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SYNTHESIS OF 3-ARYL-4,5-DIHYDRO-5-HYDROXY-1,2-OXAZOLES BY REACTION OF SUBSTITUTED BENZONITRILE OXIDES WITH THE ENOLATE ION OF ACETALDEHYDE.

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Abstract-By reaction of substituted benzonitrile oxides with the enolate ion of acetaldehyde (quantitatively generated by the known cycloreversion of THF in the presence of n-butyllithium) a number of 3-aryl-4,5-dihydro-5-hydroxy--1,2-oxazoles (previously unknown or, in two cases, only synthesized by different procedures) have been isolated in high yields. Treatment of such hydroxyisoxazolines with some common bases allows their conversion in high yields into the corresponding isoxazoles.

4,5-Dihydro-1,2-oxazoles and 1,2-oxazoles (from now on, isoxazolines and isoxazoles, respectively) are interesting compounds from a synthetic point of view, owing to numerous applications as precursors of various functional groups by ring modification and cleavage.[1]

As far as isoxazoles are concerned, their synthesis can be accomplished following a number of procedures,[2] some of which using nitrile oxides,such as 1,3-dipolar addition of nitrile oxides to alkenes (followed by oxidation)[3] or to alkynes,[4] and reaction of nitrile oxides with ß--dicarbonyl compounds in presence of base,[5] in which 5-hydroxyisoxazolines are postulated as reactive intermediates.

The latter are generally considered labile compounds. However, some stable 5-hydroxyisoxazolines, such as 3-phenyl-5-hydroxy-2-isoxazoline, have been also reported.[6] This was in fact synthesized by treatment with sodium hydroxide in methanol of 3-phenyl-5-acetoxy-2-isoxazoline (obtained in turn by 1,3-dipolar cycloaddition of benzonitrile oxide to vinyl acetate), or by hydrolysis of 3-phenyl-2-isoxazolin-5-boronic acid,[7] and, on heating to ca. 200°C or under reflux with thionyl chloride, gave once again the corresponding isoxazole (3-phenylisoxazole).[6]

Recently[8] we have investigated the reaction of the enolate ion of acetaldehyde (quantitatively obtained by the known cycloreversion of THF in the presence of n-butyllithium)[9] with arylazides, obtaining in a number of cases very good yields of 1-aryl-4,5-dihydro-5-hydroxy-1H--1,2,3-triazoles (5-hydroxy-triazolines). Owing to the similarity of azides and nitrile oxides (the two system are isoelectronic), we decided to test the reaction of the same enolate ion (obtained as above) with a series of substituted benzonitrile oxides in order to synthesize by

a new simple procedure a number of (hitherto unknown) 5-hydroxyisoxazolines, and, by their dehydration, the corresponding isoxazoles.

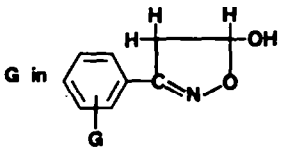
In the present paper we report the synthesis and characterization of such hydroxyisoxazolines and isoxazoles, the latter obtained by treatment of the former with some bases instead of the acidic treatment usually utilized for this purpose.[10]

RESULTS AND DISCUSSION

Various substituted benzonitrile oxides (either isolated or formed *in situ*) were allowed to react at room temperature with the enolate ion of acetaldehyde obtained by cycloreversion of THF in the presence of *n*-butyllithium. By quenching the reaction mixture with NH_4Cl/H_2O (reaction time *ca.* 1h), we isolated (and then characterized: see EXPERIMENTAL) 3-aryl-5-hydroxyisoxazolines in all cases in high yields (TABLE 1).

TABLE 1

Yields of 3-aryl-5-hydroxyisoxazolines isolated from the reaction of substituted benzonitrile oxides and the lithium enolate of the acetaldehyde in THF at room temperature.

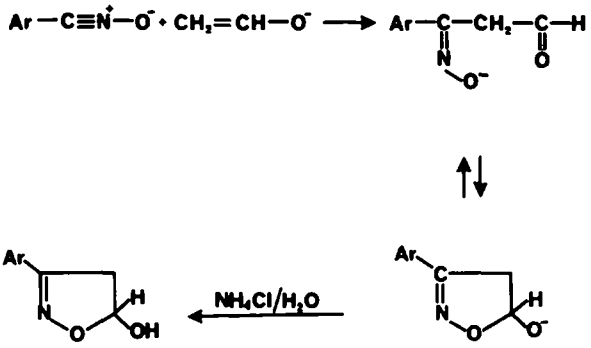


G in	Yield %
H	89
2-Chloro	83
3-Chloro	91
2,6-Dichloro	95
2,4,6-Trimethyl	97
3-Nitro	90
4-Nitro	85

Thus, not only 3-phenyl-5-hydroxy-2-isoxazoline,[6] but also all the similar terms synthesized by us are stable compounds, at variance with the very low stability[11] generally attributed to hydroxyisoxazolines (*e.g.*, as above reported, they are only postulated as intermediates in the reaction of ß-dicarbonyl compounds with nitrile oxides in the presence of hydroxides or alkoxides). Therefore, structural features are seemingly responsible for the observed stability of this kind of hydroxyisoxazolines.

As far as the mechanism of reaction is concerned, we assume a stepwise scheme, by analogy to that suggested for the formally similar reaction of the same enolate ion with arylazides affording hydroxytriazolines (SCHEME 1).

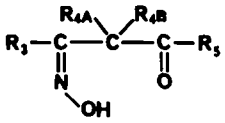
SCHEME 1



Such an hypothesis differs from the one previously suggested for the reaction in presence of base of ß-dicarbonyl compounds with benzonitrile oxide, where 1,3-dipolar cycloaddition of the latter compound to the enol form of the ß-diketone was postulated.[5] Now, because of the identical substituents (both hydrogens) on the position 4 of the isoxazoline ring, any preference for some of the otherwise possible four stereoisomers (a/a' or b/b'),

(a) (a') (b) (b')

which could give informations on the concerted or stepwise character of the reaction, cannot be observed. However, it is known[11,12] that, in the case of 5-hydroxyisoxazolines,(a/a') and (b/b') can equilibrate through the open form (c)



(c)

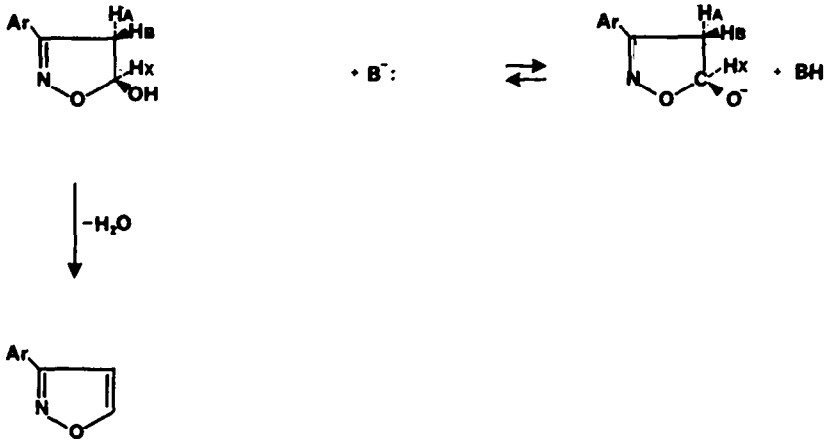
and this could well support the stepwise mechanism postulated by us, whose backbone is in fact just a similar equilibrium (involving the anionic instead of the undissociated forms).

On the other hand, 5-hydroxyisoxazolines so isolated were subjected to the action of some bases, like sodium hydroxide in EtOH or sodium methoxide in MeOH, as well as n-butyllithium or the enolate ion of acetaldehyde in THF. The enolate ion does not appreciably affect hydroxyisoxazolines (excepted for the hydrogen abstraction from hydroxy-group) even for long times of reaction and on heating under reflux. Such a behaviour was to be expected: otherwise, hardly hydroxyisoxazolines could in fact be isolated in high yields when formed from nitrile oxides and the cited enolate ion.

No appreciable reaction is also observed with n-butyllithium.

On the contrary, a similar treatment of hydroxyisoxazolines with the other above-cited bases converted them into the corresponding isoxazoles in all cases in high to nearly quantitative yields (TABLE 2). Further, it must be pointed out that simple heating under reflux and for comparable times either in methanol or in ethanol again does not appreciably affect hydroxyisoxazolines. This resembles the behaviour with bases previously observed for 5-hydroxytriazolines,[8] where triazoles could in fact be obtained in high yields in many cases. By analogy, a similar mechanism for this "base-promoted" dehydration (E_2 or an "irreversible" E_1cB) could also be hypothesized. In this light the fact that with the enolate ion of acetaldehyde (or with n-butyllithium) no appreciable dehydration of hydroxyisoxazolines is observed even after long times of reaction could be explained as follows. In presence of the enolate ion of acetaldehyde, because of its greater basicity compared to hydroxide or alkoxide ions, the equilibrium between the undissociated and dissociated form of hydroxyisoxazoline (SCHEME 2) would in fact be less shifted towards the former, likely involved in the dehydration. Correspondingly dehydration would be substantially decreased or even not observed at all. Further, a similar explanation can also be given in the case of n-butyllithium, which is much more basic compared to the enolate ion.

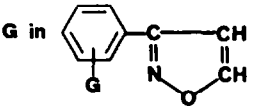
SCHEME 2



On the other hand, apart from the mechanistic aspects, these findings seem to be interesting from a synthetic point of view. In fact they clearly indicate that conversion of such hydroxyisoxazolines into the corresponding isoxazoles can satisfactorily be accomplished not only, as reported,[6] by acidic (or thermal: ca. 200°C) treatment, but also equally well simply by using some common bases.

TABLE 2

Yields of 3-arylisoxazoles obtained by dehydration of 3-aryl-5-hydroxyisoxazolines with bases at reflux temperature.

G in 		Yield %
H	a)	92
	b)	95
2-Chloro	a)	87
	b)	90
3-Chloro	a)	83
	b)	91
2,6-Dichloro	a)	quantitative
	b)	"
2,4,6-Trimethyl	a)	95
	b)	quantitative
3-Nitro	a)	90
	b)	94
4-Nitro	a)	88
	b)	95

a) base = sodium hydroxide in ethanol;

b) base = sodium methoxide in methanol.

EXPERIMENTAL

MPS taken on a Electrothermal apparatus were uncorrected. H NMR spectra were recorded on a Varian EM 360, EM 390 or XL 200 spectrometer and chemical shifts are reported in parts per million (δ) from internal Me_4Si. Absolute values of the coupling costants are reported. IR spectra were recorded on a Perkin-Elmer 681 spectrometer. Thin-layer chromatography (TLC) was performed on silica gel sheets with fluorescent indicator (stratocrom SIF, Carlo Erba). Microanalyses were performed on a Elemental Analyzer mod. 1106, Carlo Erba-instrument.

Materials. Tetrahydrofuran (THF) from commercial source (RS, Carlo Erba) was purified by distillation (twice) from sodium wire in a N_2 atmosphere. Standardized (2.4 N) n-butyllithium in hexane was from Aldrich Chemical Co..

All other chemicals were commercial grade further purified by distillation or crystallization prior to use.

Nitrile oxides. The synthesis was accomplished in all cases from aldehydes through the conversion into the corresponding oximes and then into benzohydroximinoyl chlorides. These were finally converted into nitrile oxides by treatment with Et_3N.[13-16]

Benzaldehyde oxime, m.p. 33-36°C (lit[13] 35°C); IR (neat): ν_{OH}=3700-3120 cm^{-1}; ^1H NMR (CCl_4,δ): 9.18 (s, 1H: exchange with D_2O); 7.88 (s, 1H); 7.15 (m, 5H).

2,4,6-Trimethylbenzaldehyde oxime, m.p. 124-127°C (lit[14] 124°C); IR (CH_2Cl_2): ν_{OH}= 3600 cm^{-1}, 3560-3100 cm^{-1}; ^1H NMR ($CDCl_3$,δ): 7.91 (s, 1H); 6.72 (s, 2H); 4.58 (bs, 1H: exchange with D_2O); 2.31 (s, 6H); 2.20 (s, 3H).

2-Chlorobenzaldehyde oxime, m.p. 73-76°C (lit[15] α= 75-76°C, ß=101-103°C); IR (CCl_4): ν_{OH}= 3600 cm^{-1}, 3540-3100 cm^{-1}; ^1H NMR ($CDCl_3$,δ): 8.32 (s, 1H); 7.30 (m, 4H); 1.82 (bs, 1H: exchange with D_2O).

3-Chlorobenzaldehyde oxime, m.p. 65-66°C (lit[13] 68-69°C); IR (CCl_4): ν_{OH}= 3610 cm^{-1}, 3550-3100 cm^{-1}; ^1H NMR (CCl_4,δ): 8.60 (bs, 1H: exchange with D_2O); 7.97 (s, 1H); 7.30 (m, 4H).

2,6-Dichlorobenzaldehyde oxime, m.p. 129-130°C (lit[13] 130°C); IR (CH_2Cl_2): ν_{OH}= 3590 cm^{-1}, 3490-3160 cm^{-1}; ^1H NMR (acetone-d_6,δ): 8.10 (s, 1H); 7.32 (m, 3H); 2.60 (s, 1H: exchange with D_2O).

3-Nitrobenzaldehyde oxime and 4-Nitrobenzaldehyde oxime were from Aldrich Chemical Co..

Benzohydroximinoyl chloride, m.p. 53-55°C (lit[16] 48-52°C); IR (CCl_4): ν_{OH}= 3580 cm^{-1}, 3500-3200 cm^{-1}; ^1H NMR (CCl_4,δ): 8.50 (s, 1H: exchange with D_2O); 7.40 (m, 5H).

2-Chlorobenzohydroximinoyl chloride,[13] oil; IR (CCl_4): ν_{OH}= 3600 cm^{-1}, 3540-3160 cm^{-1}; ^1H NMR (CCl_4,δ): 9.65 (s, 1H: exchange with D_2O); 7.00 (m, 4H).

3-Chlorobenzohydroximinoyl chloride, m.p. 54-58°C (lit[13] 58-61°C); IR (CCl_4): ν_{OH}= 3580 cm^{-1}, 3520-3130 cm^{-1}; ^1H NMR (CCl_4,δ): 8.53 (bs, 1H: exchange with D_2O); 7.33 (m, 4H).

2,6-Dichlorobenzohydroximinoyl chloride, m.p. 54-57°C (lit[13] 57-58°C); IR (CH_2Cl_2): ν_{OH}= 3570 cm^{-1}, 3540-3150 cm^{-1}; ^1H NMR ($CDCl_3$,δ): 8.70 (bs, 1H: exchange with D_2O); 7.12 (m, 3H).

3-Nitrobenzohydroximinoyl chloride, m.p. 94-96°C (lit[18] 101-102°C); IR ($CHCl_3$): ν_{OH}=3560 cm^{-1}, 3480-3090 cm^{-1}; ^1H NMR ($CDCl_3$,δ): 9.10 (bs, 1H: exchange with D_2O); 8.00 (m, 4H).

4-Nitrobenzohydroximinoyl chloride, m.p. 118-120°C (lit[13] 120°C); IR ($CHCl_3$): ν_{OH}= 3570 cm^{-1}, 3500-3100 cm^{-1}; ^1H NMR ($CDCl_3$,δ): 8.60 (bs, 1H: exchange with D_2O); 7.90 (m, 4H).

Benzonitrile oxide, 2-chlorobenzonitrile oxide, 3-chlorobenzonitrile oxide, 2,6-dichlorobenzonitrile oxide, 3-nitrobenzonitrile oxide and 4-nitrobenzonitrile oxide were not isolated, but prepared directly in solution of benzene by the cited procedure.[16] Their presence were checked by IR bands at 2300 cm^{-1} (C≡N) and 1370 cm^{-1} (NO).

2,4,6-Trimethylbenzonitrile oxide, m.p. 110-112°C (lit[14] 112°C); IR (CH_2Cl_2): $\nu_{C\equiv N}$= 2300 cm^{-1}, ν_{NO}= 1370 cm^{-1}; ^1H NMR ($CDCl_3$,δ): 6.70 (s, 2H); 2.31 (s, 6H); 2.20 (s, 3H).

Reaction of nitrile oxides with the enolate ion of the acetaldehyde: general procedure.

A mixture containing lithium enolate of the acetaldehyde (6 mmole) in anhydrous THF (10 ml), prepared by allowing to stand THF in the presence of n-butyllithium for ca. 16h as previously

reported,[8,9] is added dropwise and at ca. 20°C to a solution of nitrile oxide (6 mmole) in THF, using a nitrogen-flushed, three necked flask equipped with a magnetic stirrer, a nitrogen inlet and a dropping funnel. After the reaction was completed, the reaction mixture was quenched by adding aqueous NH_4Cl, the organic layer separated and the aqueous layer extracted with ethyl ether. The combined extracts were dried over Na_2SO_4 and evaporated under pressure, affording crude 5-hydroxyisoxazolines which were purified by recrystallization (solid compounds).

Reactions of 5-hydroxyisoxazolines with bases.

Solution of sodium methoxide (10 mmole) in methanol (20 ml) or sodium hydroxide (10 mmole) in ethanol (20 ml) was added to a solution of hydroxyisoxazoline (5 mmole) in the same alcohol (20 ml), using a nitrogen-flushed, 100 ml, three necked flask, equipped with a nitrogen inlet, a dropping funnel, and a reflux condenser. The reaction mixture was then heated under reflux and, when the reaction was completed (ca. 2h), was quenched with aqueous NH_4Cl. Organic layer is then separated and aqueous layer extracted with ethyl ether. The combined extracts were then dried over Na_2SO_4 and evaporated under reduced pressure affording crude isoxazoles which were purified by recrystallization or by distillation under vacuum.
By simple heating under reflux in the same alcohols without bases for even longer times no appreciable amounts of isoxazoles were observed.
Reaction with the enolate ion or n-butyllithium in THF did not afford any isoxazole even by heating under reflux for two days.

Products

3-Phenyl-5-hydroxy-2-isoxazoline, m.p. 118-124°C (hexane) (lit[7] 120-121°C); IR (CH_2Cl_2): ν_{OH}= 3590 cm^{-1}, 3480-3250 cm^{-1}; ^1H NMR (DMSO-d_6,δ): 7.57 (m, 5H); 7.08 (d, 1H: exchange with D_2O; $J_{(OH)X}$= 5.2 Hz); 5.87 (td, $1H_X$; $J_{(OH)X}$= 5.2 Hz, J_{BX}= 1.8 Hz, J_{AX}= 6.9 Hz); 3.44 (dd, $1H_A$; J_{AB}= 17.8 Hz, J_{AX}= 6.9 Hz); 3.05 (dd, $1H_B$; J_{AB}= 17.8 Hz, J_{BX}= 1.8 Hz). (Found: C, 66.26; H, 5.52; N, 8.57. Calc. for $C_9H_9NO_2$: C, 66.26; H, 5.52; N, 8.59).
3-(2,4,6-Trimethylphenyl)-5-hydroxy-2-isoxazoline, m.p. 124-126°C (hexane); IR (CH_2Cl_2): ν_{OH}= 3600 cm^{-1}, 3520-3200 cm^{-1}; ^1H NMR ($CDCl_3$,δ): 6.89 (s, 2H); 6.03 (dd, $1H_X$; J_{AX}= 6.2 Hz, J_{BX}= 1.2 Hz); 3.90 (bs, 1H: exchange with D_2O); 3.30 (dd, $1H_A$; J_{AX}= 6.2 Hz, J_{AB}= 17.8); 2.99 (dd, $1H_B$; J_{BX}= 1.2 Hz, J_{AB}= 17.8 Hz); 2.29 (s, 3H); 2.24 (s, 6H). (Found: C, 70.23; H, 7.32; N, 6.83. Calc. for $C_{12}H_{15}NO_2$: C, 70.24; H, 7.32; N, 6.83).
3-(2-Chlorophenyl)-5-hydroxy-2-isoxazoline, oil; IR (neat): ν_{OH}= 3700-3100 cm^{-1}; ^1H NMR (DMSO-d_6,δ): 7.62 (m, 4H); 7.13 (bs, 1H: exchange with D_2O); 5.92 (dd, $1H_X$; J_{AX}= 6.9 Hz, J_{BX}= 1.9 Hz); 3.48 (dd, $1H_A$; J_{AX}= 6.9 Hz, J_{AB}= 18.1 Hz); 3.12 (dd, $1H_B$; J_{BX}= 1.9 Hz, J_{AB}= 18.1 Hz). (Found: C, 54.81; H, 4.06; N, 7.11. Calc. for $C_9H_8NO_2Cl$: C, 54.82; H, 4.06; N, 7.11).
3-(3-Chlorophenyl)-5-hydroxy-2-isoxazoline, m.p. 133-136°C (benzene); IR (KBr): ν_{OH}= 3700-3100 cm^{-1}; ^1H NMR (DMSO-d_6,δ): 7.60 (m, 4H); 7.15 (d, 1H: exchange with D_2O; $J_{(OH)X}$= 6.1 Hz); 5.90 (td, $1H_X$; $J_{(OH)X}$= 6.1 Hz, J_{AX}= 7.1 Hz, J_{BX}= 1.7 Hz); 3.46 (dd, $1H_A$; J_{AX}= 7.1 Hz, J_{AB}= 18.1

Hz); 3.10 (dd, $1H_B$; J_{BX}= 1.7 Hz, J_{AB}= 18.1 Hz). (Found: C, 54.82; H, 4.05; N, 7.11. Calc. for C_9H_8NOCl: C, 54.82; H, 4.06; N, 7.11).

3-(2,6-Dichlorophenyl)-5-hydroxy-2-isoxazoline, m.p. 126-127°C (hexane-benzene) (lit[6] 125-127°C); IR (CH_2Cl_2): ν_{OH}= 3590 cm^{-1}, 3520-3100 cm^{-1}; ^1H NMR ($CDCl_3$,δ): 7.32 (m, 3H); 6.10 (d, $1H_X$; J_{AX}= 6.3 Hz); 5.00 (bs, 1H: exchange with D_2O); 3.43 (dd, $1H_A$; J_{AX}= 6.3 Hz, J_{AB}= 18.1 Hz); 3.04 (d, $1H_B$; J_{AB}= 18.1 Hz). (Found: C, 46.75; H, 3.01; N, 6.05. Calc. for $C_9H_7NO_2Cl_2$: C, 46.75; H, 3.03; N, 6.06).

3-(3-Nitrophenyl)-5-hydroxy-2-isoxazoline, m.p. 115-120°C dec. (benzene); IR (CH_2Cl_2): ν_{OH}= 3590 cm^{-1}, 3500-3140 cm^{-1}; ^1H NMR (DMSO-d_6,δ): 8.05 (m, 4H); 7.23 (d, 1H: exchange with D_2O; $J_{(OH)X}$= 6.0 Hz); 6.00 (td, $1H_X$; $J_{(OH)X}$= 6.0 Hz, J_{AX}= 7.1 Hz, J_{BX}= 2.0 Hz); 3.53 (dd, $1H_A$; J_{AX}= 7.1 Hz,J_{AB}= 18.0 Hz); 3.17 (dd, $1H_B$; J_{BX}= 2.0 Hz, J_{AB}= 18.0 Hz). (Found: C, 51.92; H, 3.85; N, 13.44. Calc. for $C_9H_8N_2O_4$: C, 51.92; H, 3.85; N, 13.46).

3-(4-Nitrophenyl)-5-hydroxy-2-isoxazoline, m.p. 135-140°C (benzene); IR (CH_2Cl_2): ν_{OH}= 3640 cm^{-1}, 3600-3260 cm^{-1}; ^1H NMR (DMSO-d_6,δ): 8.16 (m, 4H); 7.30 (d, 1H: exchange with D_2O; $J_{(OH)X}$= 5.7 Hz); 6.01 (td, $1H_X$; $J_{(OH)X}$= 5.7 Hz, J_{AX}= 7.1 Hz, J_{BX}= 2.0 Hz); 3.51 (dd, $1H_A$; J_{AX}= 7.1 Hz, J_{AB}= 17.9 Hz); 3.13 (dd, $1H_B$; J_{BX}= 2.0 Hz, J_{AB}= 17.9 Hz). (Found: C, 51.92; H, 3.85; N, 13.45. Calc. for $C_9H_8N_2O_4$: C, 51.92; H, 3.85; N, 13.46).

3-Phenylisoxazole, b.p. 122-124°C/12mmHg (lit[17] 75°C/2mmHg, m.p. 12-14°C); ^1H NMR ($CDCl_3$,δ): 8.30 (d, 1H; J≈2 Hz); 7.53 (m, 5H); 6.50 (d, 1H; J≈2 Hz). (Found: C, 74.48; H, 4.83; N, 9.65. Calc. for C_9H_7NO: C, 74.48; H, 4.83; N, 9.65).

3-(2,4,6-Trimethylphenyl)isoxazole, m.p. 103-104°C (ethyl ether); ^1H NMR ($CDCl_3$,δ): 8.16 (d, 1H; J≈2 Hz); 6.58 (s, 2H); 6.00 (d, 1H; J≈2 Hz); 2.20 (s, 3H); 2.00 (s, 6H). (Found: C, 77.00; H, 6.92; N, 7.49. Calc. for $C_{12}H_{13}NO$: C, 77.00; H, 6.95; N, 7.49).

3-(2-Chlorophenyl)isoxazole, b.p. 85°C/0.3mmHg (lit[6] 90°C/0.5mmHg); ^1H NMR ($CDCl_3$,δ): 8.10 (d, 1H; J≈2 Hz); 7.25 (m, 4H); 6.50 (d, 1H; J≈2 Hz). (Found: C, 60.32; H, 3.35; N, 7.82. Calc. for C_9H_6NOCl: C, 60.33; H, 3.35; N, 7.82).

3-(3-Chlorophenyl)isoxazole, b.p. 120°C/10mmHg; ^1H NMR ($CDCl_3$,δ): 8.10 (d, 1H; J≈2 Hz); 7.26 (m, 4H); 6.33 (d, 1H; J≈2 Hz). (Found: C, 60.33; H, 3.35; N, 7.82. Calc. for C_9H_6NOCl: C, 60.33; H, 3.35; N, 7.82).

3-(2,6-Dichlorophenyl)isoxazole, m.p. 59-60°C (hexane) (lit[6] 61-62°C); ^1H NMR ($CDCl_3$,δ): 8.57 (d, 1H; J≈2 Hz); 7.38 (m, 3H); 6.45 (d, 1H; J≈2 Hz). (Found: C, 50.70; H, 2.35; N, 6.55. Calc. for $C_9H_5NO_2Cl_2$: C, 50.70; H, 2.35; N, 6.57).

3-(3-Nitrophenyl)isoxazole, m.p. 77-79°C (hexane); ^1H NMR ($CDCl_3$,δ): 8.25 (d, 1H; J≈2 Hz); 7.90 (m, 4H); 6.56 (d, 1H; J≈2 Hz). (Found: C, 56.83; H, 3.16; N, 14.72. Calc. for $C_9H_6N_2O_3$: C, 56.84; H, 3.16; N, 14.74).

3-(4-Nitrophenyl)isoxazole, m.p. 169-170°C dec. (ethyl ether); ^1H NMR (acetone-d_6,δ): 8.65 (d, 1H; J≈2 Hz); 8.05 (m, 4H); 6.95 (d, 1H; J≈2 Hz). (Found: C, 56.84; H, 3.16; N, 14.72. Calc. for $C_9H_6N_2O_3$: C, 56.84; H, 3.16; N, 14.74).

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