A New Method for the Generation of α-Nitrosoolefins from Ketooximes and its Application to the Synthesis of 5,6-Dihydro-4*H*-1,2-oxazine Derivatives [1]

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Reaction of ketooximes containing α-methylene group with chloramine-T followed by treatment with triethylamine leads to the formation of α-nitrosoolefins *via* α-nitrosochloride, which can react *in situ* intermolecularly with olefinic compounds to produce 5,6-dihydro-4*H*-1,2-oxazine derivatives in good yield.

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[4+2] Cycloaddition of α-nitrosoolefins with olefinic compounds are of synthetic interest since the product 5,6-dihydro-4*H*-1,2-oxazines are versatile intermediates for the synthesis of bifunctional compounds [2-4]. The reduced product tetrahydro-4*H*-1,2-oxazines plays an important role as partial structure in agricultural and horticultural, fungicides, herbicides and broad spectrum of bacteriocides [5]. Compounds possessing the oxazine moiety are also potential glycosidase inhibitors [6]. The usual method of generating them is the elimination of hydrogen halide from α-monohaloketooximes with triethylamine [7]. However α-nitrosoolefins are highly reactive and unstable, hence they are usually only generated *in situ*. The yield of cycloaddition products often is low or side reactions predominate, hence new procedure for the formation of α-nitrosoolefins remain of interest.

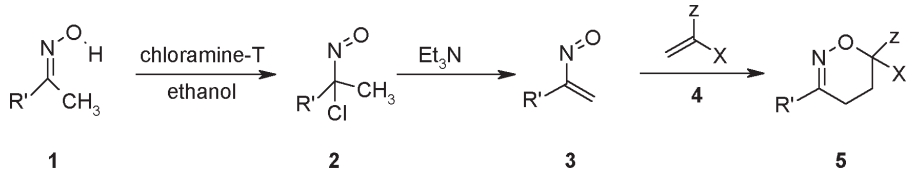
Rai *et al* [8] extensively used chloramine-T for the preparation of biologically active heterocycles *via* [3+2] cycloaddition reaction of 1,3-dipolar species such as nitrile oxides and nitrile imines with olefinic compounds. We have successfully isolated the reactive intermediate nitrile oxides by the oxidation of aldoximes with chloramine-T. During the course of these studies, we have observed that treatment of cyclohexanone oxime with chloramine-T produced a blue colour suggestive of formation of 1-chloro-1-nitrosocyclohexane [6]. With this success, we now report the use of chloramine-T as a new efficient reagent for the conversion of ketooxime bearing reactive methylene group into α-nitrosochloride, which is suitable for *in situ* generation of α-nitrosoolefins during [4+2] cycloaddition to olefins. Typically, the cycloaddition is carried out by refluxing an equimolecular mixture of a ketooxime, chloramine-T trihydrate in ethanol followed by addition of triethylamine and an alkene in ethanol at rt. In general 5,6-dihydro-4*H*-1,2-oxazine derivatives are thus obtained in good yield .

The reaction with chloramine-T proceeds with aromatic as well as aliphatic ketooximes bearing α-hydrogen (*e.g.* **1a-f**) and with styrene, acrylonitrile and with 1-methylstyrene.

The probable mechanism for the formation of α-nitrosoolefins involves the interaction of ketoxime with chloramine-T to form α-nitrosochloride followed by the elimination of HCl in the presence of triethylamine (Scheme 2).

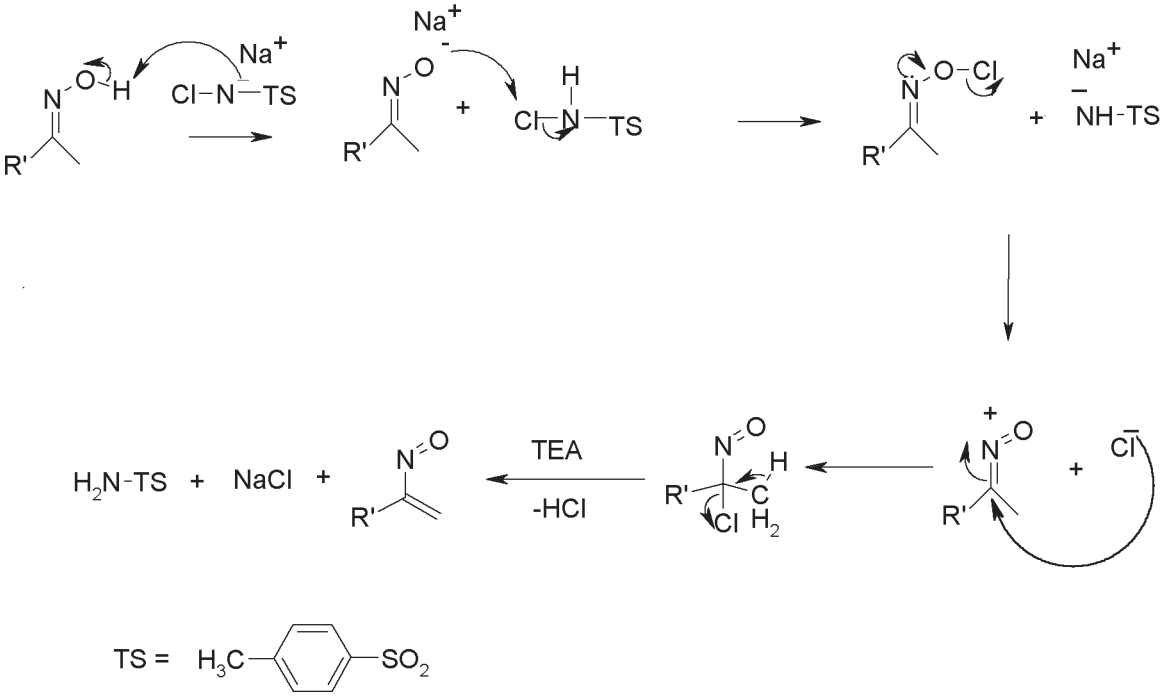
The structure proof is based on ^{1}H nmr, ^{13}C nmr, ms studies and elemental analyses of the 5,6-dihydro-4*H*-1,2-oxazine derivatives. As expected, the cycloaddition was regioselective. ^{1}H nmr indicated the presence of a single isomer in all cases studied. All ^{1}H nmr spectra of **5** (when X=H), showed the signals due to C_6 as a doublet of doublet in the region 4.5-5.5 δ ppm while in **5** (when X=CH_3) shows no signal in the said region and those due to C_5 pro-

Scheme 1



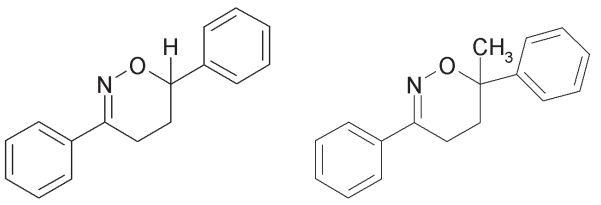
1	R'	4	X	Z
a	Ph	**a**	H	Ph
b	p-Cl-C_6H_4-	**b**	H	CN
c	p-NO_2-C_6H_4-	**c**	Me	Ph
d	Isobutyl			
e	Ethyl			
f	Furyl			

Scheme 2



tons a multiplet in the region δ 1.9–2.5 ppm and those due to C_4 as a triplet in the region δ 2.0–2.8 ppm.

In the ^{13}C nmr spectra, all oxazines gave consistent signals for the newly formed ring carbons. For instance, the signals due to C_6 appears in **5** (when X=H) as doublet in the region δ 70–80 ppm while **5** (when X=CH_3) appears as singlet in the region δ 70–80 ppm and those due to C_5 and C_4 appears as triplets in the region δ 15–25 ppm and δ 25–30 ppm repectively. All oxazines show MH^+ as base peak and stable molecular ion peak with relative abundance ranging from 7-20%. The formation of the products was further supported by correct elemental analyses.



5a **5c**

In summary we have demonstrated for the first time that oxazines can be easily synthesized by the reaction of ketooximes bearing α-methylene group with alkenes in presence of chloramine-T and triethylamine in almost 60-83% yield.

The known compounds were identified by the comparison of the spectral data with those described in the literature [9].

EXPERIMENTAL

Melting points were determined on Thomas Hoover melting point apparatus and are uncorrected. ^1H NMR spectra were recorded on a Bruker AM 300 MHz spectrometer using $CDCl_3$ as solvent and tetramethylsilane as internal standard. ^{13}C NMR spectra were measured on Jeol 400 (100 MHz) instrument. The chemical shifts are expressed in δ and following abbreviations were used: s=singlet, d=doublet, t=triplet and m=multiplet. Mass spectra were obtained on a Finnigan 4021 mass spectrometer at an ionizing energy of 35 eV. Elemental analyses were obtained on a Vario-EL instrument. Thin layer chromatography (TLC) was done with pre-coated silica gel G plates using chloroform-acetone (8:2) as eluent.

3,6-Diphenyl-5,6-dihydro-4*H*-1,2-oxazine (**5a**).

Typical Procedure.

A mixture of 0.50 g (3.7 mmoles) of **1a** and 1.05 g (3.73 mmoles) of chloramine-T trihydrate in ethanol (20 ml) were refluxed for 2 hour. The mixture was cooled to room temperature, triethylamine (1 ml) was added and stirred at room temperature for 15 minutes. After this, solution of 0.39 g (3.75 mmoles) of **4a** in ethanol (5 ml) was added and stirred for 1 hour. It was then concentrated under reduced pressure and the residue is extracted with CH_2Cl_2 (25 ml). This extract was then washed with water (15 ml), with 1 *N* aq. NaOH (2 × 15 ml) and dried (Na_2SO_4). The solvent was evaporated and the remaining pale yellow solid was recrystallized from alcohol-*n*-hexane to gave **5a**

as a creamy white crystalline solid, yield 0.630 g (72%), mp 159-161 °C (lit. mp 160-162 °C) [9]; ^{1}H nmr (deuteriochloroform): δ 2.18 (m, 2H, CH_2), 2.73 (t, 2H, CH_2), 4.82 (dd, 1H, J=10.3Hz & 2.7Hz, CH), 7.35-7.50 (m, 8H, ArH), 7.72-7.78 (m, 2H, ArH).

Anal. Calcd. for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 80.93; H, 6.44; N, 5.84.

The same procedure was used in all cases.

3-Phenyl-5,6-dihydro-4*H*-1,2-oxazine-6-carbonitrile (**5b**).

This compound was obtained from 0.50 g (3.7 mmoles) of **1a**, 0.2 g (3.76 mmol) of **4b**, 1.05 g (3.73 mmoles) of chloramine-T trihydrate and triethylamine as a pale yellow crystalline solid, yield 0.550 g (80%), mp 100-102 °C; ^{1}H nmr (deuteriochloroform): δ 2.08 (m, 2H, CH_2), 2.72 (t, 2H, CH_2), 5.14 (dd, 1H, J=9.6 & 2.4Hz, CH), 7.30-7.50 (m, 5H, ArH); ^{13}C nmr (deuteriochloroform): δ 15.1 (t), 27.4 (t), 72.10 (d), 119.6 (s), 128.9 (d), 129.2 (d), 130.6 (d), 132.1 (s), 165.1 (s); ms m/z: 187 (MH+, 100), 186 (M+,6), 117 (10), 103 (13).

Anal. Calcd. for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41; N, 15.04. Found: C, 70.98; H, 5.49; N, 15.01.

6-Methyl-3,6-diphenyl-5,6-dihydro-4*H*-1,2-oxazine (**5c**).

This compound was obtained from 0.50 g (3.7 mmoles) of **1a**, 0.44 g (3.70 mmol) of **4c**, 1.05 g (3.73 mmoles) of chloramine-T trihydrate and triethylamine as a off white crystalline solid, yield 0.620 g (67%), mp 128-130°C (lit mp 128-129°C) [9]; ^{1}H nmr (deuteriochloroform): δ 1.59 (s, 3H, CH_3), 2.12 (t, 2H, CH_2), 2.42 (t, 2H, CH_2), 7.17-7.35 (m, 8H, ArH), 7.60-7.76 (m, 2H, ArH).

Anal. Calcd. for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.22; H, 6.85; N, 5.59.

3-(4-Chlorophenyl)-6-phenyl-5,6-dihydro-4H-1,2-oxazine (**5d**).

This compound was obtained from 0.50 g (2.94 mmol) of **1b**, 0.31 g (2.98mmol) of **4a**, 0.84 g (2.95 mmol) of chloramine-T trihydrate and triethylamine as a pale yellow oil, yield 0.560 g (70%); ^{1}H nmr (deuteriochloroform): δ 2.02 (m, 2H, CH_2), 2.66 (t, 2H, CH_2), 4.48 (dd, 1H, J=10.3 & 2.4Hz, CH), 7.20-7.35 (m, 5H, ArH), 7.45 (dd, 2H, ArH), 7.65 (dd, 2H, ArH); ^{13}C nmr (deuteriochloroform): δ 22.2 (t), 29.6 (t), 80.2 (d), 125.4 (d), 128.4 (d), 128.6 (d), 129 (d),129.6 (s), 130.8 (d), 134.2 (s), 138.2 (s), 164.1 (s); ms m/z: 272 (MH$^+$, 100), 271 (M$^+$, 8), 151 (20), 137 (10), 120 (17), 106 (4), 77 (38).

Anal. Calcd. for $C_{16}H_{14}ClNO$: C, 70.72; H, 5.19; N, 5.15. Found: C, 70.70; H, 5.22; N, 5.17.

3-(4-Chlorophenyl)-5,6-dihydro-4*H*-1,2-oxazine-6-carbonitrile (**5e**).

Obtained from 0.50 g (2.94 mmol) of **1b**, 0.20 g (3.76 mmol) of **4b**, 0.84 g (2.95 mmol) of chloramine-T trihydrate and triethylamine as a pale yellow oil, yield 0.530 g (81%); ^{1}H nmr (deuteriochloroform): δ 2.11 (m, 2H, CH_2), 2.74 (t, 2H, CH_2), 5.22 (dd, 1H, J=10.1 & 2.9Hz, CH), 7.33 (d, 2H ArH), 7.62 (d, 2H, ArH); ^{13}C nmr (deuteriochloroform): δ 15.1 (t), 29.2 (t), 71.40 (d), 118.5 (s), 129.6 (d), 130 (s), 131.8 (d), 134.2 (s), 163.6 (s); ms m/z: 221 (MH$^+$, 100), 220 (M$^+$, 6), 151 (18), 137 (10).

Anal. Calcd. for $C_{11}H_9ClN_2O$: C, 59.88; H, 4.11; N, 12.70. Found: C, 59.85; H, 4.15; N, 12.68.

3-(4-Chlorophenyl)-6-methyl-6-phenyl-5,6-dihydro-4*H*-1,2-oxazine) (**5f**).

This compound was obtained from 0.50 g (2.94 mmol) of **1b**, 0.44 g (3.7 mmol) of **4c**, 0.84 g (2.95 mmol) of chloramine-T trihydrate and triethylamine as a pale yellow oil to yield 0.550 g (65%); ^{1}H nmr (deuteriochloroform): δ 1.41 (S, 3H, CH_3), 1.98 (t, 2H, CH_2), 2.73 (t, 2H, CH_2), 7.28-7.37 (m, 5H, ArH), 7.51 (dd, 2H, ArH), 7.68 (dd, 2H, ArH); ^{13}C nmr (deuteriochloroform): δ 24.6 (q), 27.0 (t), 28.1 (t), 80..4 (s), 123.7 (d), 128.0 (d), 128.6 (d), 129.4 (d), 129.9 (d), 131.2 (s), 137.1 (s), 139.2 (s), 164.1(s); ms m/z: 286 (MH$^+$, 100), 285 (M$^+$,11), 151 (15), 137 (11), 134 (8), 120 (18), 77 (40).

Anal. Calcd. for $C_{17}H_{16}ClNO$: C, 71.45; H, 5.64; N, 4.90. Found: C, 71.48; H, 5.67; N, 4.88.

3-(4-Nitrophenyl)-6-phenyl-5,6-dihydro-4*H*-1,2-oxazine (**5g**).

This compound was obtained from 0.50 g (2.77 mmol) of **1c**, 0.29 g (2.78 mmol) of **4a**, 0.79 g (2.81 mmol) of chloramine-T trihydrate and triethylamine as a yellow crystalline solid to yield 0.587 g (75%), mp 186-188 °C (lit mp 188-189 °C) [9]; ^{1}H nmr (deuteriochloroform): δ 2.16 (m, 2H, CH_2) 2.74 (t, 2H, CH_2), 4.78 (dd, 1H, J=10.1 & 2.9Hz, CH), 7.31-7.42 (m, 5H ArH), 7.84 (dd, 2H, ArH), 8.12 (dd, 2H, ArH).

Anal. Calcd. for $C_{16}H_{14}N_2O_3$: C, 68.07; H, 5.0; N, 9.92. Found: C, 68.09; H, 4.98; N, 9.94.

3-(4-Nitrophenyl)-5,6-dihydro-4*H*-1,2-oxazine-6-carbonitrile (**5h**).

This compound was obtained from 0.50 g (2.77 mmol) of **1c**, 0.15 g (2.83 mmol) **4b**, 0.15 g (2.83 mmol), 0.79 g (2.81 mmol) of chloramine-T trihydrate and triethylamine as a yellow oil to yield 0.532 g (83%); ^{1}H nmr (deuteriochloroform): δ 2.07 (m, 2H, CH_2), 2.73 (t, 2H, CH_2), 4.89 (dd, 1H, J=9.4 & 2.6 Hz, CH), 7.93 (dd, 2H ArH), 8.13 (dd, 2H, ArH); ^{13}C nmr (deuteriochloroform): δ 16.2 (t), 28.6 (t), 71.5 (d), 119.6 (s), 123.1 (d), 128.6 (d), 139.2 (s), 151.4 (s), 162.6 (s); ms m/z: 232 (MH$^+$, 100), 231 (M$^+$, 8), 162 (14), 148 (02).

Anal. Calcd. for $C_{11}H_9N_3O_3$: C, 57.14; H, 3.92; N, 18.17. Found: C, 57.19; H, 3.90; N, 18.16.

6-Methyl-3-(4-nitro-phenyl)-6-phenyl-5,6-dihydro-4*H*-1,2-oxazine (**5i**).

This compound was obtained from 0.50 g (2.77 mmol) of **1c**, 0.33 g (2.78 mmol) **4c**, 0.79 g (2.81 mmol) of chloramine-T trihydrate and triethylamine as a pale yellow crystalline solid to yield 0.575 g (70%), mp 167-169 °C (lit mp 168-172 °C) [9]; ^{1}H nmr (deuteriochloroform): δ 1.45 (s, 3H, CH_3), 1.98 (t, 2H, CH_2), 2.19 (t, 2H, CH_2), 7.37-7.5 (m, 5H, ArH), 7.73 (dd, 2H, ArH), 8.19 (dd, 2H, ArH).

Anal. Calcd. for $C_{17}H_{16}N_2O_3$: C, 68.44; H, 6.08; N, 9.39. Found: C, 68.49; H, 6.06; N, 9.37.

3-Isobutyl-6-phenyl-5,6-dihydro-4*H*-1,2-oxazine (**5j**).

This compound was obtained from 0.50 g (4.34 mmol) of **1d**, 0.46 g (4.35mmol) of **4a**, chloramine-T (1.23 g, 4.37 mmol) and triethylamine as a yellow oil to yield 0.594 g (63%); ^{1}H nmr (deuteriochloroform): δ 1.01 (s, 6H, CH_3), 1.31-1.37 (m, 4H, CH_2), 1.84 (m, 1H, CH), 2.02 (m, 2H, CH_2), 4.53 (dd, 1H, J=9.8 & 2.5 Hz, CH), 7.22-7.64 (m, 5H, ArH); ^{13}C nmr (deuteriochloroform): δ 20.4 (d), 22.8 (q), 23.1 (t), 28.5 (t), 43.1 (t), 80.2 (d), 124.8 (d), 127.9 (d), 128.5 (d) 137.6 (s), 163.8(s); ms m/z: 218 (MH$^+$, 100), 120 (12), 106 (15), 97 (28), 83 (6), 77 (10).

Anal. Calcd. for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.32; H, 8.84; N, 6.44.

3-Isobutyl-5,6-dihydro-4*H*-1,2-oxazine-6-carbonitrile (**5k**).

This compound was obtained from 0.50 g (4.34 mmol) of **1d**, 0.24 g (4.52 mmol) of **4b**, 1.23 g (4.37 mmol) of chloramine-T trihydrate and triethylamine as a pale yellow oil to yield 0.490 g (69%); ^{1}H nmr (deuteriochloroform): δ 1.05 (s, 6H, CH_3), 1.29-1,34 (m, 4H, CH_2), 1.85 (m, 1H, CH), 2.07 (m, 2H, CH_2), 4.33 (dd, 1H, J=9.9 & 2.5Hz CH); ^{13}C nmr (deuteriochloroform): δ 18.2 (t), 20.4 (d), 23.4 (q), 27.1 (t), 44.2 (t), 71.4 (d), 119.2 (s), 164.1 (s); ms m/z: 167 (MH^+, 100), 97 (10), 83 (8).

Anal. Calcd. for $C_9H_{14}N_2O$: C, 65.03; H, 8.49; N, 16.85. Found: C, 64.99; H, 8.52; N, 16.87.

3-Isobutyl-6-methyl-6-phenyl-5,6-dihydro-4*H*-1,2-oxazine (**5l**).

This compound was obtained from 0.50 g (4.34 mmol) of **1d**, 0.52 g (4.40 mmol) of **4c**, 1.23 g (4.37 mmol) of chloramine-T trihydrate and triethylamine as a pale yellow oil to yield 0.580 g (58%); ^{1}H nmr (deuteriochloroform): δ 1.04 (s, 6H, CH_3), 1.33-1.39 (m, 4H, CH_2), 1.51 (s, 3H, CH_3), 1.89 (m, 1H, CH), 1.99 (m, 2H, CH_2), 7.30-7.40 (m, 5H, ArH); ^{13}C nmr (deuteriochloroform): δ 20.9 (d), 23.0 (q), 25.8 (q), 26.4 (t), 27.8 (t), 43.2 (t), 80.3 (s), 124.8 (d), 127.9 (d), 128.2 (d), 137.1 (s), 163.5 (s); ms m/z: 232 (MH^+, 100), 134 (8), 120 (25), 97 (2), 83 (7),77 (11).

Anal. Calcd. for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.05. Found: C, 77.81; H, 9.19; N, 6.07.

3-ethyl-6-phenyl-5,6-dihydro-4*H*-1,2-oxazine (**5m**).

This compound was obtained from 0.50 g (5.70 mmol) of **1e**, 0.60 g (5.76 mmol) of **4a**, 1.62 g (5.76 mmol) of chloramine-T trihydrate and triethylamine as a pale yellow oil to yield 0.673 g (63%); ^{1}H nmr (deuteriochloroform): δ 1.07 (t, 3H, CH_3), 1.33 (t, 2H, CH_2), 1.44 (m, 2H, CH_2), 2.02 (m, 2H CH_2), 4.53 (dd, 1H, J=10.2 & 2.8Hz, CH), 7.2-7.4 (m, 5H, ArH); ^{13}C nmr (deuteriochloroform): δ 7.5 (q), 23.9 (t), 26.9 (t), 27.5 (t), 81.1 (d), 125.4 (d), 127.6 (d), 128.0 (d), 137.2 (s), 163.4 (s); ms m/z: 190 (MH^+, 100), 189 (M^+, 7), 106 (20), 77 (30), 69 (6), 55 (10).

Anal. Calcd. for $C_{12}H_{15}NO$: C, 76.16; H, 7.99; N, 7.40. Found: C, 76.10; H, 8.03; N, 7.44.

3-Ethyl-5,6-dihydro-4*H*-1,2-oxazine-6-carbonitrile (**5n**).

This compound was obtained from 0.50 g (5.70 mmol) of **1e**, 0.31 g (5.84 mmol) of **4b**, 1.62 g (5.76 mmol) of chloramine-T trihydrate and triethylamine as a pale yellow oil to yield 0.547 g (69%); ^{1}H nmr (deuteriochloroform): δ 1.06 (t, 3H, CH_3), 1.33 (t, 2H, CH_2), 1.43 (m, 2H, CH_2), 2.04 (m, 2H, CH_2), 4.26 (dd, 1H, J=9.9 & 2.6 Hz, CH), 7.23-7.40 (m, 5H, ArH); ^{13}C nmr (deuteriochloroform): δ 8.5 (q), 17.2 (t), 27.0 (t), 27.8 (t), 73.3 (d), 118.9 (s), 163.9 (s); ms m/z: 139 (MH^+, 100), 138 (M^+, 9) 69 (4), 55 (12) .

Anal. Calcd. for $C_7H_{10}N_2O$: C, 60.85; H, 7.30; N, 20.27. Found: C, 60.80; H, 7.33; N, 20.30.

3-Ethyl-6-methyl-6-phenyl-5,6-dihydro-4*H*-1,2-oxazine (**5o**).

This compound was obtained from 0.50 g (5.70 mmol) of **1e**, 0.68 g (5.76 mmol) of **4c**, 1.62 g (5.76 mmol) of chloramine-T trihydrate and triethylamine as pale yellow oil to yield 0.653 g (56%); ^{1}H nmr (deuteriochloroform): δ 1.07 (t, 3H, CH_3), 1.30 (t, H, CH_2), 1.43 (m, 2H, CH_2), 1.59 (s, 3H, CH3), 1.99 (t, 2H, CH2), 7.28-7.40 (m, 5H, ArH); ^{13}C nmr (deuteriochloroform): δ 7.9 (q), 24.2 (q), 26.2 (t), 27.0 (t), 27.1 (t), 80.6 (s), 126.1 (d), 128.4 (d), 128.9 (d), 139.9 (s), 165.0 (s); ms m/z: 204 (MH^+, 100), 203(M^+, 6), 135 (8),120 (28), 77 (30), 69 (6), 55 (13).

Anal. Calcd. for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.75; H, 8.46; N, 6.93.

3-Furan-2-yl-6-phenyl-5,6-dihydro-4*H*-1,2-oxazine (**5p**).

This compound was obtained from 0.5 g (4.0 mmol) of **1f**, 0.42 g (4.03 mmol) of **4a**, 1.14 g (4.05 mmol) of chloramine-T trihydrate and triethylamine as a yellow oil to yield 0.635 g (70%); ^{1}H nmr (deuteriochloroform): δ 1.33 (t, 2H, CH_2), 1.88 (m, 2H, CH_2), 4.54 (dd, 1H, , J=9.2 & 2.3 Hz, CH), 6.32-6.37 (m, 2H, furyl), 7.20-7.30 (m, 5H, ArH), 7.43 (d, 1H, furyl); ^{13}C nmr (deuteriochloroform): δ 21.0 (t), 27.1 (t), 80.2 (d), 112.2 (d), 125.1 (d), 128.8 (d), 129.1 (d) 137.8 (s), 140.2 (d), 141 (s), 165.2 (s); ms m/z: 228 (MH^+, 100), 227 (M^+, 17), 107 (32), 93(38), 77 (21).

Anal. Calcd. for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 74.05; H, 5.74; N, 6.12.

3- Furan-2-yl-5,6-dihydro-4*H*-1,2-oxazine-6-carbonitrile (**5q**).

This compound was obtained from 0.5 g (4.0 mmol) of **1f**, 0.22 g (4.15 mmol) of **4b**, 1.14 g (4.05 mmol) of chloramine-T trihydrate and triethylamine as a yellow oil to yield 0.549 g (78%); ^{1}H nmr (deuteriochloroform): δ 1.32 (t, 2H, CH_2), 1.87 (m, 2H, CH_2), 4.23 (dd, 1H, J=9.6 & 2.4Hz, CH), 6.30-6.36 (m, 2H, furyl), 7.42 (d, 1H, furyl); ^{13}C nmr (deuteriochloroform): δ 15.1 (t), 29.0 (t), 72.1 (d), 112.0 (d), 119.3 (s), 140.2 (d) 143.2 (s), 163.5 (s); ms m/z: 177 (MH^+, 100), 176(M^+, 20), 107 (29), 93 (38).

Anal. Calcd. for $C_9H_8N_2O_2$: C, 61.36; H, 4.58; N, 15.90. Found: C, 61.30; H, 4.60; N, 15.93.

3-Furan-2-yl-6-methyl-6-phenyl-5,6-dihydro-4*H*-1,2-oxazine (**5r**).

This compound was obtained from 0.5 g (4.0 mmol) of **1f**, 0.51 g (4.32 mmol) of **4c**, 1.14 g (4.05 mmol) of chloramine-T trihydrate and triethylamine as a yellow oil to yield 0.616 g (64%); ^{1}H nmr (deuteriochloroform): δ 1.33 (t, 2H, CH_2), 1.52 (s, 3H, CH_3), 1.93 (m, 2H, CH_2), 6.30-6.36 (m, 2H, furyl), 7.19-7.28 (m, 5H, ArH), 7.42 (d, 1H, furyl); ^{13}C nmr (deuteriochloroform): δ 24.2 (q), 25.7 (t), 26.7 (t), 79.8 (s), 112.1 (d), 125.1 (d),128.4 (d), 128.8 (d), 139.4 (d), 142.1 (s), 163.9 (s); ms m/z: 242 (MH^+, 100), 241 (M^+, 16), 120 (35), 107 (29),93 (32), 77 (25).

Anal. Calcd. for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.80. Found: C, 74.62; H, 6.30; N, 5.79.

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