, 1201, 1026, 757 cm^{-1}. MS: m/z 370 (M^+, 3), 326 (71), 280 (27), 234 (18), 160 (12), 104 (20), 77 (13), 46 (67), 45 (100), 44 (59).

Reaction of 2 with triethylamine

The isoxazolone 2 (74 mg, 0.2 mmol) and triethylamine (0.15 ml) were refluxed in ethanol (7 ml) for 1hour. The solvent was removed, and the solid was recrystallised from ethanol to give ethyl 2-(5-nitropyridine-2-amino) indole-3-carboxylate, 7, as yellow needles, mp 199-200°C (51 mg, 78%). (Found C, 58.8, H, 4.2, N, 17.2%, M^+ 326. 1014. Calc. for $C_{16}H_{14}N_4O_4$ requires C, 58.9, H, 4.3, N, 17.2%, M^+ 326.1015). ^1H NMR ($CDCl_3$) δ 1.55 (t, J 7Hz, 3H), 4.56 (q, J7 Hz, 2H), 7.08 (t, J 7.5 Hz, 1H), 7.36 (d, J 7.8 Hz, 1H), 7.39 (d, J 7.5 Hz, 1H), 7.57 (d, J 9.6 Hz, 1H), (7.72,1H) (m, 2H), 8.15 (dd, J 9.6, 2.1 Hz, 1H), 8.93 (bs, 1H, NH), 9.87 (bs, 1H, NH). ^{13}C NMR ($CDCl_3$) δ 14.5, 61.0, 98.9, 100.0, 114.1, 118.8, 122.5, 123.0, 127.0, 129.3, 137.0, 139.4, 152.5, IR: ν_{max} 3315, 1662, 1619, 1601, 1575, 1459, 1433, 1344, 1309, 1274, 1211, 749 cm^{-1}. MS: m/z 326 (M^+, 100), 280 (46), 234 (27), 206 (10), 130 (11), 104 (17), 103 (15), 77 (36), 51 (13), 44 (15).

Pyrolysis of 2

The isoxazolone 2 (150 mg) was pyrolysed under FVP conditions (540°C, 140-150°C, 0.05 mm, 2hours). The red sticky solid was collected from the tube and cold trap, and eluted through a short plug of silica with dichloromethane. The product, the indole 7, was recrystallised from light petroleum/ dichloromethane (1:1) as yellow needles, mp 199-200°C (65 mg, 49%), with spectral data identical with those above.

Photolysis of 2

A solution of the isoxazolone 2 (150 mg) in a acetonitrile (170 ml) was irradiated at 254 nm for 15 minutes. The solvent was removed, and tlc analysis indicated that only one product was present. The residue was passed through a short plug of silica in dichloromethane, and the resulting solid was recrystallised from light petroleum/ dichloromethane (1:1) to give indole 7 as yellow needles, mp 200°C (118 mg, 89%), whose spectral data were identical to those reported above.

Ethyl 2-(isoquinolin-1-yl)-5-oxo-3-phenylamino-2,5-dihydroisoxazole-4-carboxylate, 3

The isoxazolone 1 (100 mg, 0.4 mmol) and 1-chloroisoquinoline (70 mg, 0.42 mmol) were refluxed in chlorobenzene (5 ml) for 4 hours. The solvent was removed, and the mixture was separated by radial chromatography, eluting with ether/light petroleum (80: 20). Three fractions were isolated and identified. The first was unreacted 1-chloroisoquinoline; the second was 1-hydroxyisoquinoline, and the third fraction was the title compound, which was recrystallised from ethanol as cream needles, mp 159-161°C (68 mg, 45%). (Found C, 67.2, H, 4.4, N, 11.2%. Calc. for $C_{21}H_{17}N_3O_4$ requires C, 67.2, H, 4.6, N, 11.2%). ^1H NMR ($CDCl_3$) δ 1.43, (t, J 7 Hz, 3H), 4.44 (q, J 7 Hz, 2H), 6.73 (t, J 7.8 Hz, 1H), 6.81 (t, J 7.8 Hz, 3H), 6.98 (d, J 7.8 Hz, 2H), 7.45 (d, J 5.5 Hz, 1H), 7.22 (m, 3H), 7.99 (d, J 5.5 Hz, 1H), 8.40 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 14.5, 60.8, 79.1, 122.4, 122.9, 124.5, 124.6, 125.9, 126.7, 128.7, 128.8, 131.3, 136.0, 137.8, 140.5, 149.2, 165.0, 165.5, 166.6. IR: ν_{max} 3155, 1772, 1624, 1349, 1215, 1125, 1038, 795, 762, 744 cm^{-1}. MS: m/z 331 (M$^+$-CO_2, 74), 285 (76), 257 (15), 128 (30), 119 (34), 91 (21), 77 (24), 44 (100).

Reaction of 3 with triethylamine

The isoxazolone (37 mg) and triethylamine (0.1 ml) were refluxed in ethanol (4 ml) for 20 hours. The solvent was removed, and the residue was recrystallised from light petroleum/chloroform (4:1) to give ethyl 2-phenylaminoimidazo [2,1-a]isoquinoline-3-carboxylate, **8** as a pale cream solid, mp 100-101°C (24 mg, 71%). (Found M$^+$ 331.1350. Calc. for $C_{20}H_{17}N_3O_2$ M$^+$ 331.1321). ^{1}H NMR ($CDCl_3$) δ 1.52 (t, J 7Hz, 3H), 4.51, (q, J 7 Hz, 2H), 7.02 (t, J 7.2 Hz, 1H), 7.16 (d, J 7.8 Hz, 1H), 7.39 (t, J 7.2 Hz, 2H), 7.65 (m, 3H), 7.74 (m, 1H), 7.88 (d, J 7.8 Hz, 2H), 8.71 (m, 1H), 8.82 (bs, 1H, NH). ^{13}C NMR ($CDCl_3$) δ 14.5, 60.2, 99.3, 112.7, 117.8, 121.4, 121.9, 124.1, 124.7, 126.7, 127.8, 129.1, 129.4, 130.1, 140.9, 143.9, 161.4. IR: ν_{max} 1687, 1656, 1602, 1572, 1248, 1213, 1115, 1077, 793, 748 cm^{-1}. MS: m/z 331 (M$^+$, 7), 285 (9), 179 (9), 163 (13), 128 (28), 119 (36), 84 (100), 47 (22).

Pyrolysis of 3

The isoxazolone **3** (60 mg) was pyrolised under FVP conditions (540°C, 130-140°C, 0.15 mm, 1 hour). The product condensed at the end of the pyrolysis tube, and was collected in dichloromethane, and passed through a short silica plug. The product was recrystallised from light petroleum/chloroform (4:1) to give the imidazoisoquinoline **8** as a cream solid, mp 100-101°C (28 mg, 53%), whose spectral data were identical with those reported above.

Ethyl 5-oxo-3-phenylamino-2-(2-phenylquinazolin-4-yl)-2,5-dihydroisoxazole-4-carboxylate, 4

The isoxazolone **1** (248 mg, 1 mmol) and 4-chloro-2-phenylquinazoline (240.5 mg, 1 mmol) were refluxed in dichloromethane (6 ml) for 8 hours. The cooled solution was filtered and passed through a short plug of silica. Removal of solvent gave a white solid which was recrystallised from ethanol to give the title compound as white needles, mp 187-188°C (402 mg, 89%). (Found C, 69.1, H, 4.3, N, 12.4%, M$^+$ 452.1484. $C_{26}H_{20}N_4O_4$ requires C, 69.0, H, 4.4, N, 12.4%, M$^+$ 452.1484). ^{1}H NMR ($CDCl_3$) δ 1.47 (t, J 7.2 Hz, 3H), 4.49 (q, J 7.2 Hz, 2H), 6.74 (tt, J 7.2, 2.1 Hz, 1H), 6.79-6.86 (m, 2H), 7.07 (dd. J 7.8, 2.1 Hz, 2H), 7.42-7.52 (m, 3H), 7.70 (ddd, J 8.1, 6.9, 1.5 Hz, 1H), 7.93 (ddd, J 8.1, 6.9, 1.5 Hz, 1H), 8.03 (bd, J 8.4 Hz, 1H), 8.25-8.31 (m, 2H), 8.42 (dd, J 8.4, 1.5 Hz, 1H), 10.23 (bs, 1H, NH). ^{13}C NMR ($CDCl_3$) δ 14.4, 61.0, 79.1, 117.9, 121.7, 124.8, 126.3, 128.4, 128.5, 128.8, 129.2, 131.2, 135.0, 136.3, 136.4, 153.4, 156.8, 159.3, 164.4, 165.3, 165.8. IR: ν_{max} 3268, 3066, 1780, 1671, 1627, 1598, 1587, 1482, 1346, 1203, 1040, 773 cm^{-1}. MS: m/z 452 (M$^+$, 12), 408 (100), 362 (68), 337 (16), 232 (11), 216 (17), 205 (64), 181 (15), 102 (22), 77 (34), 51 (10), 44 (34).

Reaction of 4 with triethylamine

The isoxazolone (90 mg, 0.2 mmol) and triethylamine (0.2 ml) were refluxed in ethanol (8 ml) for 20 hours. The mixture was cooled to 0°C and the resulting precipitate was collected to give ethyl 5-phenyl-2-phenylaminoimidazo [2,1-a]quinazolin-3-carboxylate, **9** as pale cream needles, mp 150-151°C (60 mg, 74%), recrystallised from ethanol. (Found C, 73.4, H, 4.8, N, 13.7%, M$^+$ 408.1592. $C_{25}H_{20}N_4O_2$ requires C, 73.5, H, 4.9, N, 13.7%, M$^+$ 408.1586). ^{1}H NMR ($CDCl_3$) δ 0.83 (t, J 7.2 Hz, 3H), 3.70 (q, J 7.2 Hz, 2H), 7.06, (tt, J 7.5, 1.2 Hz, 1H), 7.40 (t, J 7.5 Hz, 2H), 7.51 (m, 3H), 7.64 (ddd, J 8.1, 7.2, 1.2 Hz, 1H), 7.76 (ddd, J 8.4, 7.2, 1.5 Hz, 1H), 7.85 (dd, J 8.7, 1.2 Hz, 2H), 7.92-7.96 (m, 2H), 7.98 (ddd, J 8.4, 1.2, 0.6 Hz, 1H), 8.62 (ddd, J 8.1, 1.5, 0.6 Hz, 1H), 8.72 (bs, 1H, NH). ^{13}C NMR ($CDCl_3$) δ 13.6, 60.3, 98.9, 116.5, 118.5, 119.1, 122.1, 124.1, 126.4, 127.9, 128.0, 128.7, 129.2, 130.4, 131.8, 137.4, 140.4, 143.0, 147.4, 148.0, 155.8, 161.4, IR: ν_{max} 3331, 1654, 1605, 1575, 1499, 1439, 1353, 1236, 1229, 1089, 765 cm^{-1}. MS: m/z 408 (M$^+$, 100), 362 (71), 361 (54), 334 (15), 205 (47), 181 (21), 103 (18), 77 (25), 51 (8).

When the reaction above was carried out in refluxing 2-propanol for 20 hours, the yield of **9** was 90%, and in refluxing dichloroethane for 20 hours, the yield was 75%.

Pyrolysis of 4

The isoxazolone (90 mg) was pyrolysed under FVP conditions (540°C, 155-165°C, 0.05 mm, 1.5 hours). The total pyrolysate was recrystallised from ehtanol to give ethyl 5-phenyl-2-phenylaminoimidazo [2,1-a]quinazolin-3-carboxylate as cream needles, mp 150°C (31 mg, 38%), whose spectral data were identical to those reported above.

Photolysis of 4

The isoxazolone (100 mg) in acetonitrile (120 ml) was irradiated at 254 nm for 30 minutes. The solvent was removed and the product was analysed by tlc and ^{1}H NMR spectroscopy, which indicated the presence of a trace of starting material and a mixture of products, including ethyl 5-phenyl-2-phenylaminoimidazo[2,1-a] quinazolin-3-carboxylate. Attempted chromatographic separation was unsuccessful.

Reaction of ethyl 5-oxo-3-methyl-2-(2-phenylquinazolin-4-yl)-2,5-dihydroisoxaole-4-carboxylate, 16, with base

The isoxazolone **16** [1] (80 mg) was treated with a solution of sodium (40 mg) in ethanol (5 ml) for 1hour at 25°C. Tlc showed that no reaction had occurred, and the mixture was refluxed for 30 minutes, then diluted with water (5 ml). The precipitate, colourless needles, mp 57-58°C, was collected and shown to be 4-ethoxy-2-phenylquinazoline (43 mg) by comparison of its ^{1}H nmr spectrum and mass spectrum with those of an authentic sample [27].

Acknowledgements

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