One Pot Photoredox Decarboxylation Reaction of *N*-Cyano(α-bromo-α-phenyl)methylanilines Leading to Synthesis of Four-Membered Cyclic Carbamates

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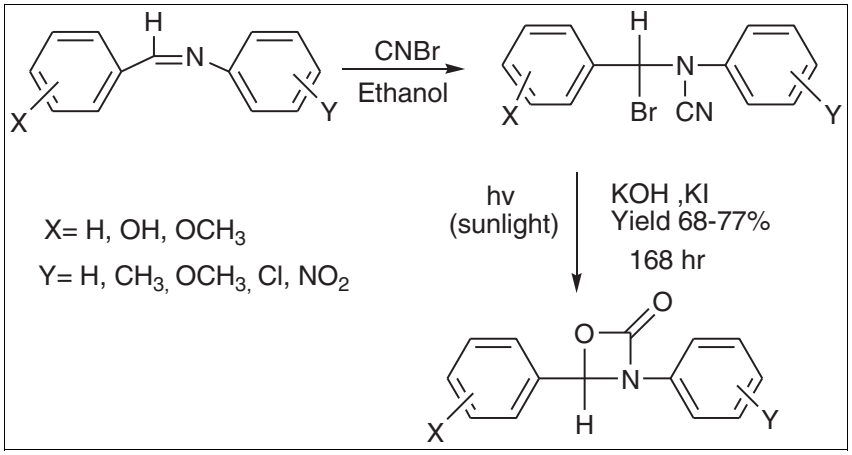

A new four-membered cyclic carbamates have been synthesized through solar irradiation of *N*-cyano(α-bromo-α-phenyl)methylanilines in their aqueous methanolic solution using iodide salt in basic medium. These compounds have been characterized as 3,4-diphenyl-1,3oxazetidin-2-one through their elemental analysis, IR, ^{1}H-NMR, ^{13}C-NMR, and mass spectral studies.

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INTRODUCTION

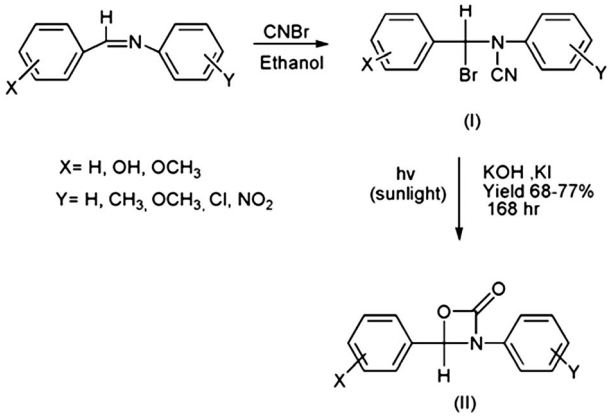
Carbon–nitrogen containing compounds are of pharmacological importance and act as antiseptic, antifungal, anticancer agent [1,2], and so forth. Carbon–nitrogen bond present in variety of substrate azomethines, azomethines-*N*-oxides, nitrilimine, azomethines ylids, and *N*-α-cyanoamines and find great importance in the synthesis of heterocyclic compounds of different ring size through their cycloaddition reaction [2–4] and photoredox reaction [5,6]. *N*-α-Cyanoamines by for the most suitable substrates [7,8] that has also been employed for the synthesis of several heterocyclic compounds of pharmacological importance. Earlier from these laboratories, a novel synthesis of substituted benzoimidazoloquinolines and a novel photoredox reaction of *N*-α-cyano-α-styryl-methylanilines have also been reported.

RESULTS AND DISCUSSION

For the present study, *N*-cyano(α-bromo-α-phenyl)methylanilines (I) have been used for the photoredox decarboxylation reaction employing solar radiation. These compounds have been prepared by synthesizing azomethines through the usual condensation reaction of variously substituted aromatic aldehyde and variously substituted anilines followed by the subsequent addition of cyanogen bromide in ethanol. These *N*-cyano(α-bromo-α-phenyl)methylanilines (I) were recrystallized and characterized through their melting points and elemental analysis and were used further for photoirradiation. To the methanolic solution of these compounds (I) were added 2% potassium iodide and 1% aqueous potassium hydroxide solution, and the reaction mixture was exposed to direct sunlight in silica glass photoreactor for a period of 1 week(168 h). These *N*-cyano(α-bromo-α-phenyl)methylanilines (I) undergo reductive photo-decarboxylation to provide four-membered cyclic carbamates (II) in good yields (Scheme 1). These carbamates have been characterized through their elemental analysis, IR, proton magnetic resonance, and high resolution mass spectra.

In their IR spectra, these carbamates (II) in Scheme 1 display a broad absorption band in the region 1702–1680 cm^{-1} that has been assigned to four-membered cyclic carbamates function. Another strong absorption band in the region 1650–1570 cm^{-1} has been assigned to aromatic carbon–carbon double bond stretching, whereas an absorption band in the region 1286–1244 cm^{-1} has been assigned to carbon–nitrogen single bond. In all these IR spectra, absorption band due to nitrile function 2250–2200 cm^{-1} is wanting indicating that cyano group has been transformed to cyclic carbamates moiety. In the 400 MHz ^{1}H-NMR, these four-membered cyclic carbamates display a multiplet signal in the region at δ 8.7–6.5 (8H—Ar) and a singlet in the region

Scheme 1. Classical synthesis of 3,4-diphenyl-1,3-oxazetidin-2-one.



at δ 13.3–12.7 (1H-phenolic) whereas a sharp singlet in the region at δ 8.8–8.5 (1H-benzylic) (vide experimental). Benzylic proton merges in aromatic region because it is deshielded by nitrogen on one side and oxygen on other side [2]. In their ^{13}C-NMR spectra, these derivatives show identical pattern, as are presentative case ^{13}C spectrum of derivative 3,4-diphenyl-1,3-oxazetidin-2-one is described. A signal in the region at δ 162.2–162.9 has been assigned to carbonyl carbon, whereas signals in the regions at δ 160.3–161.5, 145.1–146.9, and 133.4–136.7 has been assigned to carbon atom of aromatic ring bearing no hydrogen. The other aromatic carbons appear in the region at δ 132.9–116.2, whereas signals in the regions at δ 59.7–60.2 have been assigned to carbon of –OCH_3 group, and signal at δ 20.6 has been assigned to carbon of CH_3 group.

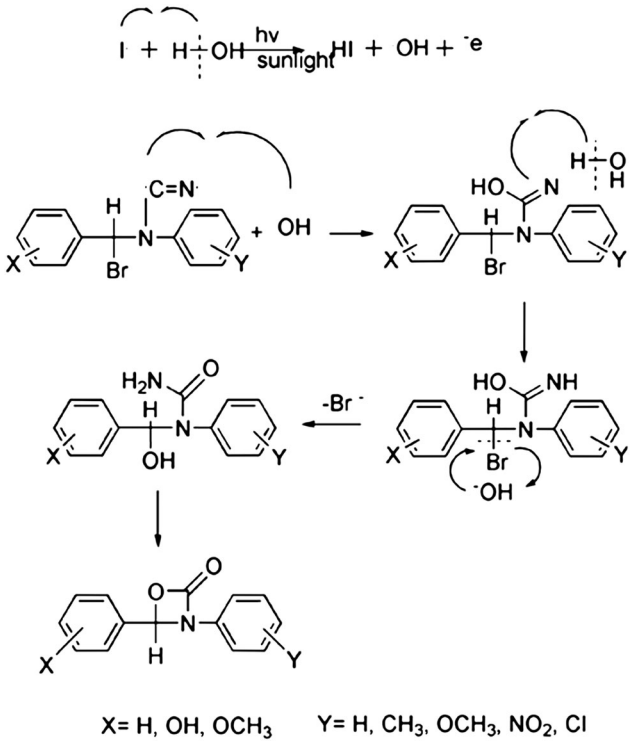
In the high-resolution mass spectra, these carbamates display M^+ and $(M-44)^+$ as the base peak along with other prominent peaks (Figure 1). The reaction seems to involve the generation of hydroxide free radical through iodide free radical in the sunlight that attack the nitrile function to form hydroxyimino radical and subsequently that is transformed to amide function, and at the same time, *C*-bromo gets hydroxylated that through nucleophilic attack forms four-membered cyclic carbamates in Scheme 2.

EXPERIMENTAL

(I) General procedure for the preparation of azomethines. Various azomethines were prepared by following an identical procedure as described in literature [2]. Synthesis of *o*-hydroxybenzylidene-*p*-nitroaniline is described as a presentative case. Salicylaldehyde 1.22 g (0.01 mol) was mixed with 1.38 g (0.01 mol) of *p*-nitroaniline in 10 mL of ethyl alcohol. The reaction mixture after gentle warming provided the required azomethines. mp 128–130°C.

(II) General procedure for the preparation of *N*-cyano(α-bromo-α-phenyl)methylanilines. To the solution of azomethines in ethyl alcohol taken in conical flask, an equimolar quantity of cyanogen bromide 1.06 g (0.01 mol) were added in a good ventilated

Scheme 2. Mechanistic pathway of 3,4-diphenyl-1,3-oxazetidin-2-one.



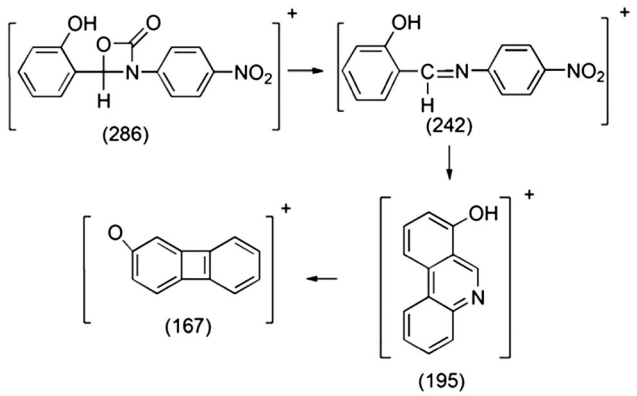
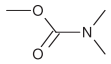


Figure 1. Mass fragmentation of 4-(2-Hydroxyphenyl)-3-(4-nitrophenyl)-,3-oxazetidin-2-one.

hood. The flask was tightly corked and shaken intermittently for half an hour. The reaction mixture was kept for overnight period. Usual work up of the reaction mixture provided the crystalline product that was recrystallised from benzene/petroleum ether. mp 160–162°C.

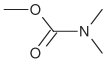
(III) General procedure for the preparation of 3,4-diphenyl-1,3-oxazetidin-2-ones. To the solution of an appropriate *N*-cyano(α-bromo-α-phenyl)methylaniline in ethanol (200 mL) was added 2% KI and 1% aqueous KOH in 250 mL conical silica glass flask. The reaction mixture was stirred with nitrogen gas to expel out any dissolved oxygen, and the reaction mixture was exposed to direct sunlight for a period of 1 week. The usual work up of the reaction mixture provided the corresponding 3,4-diphenyl-1,3-oxazetidin-2-one as white crystalline solids. These carbamates have been characterized through elemental analysis, IR, NMR, and high resolution mass spectral data. All the four-membered cyclic carbamates (S_4 to B_4) were prepared by following aforementioned similar procedure (Table 1 and Table 2).

4-(2-Hydroxyphenyl)-3-(4-nitrophenyl)-1,3-oxazetidin-2-one (S_4). mp: 196–198°C; IR (KBr Pellets) ν**:**



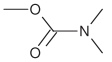
1690, (C—N) 1271, (C═C) 1586–1566, (—NO_2) 1566–1340, (—OH) 3481–3069 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.2–6.5 (m, 8H, Ar), 12.7 (s, 1H, OH), 8.6 (s, 1H, —CH—); ^{13}C-NMR ($CDCl_3$) δ: 116.2, 118.3, 119.1, 129.8, 132.5, 132.8, 136.4, 145.7, 160.3, 162.9; MS: Molecular ion peak *m/z* 286; *Anal*. Calcd for: $C_{14}H_{10}N_2O_5$: C, 58.74; H, 3.49; N, 9.79. Found: C, 59.08; H, 4.39; N, 10.5; Percentage yield = 77%.

3-(4-Chlorophenyl)-4-(2-hydroxyphenyl)-1,3-oxazetidin-2-one (S_5). mp: 197–199°C; IR (KBr Pellets) ν**:**



1690, (C—N) 1271, (C═C) 1584–1566, (—OH) 3084–2979 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.8–6.5 (m, 8H, Ar), 13.1 (s, 1H, —OH), 8.5 (s, 1H, —CH—); ^{13}C-NMR ($CDCl_3$) δ: 117.3, 119.0, 119.2, 122.5, 129.5, 132.4, 132.6, 133.4, 146.9, 161.1, 162.9; MS: Molecular ion peak *m/z* 275; *Anal*. Calcd for: $C_{14}H_{10}NO_3Cl$: C, 61.09; H,3.63; N, 5.09. Found: C, 62.27; H, 3.97; N, 5.8; Percentage yield = 72%.

4-(2-Hydroxyphenyl)-3-p-*tolyl-1,3-oxazetidin-2-one (S_2). mp: 187–189°C; IR (KBr Pellets) ν**:**



1700–1690, (C—N) 1281, (C═C) 1597–1568, (—OH) 3051–2857 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.6–6.7 (m, 8H, Ar), 13.3 (s, 1H, —OH), 8.5 (s, 1H, —CH—), 2.4 (s, 3H, —CH_3); ^{13}C-NMR ($CDCl_3$) δ: 20.6, 116.4, 118.7, 119.0, 129.7, 132.2, 132.6, 136.3, 145.1, 160.4, 162.0; MS: Molecular ion peak *m/z* 255; *Anal*. Calcd for: $C_{15}H_{13}NO_3$: C, 70.58; H, 5.09; N, 5.49. Found: C, 69.09; H, 5.97; N, 6.09; Percentage yield = 74%.

3-(4-Chlorophenyl)-4-(4-methoxyphenyl)-1,3-oxazetidin-2-one (A_5). mp: 236–238°C; IR (KBr Pellets) ν**:**

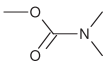


Table 1

Characterization data of azomethines and *N*-cyano(α-bromo-α-phenyl) methylanilines.

Entry	X	Y	mp of azomethines	mp of *N*-cyano(α-bromo-α-phenyl) methylanilines
S_4	2-OH	4-NO_2	128–130	160–162
S_5	2-OH	4-Cl	100–102	145–147
S_2	2-OH	4-CH_3	98–100	127–129
A_5	4-OCH_3	4-Cl	85–87	150–152
A_4	4-OCH_3	4-NO_2	79–80	145–147
A_1	4-OCH_3	4-H	60–62	146–148
B_4	4-H	4-NO_2	40–45	190–192

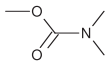
Table 2

Characterization data of 3,4-diphenyl-1,3-oxazetidin-2-one.

Entry	X	Y	Time (h)	mp (°C)	Yield (%)
S_4	2-OH	4-NO_2	163	196–198	77
S_5	2-OH	4-Cl	160	197–199	72
S_2	2-OH	4-CH_3	157	187–189	74
A_5	4-OCH_3	4-Cl	153	236–238	68
A_4	4-OCH_3	4-NO_2	162	203–205	68
A_1	4-OCH_3	4-H	156	188–190	69
B_4	4-H	4-NO_2	155	227–229	72

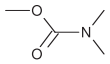
1690, (C—N) 1285, (C═C) 1582–1573 , (—OCH_3) 1171–1015 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.6–7.2 (m, 8H, Ar), 8.8 (s, 1H, —CH—), 3.8 (s, 3H, —OCH_3); ^{13}C-NMR ($CDCl_3$): δ 60.2, 116.2, 118.3, 119.5, 129.3, 132.7, 132.2, 136.7, 145.7, 160.7, 162.2; MS: Molecular ion peak *m/z* 289; *Anal*. Calcd for: $C_{15}H_{12}NO_3Cl$: C, 62.28; H, 4.15; N, 4.84. Found: C, 63.09; H, 4.89; N, 4.31; Percentage yield = 69%.

4-(4-Methoxyphenyl)-3-(4-nitrophenyl)-1,3-oxazetidin-2-one (A$_4$). mp:203–205°C; IR (KBr Pellets) ν:



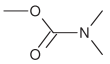
1702, (C—N) 1283, (C═C) 1581–1553, (—OCH_3) 1175–1022, (NO_2) 1553–1331 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.7–7.1 (m, 8H, Ar), 8.8 (s, 1H, —CH—), 3.9 (s, 3H, —OCH_3); ^{13}C-NMR ($CDCl_3$) δ: 59.7, 117.2, 119.1, 119.7, 122.7, 129.8, 132.3, 132.9, 133.7, 146.6, 161.4, 162.8; MS: Molecular ion peak *m/z* 300; *Anal*. Calcd for: $C_{15}H_{12}N_2O_5$: C, 60.00; H, 4.00; N, 9.33. Found: C, 59.06; H, 4.73; N, 9.87; Percentage yield = 68%.

4-(4-Methoxyphenyl)-3-phenyl-1,3-oxazetindin-2-one (A$_1$). mp: 188–190°C; IR (KBr Pellets) ν:



1680, (C—N) 1286, (C═C) 1570–1580, (—OCH_3) 1172–1012 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.5–6.9 (m, 8H, Ar) , 8.7 (s, 1H, —CH—), 3.8 (s, 3H, —OCH_3); ^{13}C-NMR ($CDCl_3$) δ: 59.8, 116.9, 119.2, 119.6, 122.4, 129.4, 132.7, 132.6, 133.9, 146.8, 161.3, 162.9; MS: Molecular ion peak *m/z* 255; *Anal*. Calcd for: $C_{15}H_{13}NO_3$: C, 70.58; H, 5.09; N, 5.49. Found: C, 69.87; H, 5.23; N, 5.89; Percentage yield = 69%.

3-(4-Nitrophenyl)-4-phenyl-1,3-oxazetidin-2-one (B$_4$). mp: 227–229°C; IR (KBr Pellets) ν:



1689, (C—N) 1244, (C═C) 1650–1570, (—NO_2) 1527–1332 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.8–6.6 (m, 8H, Ar), 8.6 (s, 1H, —CH—); ^{13}C-NMR ($CDCl_3$) δ: 117.2,119.3, 119.4, 122.8, 129.6, 132.4, 132.8, 133.4, 146.3, 161.5, 162.7; MS: Molecular ion peak *m/z* 270; *Anal*. Calcd for: $C_{14}H_{10}N_2O_4$: C, 62.22; H, 3.70; N, 10.37. Found: C, 62.97; H, 4.25; N, 10.9; Percentage yield = 72%.

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