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International Journal of Current Research
Vol. 6, Issue, 09, pp.8418-8422, September, 2014

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

ISSN: 0975-833X

RESEARCH ARTICLE

SYNTHESIS OF 1-(2-(4-SUBSTITUTEDPHENYLAMINO)-IMIDAZO[2,1-B] BENZOXAZOL-3-YL)-ETHANONE

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ARTICLE INFO

Article History:
Received 21st June, 2014
Received in revised form
06th July, 2014
Accepted 10th August, 2014
Published online 18th September, 2014

Key words:

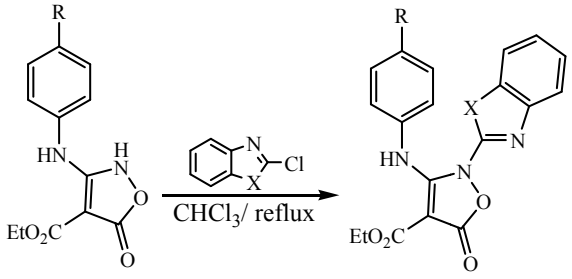
Isoxazolones, 2-chlorobenzo[d]oxazole,
Imidazobenzoxazol,
Base induced rearrangements.

ABSTRACT

4-acetyl-3-(4-substitutedphenylamino)-isoxazole-5(2H)-one, substituted on nitrogen with a 2-chlorobenzo[d] oxazole group, reacts with triethylamine (TEA) in ethanol under reflux conditions to provide a convenient synthesis of 1-(2-(4-substitutedphenylamino)-imidazo-[2,1-b]-benzoxazol-3-yl)-ethanone.

INTRODUCTION

The synthesis of 3-Arylamino isoxazol-5(2H)-one with benzoxazol substituted on nitrogen 1 has been reported (Khalafy *et al.,* 2006) by Khalafy and co-workers as shown in Scheme I.



1

1 X= O R= H, Br, Me

Scheme I

It has been reported (Khalafy *et al.,* 2006) that the 2-benzothiazol-2-yl isoxazolones 2gave the corresponding imidazobenzothiazoles3 respectively.

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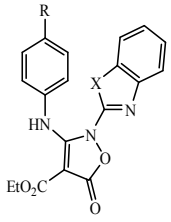
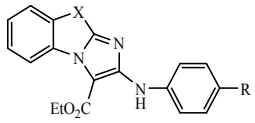


2

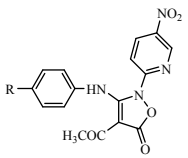
2 X= S
R=H, Br, Me, CO_2Et, NO_2



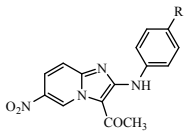
3

3 X= S
R=H, Br, Me, CO_2Et, NO_2

In previous studies we have shown (Azimi *et al.,* 2013) rearrangement of 4-acetyl-3-(4-substituted phenylamino)-isoxazol-5(2H)-ones substituted on nitrogen with an 2-chloro-5-nitropyridine group (4, R: Br, Me, OMe) to Imidazo [1, 2-a]pyridines (5, R: Br, Me, OMe) under Flash-Vacuum-Pyrolysis (F.V.P) conditions.



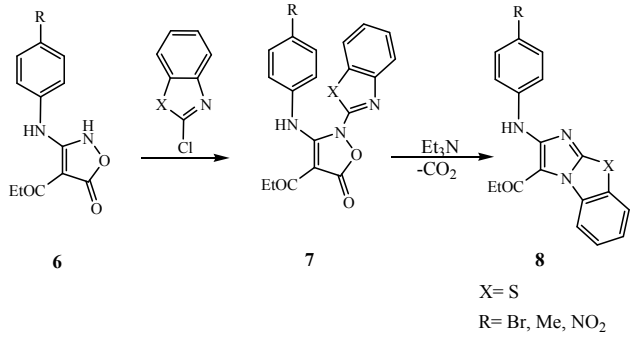
4, R: Br, Me, OMe



5, R: Br (90%), Me (93%), OMe (95%)

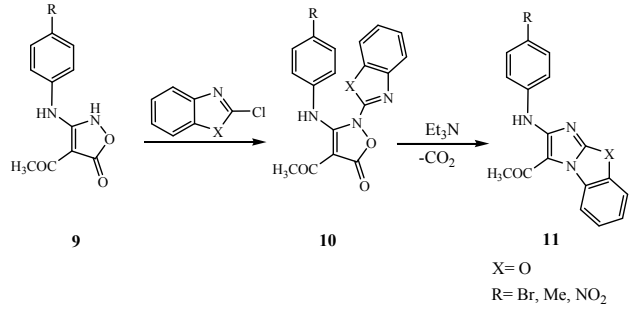
We have also reported (Azimi *et al.,* 2014) synthesis of new N-substituted derivatives of P-substituted 4-

(substitutedphenylamino)isoxazol-5(2H)-ones 6 with a 2-chlorobenzothiazole group substituted on N-2 7, and their rearrangement in the presence of triethylamine to produce 1-(2-(4-substitutedphenylamino)-imidazo[2,1-b] benzothiazole-3-yl) propan-1-one 8, as shown in (Scheme II).



Scheme II

In this paper we report the synthesis of new N-substituted derivatives of P-substituted 4-acetyl-3-(4-substitutedphenylamino)-5(2H)-one 9 with a 2-chloro benzoxazol group substituted on N-2 10, and their rearrangement in the presence of triethylamine to produce 1-(2-(4-substitutedphenylamino)-imidazo[2,1-b] benzoxazol-3-yl) ethanone11, as shown in (Scheme III).

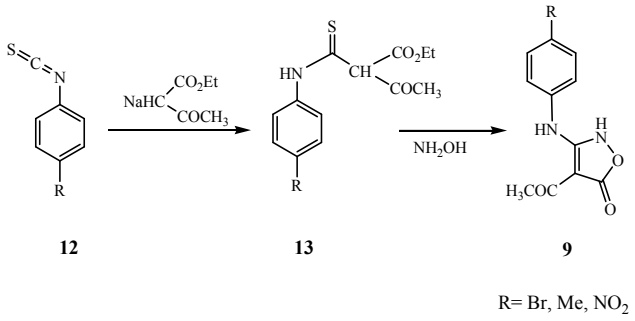


Scheme III

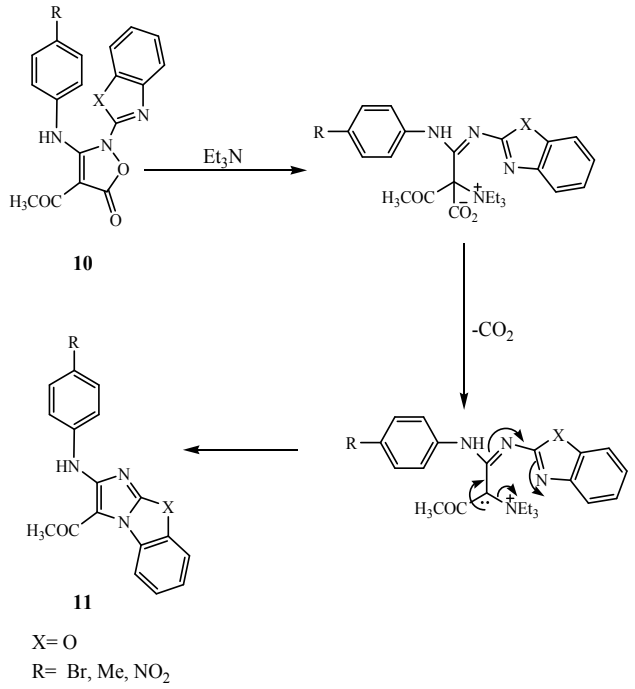
RESULTS AND DISCUSSION

The required isoxazolones10 were synthesized by reaction of 2-chlorobenzoxazol with 2H-isoxazolones 9, which in turn were made by a modification of the procedure of Worrall.(Worrall1923; Worrall1918)Thus, the reaction of the sodium salt of ethylacetoacetate in ethanol with 4-phenylisothiocyanates 12 gave the thiocarbamates13 in high yield, and these were converted to the corresponding isoxazolone7 by reaction with 2 equiv of hydroxylamine (Scheme IV).

N-arylation of 9 with 2-chlorobenzoxazol in toluene under reflux conditions gave the corresponding N-substituted isoxazolones10 in medium yield. The rearrangement of N-substituted isoxazolones10, as shown in (Scheme III), proceeded in 45-70% yield in refluxing ethanol for 72 h in the presence of triethylamine (TEA). The reaction pathway leading to the imidazobenzoxazol is consistent with our earlier suggestion for the formation of imidazopyridines, which is consistent with the electronic requirements of the reaction, as shown in (Scheme V), or with the alternative pathway suggested by Prager and co-workers. (Prager *et al.,*1994)



Scheme IV



Scheme V

Experimental

Freshly distilled solvents were used throughout, and anhydrous solvents were dried according to Perrin and Armarego. (Perrin and Armarego1988) Melting points were determined on a Philip Harris C4954718 apparatus and are uncorrected. Infrared spectra were recorded on a Thermonicolet (Nexus 670) FT-infrared spectrometer, using sodium chloride cells and measured as Nujol mulls or KBr. ^{1}H (300 MHz) and ^{13}C (300 MHz) NMR measurements were recorded on a Bruker 300 spectrometer in DMSO-d_6 or $CDCl_3$ using TMS as the internal reference. High resolution mass spectra were recorded on a Varian Matt 311 spectrometer. Mass spectra were registered in a HP 5973 MSD connected to HP 6890 GC interfaced by a Pentium PC and relative abundances of fragments are quoted in parentheses after the m/zvalues. Microanalyses were performed on a Leco Analyzer 932.

Ethyl- 2-((4-bromophenyl)carbamothioyl)-3-oxobutanoate (13, R: Br)

In a 100 mL round-bottomed flask, absolute ethanol (60 mL) was reacted with sodium (2.9 g, 0.126 mol) and after cooling to room temperature ethylacetoacetate (20 g, 18.90 mL, 0.155mol) was added. The reaction mixture was stirred at room temperature for 30 min; 4-bromophenyl isothiocyanate (26.82 g, 0.126 mol) was added and the stirring was continued for a further 8 h, during which a yellowish white precipitate of sodium ethyl-2-((4-bromophenyl) carbamothioyl)- 3-oxobutanoate salt was formed. The salt was collected and washed with light petroleum ether (b.p. 30-55 ºC) (4 × 50 mL) to give yellow crystals m.p. 161-167 ºC (30.14 g, 70%). The pure salt was dissolved in water (50 mL) and neutralized with dropwise addition of HCl (10%) to maintain the pH at 7. The product was extracted with dichloromethane (CH_2Cl_2) and the extract was washed with water (4 × 50 mL) and dried over anhydrous Na_2SO_4. Removal of solvent gave (13, R: Br) as a yellow oil (19.8g, 68%).

^{1}H-NMR($CDCl_3$)(δppm): 1.3 (t, J=7.1Hz, 3H), 2.9 (s, J=7.1Hz, 3H), 4.12 (q, J=7.1Hz, 2H), 5.09 (s, 1H), 7.55 (d, J=8.6Hz, 2H), 7.73 (d, J=8.6Hz, 2H), 10.9 (bs, 1H, NH).
^{13}C-NMR($CDCl_3$)(δppm): 14.1, 27.8, 63.63, 79.1, 128.37, 132.37, 137.89, 166.08, 188.05.
FT-IR: 3285, 1759, 1723, 1548, 1431, 1285, 1146, 1023, 831 cm^{-1}.

Ethyl-2-((4-methylphenyl)carbamothioyl)-3- oxobutanoate (13, R: Me)

This compound was prepared as described above, using 4-methylphenyl isothiocyanate (1.34 g, 9 mmol) and stirring for a further 2 h after addition of 4-methylphenyl isothiocyanate to the ethylacetoacetate salt to give ethyl-2-((4-methylphenyl)carbamothioyl)-3-oxobutanoate (1.92, 71.25%) as pale yellow solid, m.p. 56-59 ºC.

^{1}H-NMR($CDCl_3$)(δppm): 1.3 (t, J=7.1Hz, 3H), 2.9 (s, J=7.1Hz, 3H), 2.35 (s, J=7.1Hz, 3H), 4.12 (q, J=7.1Hz, 2H), 5.09 (s, 1H), 7.23 (d, J=8.3Hz, 2H), 7.66 (d, J=8.3Hz, 2H), 10.77 (bs, 1H, NH).
^{13}C-NMR($CDCl_3$)(δppm): 14.2, 23.57, 27.8, 63.47, 79.2, 126.64, 129.86, 136.41, 166.16, 187.68.
FT-IR : 3284,1760, 1723, 1515, 1430, 1315, 1223, 1148, 1020, 831 cm^{-1}.

Ethyl-2-((4-nitrophenyl)carbamothioyl)-3- oxobutanoate (13, R: NO_2)

This compound was prepared as described above, using 4-nitrophenyl isothiocyanate (1.62 g, 9 mmol) and stirring for a further 2 h after addition of 4-nitrophenyl isothiocyanate to the ethylacetoacetate salt to give ethyl-2-((4-nitrophenyl)carbamothioyl)-3-oxobutanoate (1.9, 69.25%) as pale yellow solid, m.p. 51-54 ºC.

^{1}H-NMR($CDCl_3$)(δppm): 1.3 (t, J=7.1Hz, 3H), 2.9 (s, J=7.1Hz, 3H), 4.12 (q, J=7.1Hz, 2H), 5.09 (s, 1H), 6.8 (d, J=8.3Hz, 2H), 7.89 (d, J=8.3Hz, 2H), 10.77 (bs, 1H, NH).
^{13}C-NMR($CDCl_3$)(δppm): 14.2, 27.9, 62.47, 79, 123.64, 129.86, 136.41, 143.43, 166.16, 187.68, 199.
FT-IR : 3284,1760, 1723, 1515, 1430, 1350, 1315, 1223, 1148, 1020, 831 cm^{-1}.

4-acetyl-3-(4-bromo phenylamino) isoxazol-5(2H)-ones (9, R: Br)

To a solution of hydroxylamine hydrochloride (7.06 g, 102 mmol) in water (30 mL), sodium bicarbonate (10.17 g, 102 mmol) was added slowly. Ethanol (80 mL) was added and the resulting potassium chloride was filtered off. Ethyl-2-(4-bromophenyl) carbamothioyl)-3-oxobutanoate (13, R: Br) 12.71g, 34 mmol) was added to the filtrate and the mixture was stirred at room temperature for 24 hours. The reaction mixture was acidified with dilute HCl and the white precipitate was collected and recrystallized from acetone to give the title product (8.78 g, 79%) as colourless needles, m.p: 200-202 ºC (dec.);

^{1}H-NMR (D_6-DMSO)δ(ppm) 2.25(s, J=7.1Hz, 3H, CH_3), 7.37(d, J=8.4Hz, 2H, Ar), 7.57(d, J=8.4Hz, 2H, Ar), 8.30 (bs, 1H, NH), 9.39 (bs, 1H, NH).

^{13}C-NMR (D_6-DMSO)δ(ppm) 15.31, 74.69, 118.02, 125.08, 132.94, 137.10, 163.53, 164.74, 167.39.

FT-IR ν_{max} 3250, 2950, 2740, 1723, 1696, 1666, 1607, 1563, 1456, 1398, 1316, 1183, 1018, 818 cm^{-1}.

4-acetyl-3-(4-methyl phenylamino) isoxazol-5(2H)-ones(9, R: Me)

This compound was prepared as described above using Ethyl-2-(4-methylphenyl) carbamothioyl)-3-oxobutanoate(13, R: Me) and Refluxing for 24 hours gave colourless crystals (85%), m.p: 164-166 ºC (dec.).

^{1}H-NMR (D_6-DMSO+$CDCl_3$)δ(ppm) 2.30 (s, J=7.0Hz, 3H, CH_3), 2.35 (s, 3H, Me), 6.78 (d, J=9.2Hz, 2H, Ar), 6.79 (bs, 1H, NH), 6.80(d, J=9.2Hz, 2H, Ar), 8.85 (bs, 1H, NH).
^{13}C-NMR (D_6-DMSO+$CDCl_3$,400 MHz)δ(ppm) 14.52, 20.85, 74.69, 121.53, 130.13, 133.29, 135.64, 163.59, 165.51, 166.74.
FT-IR ν_{max} 3669, 2979, 2746, 1705, 1669, 1615, 1331, 1208, 1115, 1023, 800 cm^{-1}.

4-acetyl-3-(4-nitrophenylamino)isoxazole-5(2H)-ones (9, R: NO_2)

The compound was prepared as described above using Ethyl-2-(4-nitrophenyl) carbamothioyl)-3-oxobutanoate(13, R: NO_2) (1.3 g, 4 mmol) and refluxing for 24 h to give the desired product as colourless crystals (0.5 g,65%), m.p. 162-164 ºC.
^{1}H-NMR (d_6-DMSO + $CDCl_3$)(δppm): 2.3 (s, J=7.0Hz, 3H, CH_3), 6.72 (d, J=9.2Hz, 2H), 6.84(bs, 1H, NH), 7.94 (d, J=9.2Hz, 2H), 8.8 (bs, 1H, NH).
^{13}C-NMR (d_6-DMSO+ $CDCl_3$)(δppm): 15.4, 74.69, 118.02, 125.08, 132.94, 137.10, 165.50, 167.74, 171.39.
FT-IR:3669, 2979, 2746, 1705, 1669, 1615, 1350, 1331, 1208, 1115, 1023, 800 cm^{-1}.

4-acetyl-3-(4-bromophenylamino)-2-(benzoxazol-2-yl)-isoxazol-5(2H)-ones (10, R: Br)

4-acetyl-3-(4-bromophenylamino)-isoxazole-5(2H)-one (9, R: Br)(116 mg, 0.4 mmol) and 2-chlorobenzoxazol (46 mg, 0.3 mmol) were refluxed in toluene (8 mL) for 72 h. The solvent was removed under reduced pressure. On addition of n-hexane (10 mL) to the residue (colourless oil) a white precipitate was formed. The precipitate was filtered and recrystallized from ethanol to give4-acetyl-3-(4-bromophenylamino)-2-(benzoxazol-2-yl)-isoxazol-5(2H)-onesas white prisms (81.8 mg, 61%) m.p. 156-157 ºC.

^{1}H-NMR (d_6-DMSO)(δppm): 2.3 (s, J=7.0Hz, 3H, CH_3), 6.37(d, J=8.4Hz, 2H), 7.3 (d, J=8.4Hz, 2H), 7.6 (t, J=8.4Hz, 2H), 8.7 (d, J=8.4Hz, 2H), 8.30 (bs, 1H, NH).
^{13}C-NMR (d_6-DMSO)(δppm): 26.1, 59.96, 84, 119.02, 124, 126.3, 132.94, 137.10, 163.53, 164.74, 167.39.
FT-IR :3250, 2950, 2740, 1723, 1696, 1666, 1607, 1563, 1456, 1402, 1398, 1301, 1183, 1018, 818 cm^{-1}.
MS *m/z*:(%) 413.4 (M+, 12%), 411 (M+, 11%), 405 (82), 397 (71), 371 (48), 369 (40), 334 (25), 294 (28), 291 (27), 290 (100), 262 (30), 224 (27), 177 (33), 161 (34), 150 (40), 135 (26), 134 (33), 108 (29), 44 (65).

4-acetyl-3-(4-methylphenylamino)-2-(benzoxazol-2-yl)-isoxazol-5(2H)-ones (10, R: Me)

This compound was prepared as described above, using the corresponding isoxazolone (9, R: Me) (61 mg, 0.27 mmol) and 2-chlorobenzoxazole (41.3 mg, 0.27 mmol) to give the desired product as white prisms (44 mg, 51%) after recrystalization from ethanol, m.p. 160-163 ºC.

^{1}H-NMR (d_6-DMSO)(δppm): 2.3 (s, J=7.0Hz, 3H, CH_3), 2.35 (s, 3H, Me), 6.37(d, J=8.4Hz, 2H), 7.5 (d, J=8.4Hz, 2H), 7.8 (t, J=8.4Hz, 2H), 8.3 (d, J=8.4Hz, 2H), 8.33 (bs, 1H, NH).
^{13}C-NMR (d_6-DMSO)(δppm): 24.3, 26.1, 59.96, 84, 118.02, 121, 125.3, 132.94, 137.10, 163.53, 164.74, 167.39.
FT-IR:3250, 2950, 2740, 1723, 1696, 1666, 1607, 1563, 1456, 1402, 1398, 1301, 1183, 1018, 818 cm^{-1}.
MS *m/z*:(%) 349.1 (M+, 12%), 341 (48), 325 (40), 314 (25), 294 (28), 291 (27), 290 (100), 262 (30), 224 (27), 177 (33), 161 (34), 150 (40), 135 (26), 134 (33), 108 (29), 44 (65).

4-acetyl-3-(4-nitrophenylamino)-2-(benzoxazol-2-yl)-isoxazol-5(2H)-ones (10, R: NO_2)

This compound was prepared as described above, using the corresponding isoxazolone (9, R: NO_2) (89 mg, 0.34 mmol) and 2-chlorobenzoxazole (52.1 mg, 0.34 mmol) to give the desired product as white prisms (43 mg, 49%) after recrystalization from ethanol, m.p. 168-170 ºC.

^{1}H-NMR (d_6-DMSO)(δppm): 2.3 (s, J=7.0Hz, 3H, CH_3), 6.7(d, J=8.4Hz, 2H), 7.6 (t, J=8.4Hz, 2H), 7.9 (d, J=8.4Hz, 2H), 8.3 (d, J=8.4Hz, 2H), 8.33 (bs, 1H, NH).
^{13}C-NMR (d_6-DMSO)(δppm): 26.1, 59.96, 84, 118.02, 121, 125.3, 132.94, 137.10, 163.53, 164.74, 167.39.
FT-IR :3250, 2950, 2740, 1723, 1696, 1666, 1607, 1563, 1456, 1450, 1402, 1398, 1301, 1183, 1018, 818 cm^{-1}.
MS *m/z*:(%) 380.1 (M+, 12%), 372 (48), 356 (40), 334 (25), 294 (28), 291 (27), 290 (100), 262 (30), 224 (27), 177 (33), 161 (34), 150 (40), 135 (26), 134 (33), 108 (29), 44 (65).

1-(2-(4-bromophenylamino)-imidazo-[2,1-b]-benzoxazol-3-yl)-ethanone (11, R: Br)

The isoxazolone (10, R: Br) (90.2 mg, 0.22 mmol) and triethylamine (0.4 mL) were refluxed in ethanol (10 mL) for 24 hours. The reaction mixture was left to cool to room tempreture and resulting precipitate was colleted to afford 1-(2-(4-bromophenylamino)-imidazo-[2,1-b] benzoxazole-3-yl)-ethanone as white needles (44 mg, 51%), mp 180-184 ^{o}C.

^{1}H-NMR (d_6-DMSO)(δppm): 2.55 (t, J=7.1Hz, 3H), 6.6(d, J=8.4Hz, 2H), 7.2 (t, J=8.4Hz, 1H), 7.3 (t, J=8.4Hz, 1H), 7.5 (d, J=8.4Hz, 2H), 8.2 (bs, 1H, NH).
^{13}C-NMR (d_6-DMSO)(δppm): 26.6, 46, 84, 118.02, 121, 125.3, 132.94, 137.10, 143.53, 144.74, 147.39.
FT-IR :3250, 2950, 2740, 1723, 1696, 1666, 1607, 1563, 1456, 1450, 1402, 1398, 1301, 1183, 1018, 818 cm^{-1}.
MS *m/z*:(%) 369.1 (M+, 12%), 357 (48), 340 (40), 334 (25), 298 (28), 295 (27), 293 (100), 262 (30), 224 (27), 179 (33), 161 (34), 153(40), 145 (26), 134 (33), 108 (29), 44 (65).

1-(2-(4-methylphenylamino)-imidazo-[2,1-b]-benzoxazole-3-yl)-ethanone (11, R: Me)

The isoxazolone (10, R: Me) (76.7 mg, 0.22 mmol) and triethylamine (0.4 mL) were refluxed in ethanol (10 mL) for 24 hours. The reaction mixture was left to cool to room tempreture and resulting precipitate was colleted to afford 1-(2-(4-methylphenylamino)-imidazo-[2,1-b]-benzothiazole-3-yl)-ethanone as white needles (43 mg, 50%), mp 153-157 ^{o}C.

^{1}H-NMR (d_6-DMSO)(δppm): 2.35 (s, J=7.1Hz, 3H), 2.55 (s, J=7.1Hz, 3H), 6.3 (d, J=8.4Hz, 2H), 6.9 (d, J=8.4Hz, 2H), 7.3 (t, J=8.4Hz, 1H), 7.5 (t, J=8.4Hz, 1H), 7.7 (d, J=8.4Hz, 2H), 8.2 (bs, 1H, NH).
^{13}C-NMR (d_6-DMSO)(δppm): 24.3, 26.7, 84, 118.02, 121, 125.3, 132.94, 137.10, 143.53, 144.74, 147.39.
FT-IR :3250, 2950, 2740, 1723, 1696, 1666, 1607, 1563, 1456, 1450, 1402, 1398, 1301, 1183, 1018, 818 cm^{-1}.
MS *m/z*:(%) 305.11 (M+, 12%), 300 (48), 298 (28), 295 (27), 293 (100), 262 (30), 224 (27), 179 (33), 161 (34), 153(40), 145 (26), 134 (33), 108 (29), 44 (65).

1-(2-(4-nitrophenylamino)-imidazo-[2,1-b]-benzoxazole-3-yl)-ethanone (11, R: NO_2)

The isoxazolone (10, R: NO_2) (83.6 mg, 0.22 mmol) and triethylamine (0.4 mL) were refluxed in ethanol (10 mL) for 24 hours. The reaction mixture was left to cool to room tempreture and resulting precipitate was colleted to afford 1-(2-(4-nitrophenylamino)-imidazo [2,1-b]-benzoxazole-3-yl)-ethanoneas white needles (40 mg, 47%), mp 199-204 ^{o}C.

^{1}H-NMR (d_6-DMSO)(δppm): 2.55 (s, J=7.1Hz, 3H), 6.7 (d, J=8.4Hz, 2H), 7.3 (t, J=8.4Hz, 1H), 7.5 (t, J=8.4Hz, 1H), 7.9 (d, J=8.4Hz, 2H), 8.6 (bs, 1H, NH).

^{13}C-NMR (d_6-DMSO)(δppm): 26.6, 70.96, 84, 118.02, 121, 125.3, 132.94, 137.10, 143.53, 144.74, 147.39.
FT-IR :3250, 2950, 2740, 1723, 1696, 1666, 1607, 1563, 1456, 1450, 1402, 1398, 1353, 1301, 1183, 1018, 818 cm^{-1}.
MS *m/z*:(%) 336.11 (M+, 11%), 323 (48), 310 (40), 304 (25), 298 (28), 295 (27), 293 (100), 262 (30), 224 (27), 179 (33), 171 (34), 153(40), 149 (26), 134 (33), 108 (29), 44 (65).

Conclusion

In conclusion we have shown that a variety of N-substituted isoxazolones10, rearranged with Triethylamine to give imidazo-[2,1-b]-benzoxazole. These rearrangements, therefore, appear to be generally applicable to the synthesis of imidazoheterocycles which are suitable synthetic intermediates for a series of polycyclic heterocycles with possible pharmaceutical applications.

Acknowledgment

We thanks Islamic Azad University branch of Piranshahr for financial support.

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