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BENZOPHENONE SENSITIZED ONE-POT PHOTOREDOX REACTION OF N-(A-CYANO-A-SUBSTITUTED PHENYL)-METHYLANILINES LEADING TO THE SYNTHESIS OF BENZOIMIDAZOLOQUINOLINES

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ABSTRACT

N-(α-cyano-α-substituted phenyl)-methylanilines (I) on exposure to bright sunlight using soda glass photoreactor are transformed smoothly, with insertion of one methylene group from the solvent (methanol), into substituted benzoimidazoloquinolines (II) with improved yields under benzophenone sensitized conditions employing basic aqueous alcoholic medium in the presence of iodide salt. These compounds have been characterized through their, elemental analysis, IR, ^{1}H NMR, ^{13}C NMR and mass spectral studies.

Keywords: Azomethines, N-(α-cyano-α-substituted phenyl)-methylanilines, benzophenone,

INTRODUCTION

Upon exposure with ultraviolet radiations organic nitriles have provided a variety of new heterocyclic compounds depending on the reaction conditions employed[1,2,3]. Consequentely, with the idea to utilise the solar radiations for these photochemical reactions, these N-(α- cyano-α-substituted phenyl)-methylanilines (I) have been subjected to solar radiations, as these compounds (I) have been reported to undergo photodecomposition on exposure to sunlight. Earlier from these laboratories the synthesis of substituted benzoimidazoloquinolines[4] and a photoredox reaction of N-(α-cyano-α-substituted phenyl)-methylanilines under unsensitised condition and consuming longer time period with poor yields have been reported[5].

EXPERIMENTAL

All the chemicals and solvents (Aldrich company U.S.A and B.D.H standard) used for this photoredox reaction were of high purity and were used without further purification. These reactions were monitored intermitantly by percolated alumina, silica gel 60 F 254 thin layer plates procured from Merck Company. All melting points were measured with an open capillary apparatus are uncorrected. All the compounds were characterized through their IR, ^{1}H NMR, ^{13}C NMR, mass spectral studies and elemental analysis. IR spectra were recorded on a Perkin Elmer RXIFT infrared spectrometer using KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker advance spectrometer using TMS as internal standard. Mass spectra was recorded on Thermo scientific LTQ-XLLCMS. Elemental analysis was carried out using Elementar Vario Micro cube CHN analyzer.

General procedure for the synthesis of 3-hydroxy-9-methyl-2-oxo-1,2,2a,11-tetrahydro-benzo [3,4-a] imidazolo [3,4-a] quinoline (I)

General procedure for the preparation of azomethines variously substituted azomethines were prepared by following identical procedure

as described in literature[8]. Synthesis of 2-(3-methylbenzylideneamino) phenol is described as a representative case. 2-Hydroxybenzaldehyde 1.22 g (0.01 mol) were mixed with 1.07 g (0.01 mol) of m-toluidine in 10cc of ethyl alcohol. The reaction mixture after gentle warming provided the required azomethine. M.p. 79-81^{0}C.

(II) General Procedure for the preparation of N-(α-cyano-α-substituted phenyl)-methylanilines

To the aqueous methanolic solution of azomethine 2.11 g (0.01 mol) taken in conical flask, an equimolar quantity of sodium cyanide 1.06 g (0.01 mol) were added in good ventilated hood. The reaction mixture was kept for overnight period. Usual work up of reaction mixture provided the crystalline product which was recrystallized from petroleum ether. M.p. 98-100^{0}C.

(III) General Procedure for the preparation of 2-oxo-1,2,2a,11-tetrahydro-benzo[3,4-a] imidazolo[3,4-a] quinoline

An alcoholic solution of doubly recrystallized 3.2 g (0.01 mol) of N-(α-cyano-α-substituted phenyl)-methyl-3-toluidine in methanol (300 ml) was taken in a one litre capacity conical soda glass flask. To this mixture were added potassium hydroxide (2.0 g), potassium iodide (7.5 g) and few crystal of benzophenone. To ensure the expulsion of dissolved oxygen in the reaction mixture it was flushed with nitrogen gas for a period of half an hour to provide an inert atmosphere. Finally the flask stoppered tightly and exposed to sunlight for one week (40 hour approximately) turning the reaction mixture dark brown. After this period, excess of methanol was pulled off in vacuo. The mother liquor was extracted with solvent ether. The etheral layer was dried over anhydrous magnesium sulphate and on pulling off the ether in vacuo provided the crude product which on recrystallization from petroleum ether yielded cream coloured crystalline 3-hydroxy-9-methyl-2-oxo-1,2,2a,11-tetrahydro-benzo[3,4-a] imidazolo[3,4-a]quinoline in 78% yield m.pt 225-27^{0}C (Scheme 1). These benzoimidazoloquinolines have been characterized through elemental analysis, IR, ^{1}H NMR, ^{13}C NMR and high resolution mass spectral data[8].

General Procedure for the preparation of 2-oxo-1,2,2a,11-tetrahydro-benzo[3,4-a] imidazolo[3,4-a] quinoline

All these benzoimidazoloquinolines (IIa to IIi) were prepared by following identical procedure (table 1 and table 2).

10-Methyl-2-oxo-1,2,2a,11-tetrahydrobenzo[3,4-a]imidazolo[3,4-a]quinoline (IIa) M.p.: 153-55^{0}C; Yield 75%; IR (Potassium bromide): 3366-3310 (-N-H), 1715 (), 1610-1585 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.3 (s, 3H, -CH_3), 6.6 (m, 2H, -CH_2), 5.3 (s, H, -CH), 7.0-8.1 (m, 7H, Ar), 1.5 (s, 1H, -NH); ^{13}C NMR (400MHz, $CDCl_3$) δ: 22.6, 116.3, 117.7, 118.7, 120.3, 121.5, 126.4, 127.7, 128.4, 131.5, 131.6, 132.5, 137.6, 141.7, 147.3, 156.4, 158.3; MS: Molecular ion peak m/z 250.22; Anal.Calcd for $C_{16}H_{14}N_2O$: C, 76.77; H, 5.67; N, 11.23; Found: C, 76.27; H, 5.36; N, 11.10.

9-Methyl-2-oxo-1,2,2a,11-tetrahydro-benzo[3,4,-a]imidazolo[3,4-a]quinoline (IIb). M.p.: 232-35^{0}C; Yield: 74%; IR (Potassium bromide): 3372-3329 (-N-H), 1711 (), 1603-1582 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.1 (s, 3H, -CH_3), 6.8 (m, 2H, -CH_2), 5.4 (s, H, -CH), 7.2-8.0 (m, 7H, Ar), 1.5 (s, 1H, -NH); ^{13}C NMR (400MHz, $CDCl_3$) δ: 23.5, 116.5,117.7, 118.5, 120.3, 120.8, 126.4, 127.8, 128.8, 131.3, 131.4, 132.4, 137.5, 141.8, 147.6, 155.4, 159.3; MS: Molecular ion peak m/z 250.43; Anal.Calcd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19; Found: C, 76.23; H, 5.32; N, 11.03.

9-Chloro-2-oxo-1,2,2a,11-tetrahydro-benzo[3,4,-a]imidazolo[3,4-a]quinoline (IIc). M.p.: 128-30^{0}C; Yield: 73%; IR (Potassium bromide): 3386-3317 (-N-H), 1720 (), 1610-1590

(C=C) cm^{-1}; ^1H NMR (400MHz, $CDCl_3$) δ : 6.6 (m, 2H, $-CH_2$), 5.5 (s, H, -CH), 6.8-7.9 (m, 7H, Ar), 1.3 (s, 1H, -NH); ^{13}C NMR (400MHz, $CDCl_3$) δ: 116.4, 117.3, 118.2 121.3, 121.4, 126.3, 127.4, 128.6, 131.5, 131.4, 132.2, 137.4, 140.8, 146.6, 156.4, 158.3; MS: Molecular ion peak m/z 270.87; Anal.Calcd for $C_{15}H_{11}ClN_2O$: C, 66.55; H, 4.10; N, 10.35; Found: C, 66.03; H, 4.02; N, 10.11.

3-Hydroxy-10-methyl-1,2,2a,11-tetrahydro-benzo[3,4,-a]imidazolo[3,4-a]quinoline (IId). M.p.: 232-34°C; Yield: 76%; IR (Potassium bromide): 3373-3310 (-N-H), 1723 (), 1615-1566 (C=C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 2.3 (s, 3H, $-CH_3$), 6.7 (m, 2H, $-CH_2$) , 5.1 (s, H, -CH), 7.2-8.0 (m, 6H, Ar), 8.2 (s, 1H, -OH), 1.2 (s, 1H, -NH); ^{13}C NMR (400MHz, $CDCl_3$) δ: 22.6, 116.3, 117.5, 119.2 120.3, 120.4, 126.6, 127.7, 128.4, 130.5, 130.2, 132.4, 137.2, 140.5, 146.4, 155.4, 159.3; MS: Molecular ion peak m/z 266.56; Anal. Calcd. for $C_{16}H_{14}N_2O_2$: C ,72.27; H, 5.28; N, 10.34; Found: C, 72.02; H, 5.09; N, 10.24.

3-Hydroxy-9-methyl-2-oxo-1,2,2a,11-tetrahydro-benzo[3,4.-a]imidazolo[3,4-a]quinoline(IIe). M.p.: 225-27°C; Yield: 78%; IR (Potassium bromide): 3376 (-N-H), 1725 (), 1615-1566 (C=C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 2.5 (s, 3H, $-CH_3$), 6.9 (m, 2H, - CH_2) , 5.3 (s, H, -CH), 7.1-8.2 (m, 6H, Ar), 8.3 (s, 1H, -OH), 0.6(s, 1H, -NH); ^{13}C NMR (400MHz, $CDCl_3$) δ: 21.4 ,112.7, 117.8, 118.6, 120.5, 120.7, 123.9, 127.5, 128.8, 131.2, 131.2, 132.7, 136.3, 140.7, 147.6, 155.7, 159.2; MS: Molecular ion peak m/z 266.23 and others prominent peak are at m/z 221.21, 206.25, 191.31, 163.31, 107.25, 77.25; Anal. Calcd. for $C_{16}H_{14}N_2O_2$: C ,72.16; H, 5.30; N, 10.50; Found: C, 72.07; H, 5.27; N, 10.32.

9-Chloro-3-hydroxy-2-oxo-1,2,2a,11-tetrahydro-benzo[3,4,-a]imidazolo[3,4-a]quinoline(IIf). M.p.: 200-02 °C; Yield: 72%; IR (Potassium bromide): 3373 (-N-H), 1725 (), 1590-1575 (C=C) cm-1; ^1H NMR (400 MHz, $CDCl_3$) δ: 6.4 (m, 2H, $-CH_2$), 5.6 (s, H, -CH-), 6.8-7.8 (m, 6H, Ar), 1.2 (s, 1H, -NH), 8.1 (s, 1H, OH); ^{13}C NMR (400MHz, $CDCl_3$) δ: 112.4, 117.4, 117.9, 121.2, 121.4, 123.5, 127.4, 128.3, 130.2, 130.6, 132.7, 136.3, 140.3, 147.4, 155.4, 158.2; MS: Molecular ion peak m/z 286; Anal.Calcd for $C_{15}H_{11}ClN_2O_2$: C, 62.84; H, 3.87; N, 9.77; Found: C, 62.14; H, 3.23; N,9.28.

5-Methoxy-10-methyl-2-oxo-1,2,2a,11-tetrahydro-benzo[3,4,-a]imidazolo[3,4-a]quinoline (IIg). M.p.: 137-39°C; Yield: 71%; IR (Potassium bromide): 3365 (-N-H), 1725 (), 1600-1585 (C=C) cm^{-1}; ^1H NMR(400MHz, $CDCl_3$) δ: 6.2 (m, 2H, $-CH_2$), 5.6 (s, H, -CH), 6.8-7.9 (m, 6H, Ar), 1.2 (s, 1H, -NH), 2.7 (s, 3H, CH_3), 3.4 (s, 3H, $-OCH_3$); ^{13}C NMR (400MHz, $CDCl_3$) δ: 24.7, 114.4, 117.2, 117.5, 121.4, 121.6, 123.6, 127.3, 128.6, 130.4, 130.4, 132.3, 136.5, 140.6, 147.7, 154.6, 158.8; MS: Molecular ion peak m/z 280; Anal.Calcd for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99; Found C, 72.15; H, 5.23; N, 9.16.

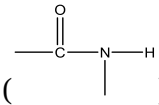
5-Methoxy-9-methyl-2-oxo-1,2,2a,11tetrahydro-benzo[3,4,-a]imidazolo[3,4-a]quinoline (IIh)., M.p.: 127-29 °C, Yield: 72%; IR (Potassium bromide): 3360 (-N-H), 1720 (), 1600-1580 (C=C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 6.3 (m, 2H, $-CH_2$), 5.5 (s, 1H, -CH), 6.8-8.1 (m, 6H, Ar), 1.3 (s,1H, -NH), 2.5 (s, 3H, CH_3), 3.2 (s, 3H, $-OCH_3$); ^{13}C NMR (400MHz, $CDCl_3$) δ: 23.7, 112.4, 116.7, 117.4, 117.6, 120.4, 120.6, 126.6, 127.5, 128.4, 131.4, 131.3, 132.5, 136.7, 140.5, 147.5, 153.7, 158.4; MS: Molecular ion peak m/z 280; Anal.Calcd for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99; Found: C, 72.12; H, 5.23; N, 9.14.

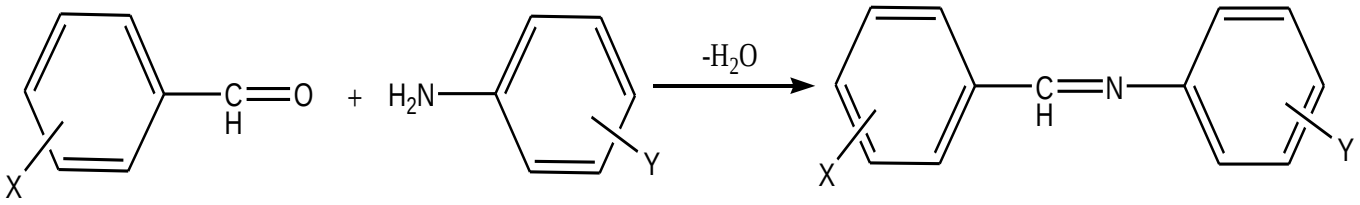
5-Methoxy-9-chloro-2-oxo-1,2,2a,11-tetrahydro-benzo[3,4,-a]imidazolo[3,4-a]quinoline(Ii).

M.p.: 122-25 ^{0}C; Yield: 73%; IR (Potassium bromide): 3360 (-N-H), 1720 (), 1610-1585 (C=C) cm^{-1} ; ^{1}H NMR (400MHz, $CDCl_3$) δ: 6.3 (m, 2H, -CH_2), 5.4 (s, H, -CH-), 6.8-7.9 (m, 6H, Ar), 1.3 (s, 1H, -NH), 3.2 (s, 1H, -OCH_3); ^{13}C NMR (400MHz, $CDCl_3$) δ: 112.6, 117.7, 117.6, 117.5, 121.3, 121.5, 126.7, 127.4, 128.7, 130.5, 130.5, 132.5, 136.7, 140.7, 147.6, 153.7, 158.4; MS: Molecular ion peak m/z 300; Anal.Calcd for $C_{16}H_{13}ClN_2O_2$: C, 63.90; H, 4.36; N, 9.31; Found: C, 63.11; H, 4.04; N, 9.09.

RESULTS AND DISCUSSION

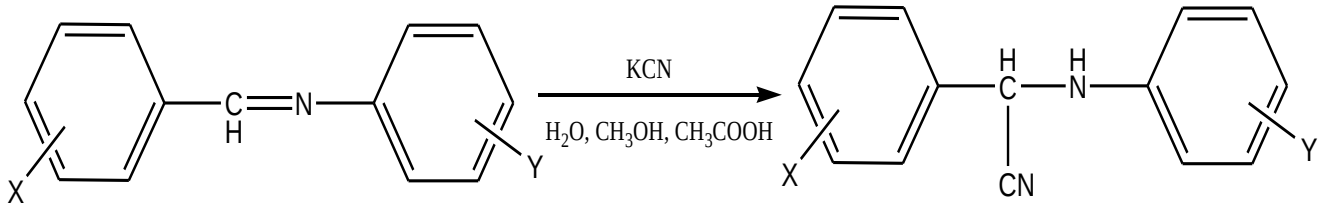
Present study describes the synthesis of variously substituted N-(α-cyano-α-substituted phenyl)-methylanilines which have been obtained by the hydrocyanic acid addition on substituted open chain azomethines and subsequently their photoredox reaction under sensitized conditions. To the methanolic solution of these N-(α-cyano-α-substituted phenyl)- methylanilines were added an aqueous solution of potassium hydroxide, potassium iodide and benzophenone and this reaction mixture was exposed to direct sunlight in soda glass reactor.

Under the sensitized conditions, these N-(α-cyano-α-substituted phenyl)-methylanilines smoothly transformed to provide a new fused heterocyclic ring system (II) in lesser time as required under unsensitized conditions[6] (Scheme 1). These compounds have been characterized as substituted 2-oxo-1,2,2a,11-tetrahydrobenzo[3,4-a]imidazolo[3,4-a] quinoline derivatives through their elemental analysis, IR, proton magnetic resonance, ^{13}C NMR and high resolution mass spectra. In infrared spectrum of 3-Hydroxy-9-methyl-2-oxo-1,2,2a,11-tetrahydrobenzo[3,4-a]imidazolo[3,4-a]quinoline shows medium intensity absorption bands in the region 3376-3315 cm^{-1} which has been assigned to the secondary amide function (-N-H-stretching). The lower position of these bands indicates the presence of either inter or intramolecular hydrogen bonding in these products. Strong infrared absorption band at 1725 cm^{-1} has been assigned to the cyclic amido carbonyl function (). Absorption bands in the region 1654-1566 cm^{-1} has been assigned to the aromatic carbon-carbon double bond stretching vibrations. Weak intensity absorption bands in the region 1410-1400 cm^{-1} correspond to carbon-nitrogen single bond vibrations. The various infrared absorption bands indicate that transformation of nitrile function present in α-cyanoamines has occurred as absorption band corresponding to the nitrile function is missing.



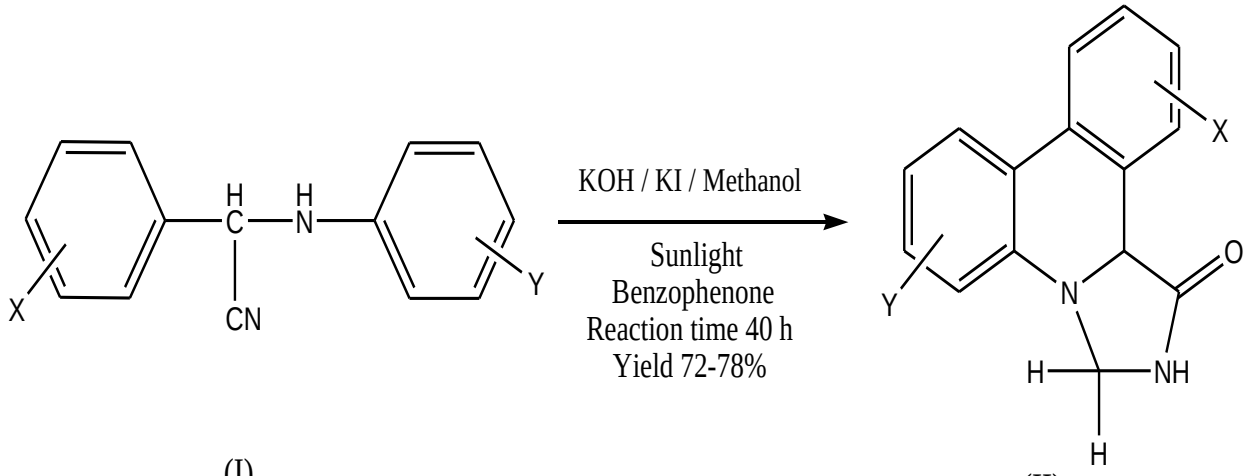
Where X= -H, 2-OH, 4-OCH_3
Y= 2-CH_3, 3-Cl, 3-CH_3

Preparation of azomethines



(I)

Preparation of N-(α-cyano-α-substituted phenyl)-methylanilines

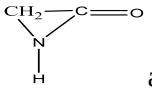


(I) (II)

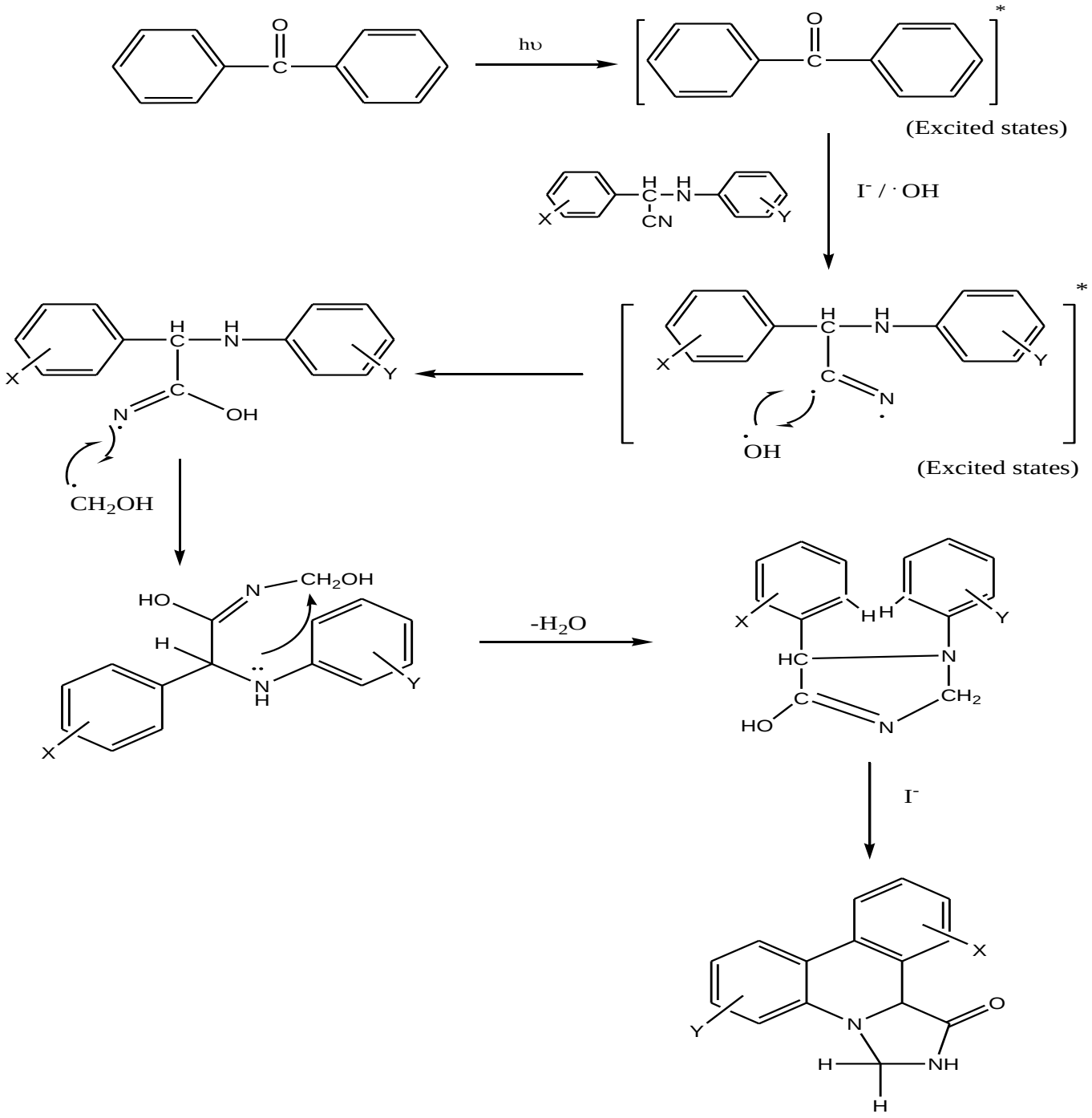
Scheme 1. Synthesis of 2-oxo-1,2,2a,11-tetrahydrobenzo[3,4-a]imidazolo[3,4-a]quinolines

In the high resolution (400 MHz) proton magnetic resonance spectrum of 3-Hydroxy-9-methyl-2-oxo-1,2,2a,11-tetrahydro-benzo[3,4-a] imidazolo [3,4-a] quinoline shows multiplet at δ 8.2-7.1 (equivalent to six protons) which has been assigned to aromatic protons, another multiplet at δ 6.9 (equivalent to two proton) which has been assigned to the methylenic protons (-CH_2-), a broad singlet at δ 5.3 (equivalent to one proton) has been assigned to the methynic proton (-CH-), a singlet at δ 2.5 (equivalent to three protons) has been assigned to one methyl group and a broad absorption signal at δ 0.6 (equivalent to one proton) has been assigned an amido proton (-N-H), on deuterium exchange the signal for this (-N-H-) proton disappears confirming the presence of one active proton on the amine function.

In their ^{13}C NMR spectra, compound 3-Hydroxy-9-methyl-2-oxo-1,2,2a,11-tetrahydro-benzo[3,4-a]imidazolo [3,4-a]quinoline displays signal at δ 159.2 has been assigned to carbonyl carbon while another signal at δ 155.7 has been assigned to phenolic carbon. The aniline carbon displays its signal at δ 147.6 and the tolylic carbon displays its signal at δ 140.7. The other signals at δ 132.7, 120.7, 120.5, 128.8, 131.2, 131.2, 127.5, 136.3 corresponds to C-10, C-8, C-7, C-6b, C-5, C-4, C-6, C-2b. The signal at δ 119.5 has been assigned to carbon atom of benzylic group while a signal at δ 118.6 assigned to carbon atom of methylene group. The signal at δ 21.4 assigned to carbon atom of methyl group.

In high resolution mass spectra of 3-Hydroxy-9-methyl-2-oxo-1,2,2a,11-tetrahydro-benzo [3,4-a] imidazolo[3,4-a]quinoline, the molecular ion peak appears at m/z 266. The base peak appears at m/z 193 due to the loss of a neutral molecule aziridinones molecule  and phenolic group OH. The molecular ion peak loses hydrogen cyanide H-N-C=O to give a peak at m / z 221. The other ion peak appears at m / z 206 with the loss of methyl (-CH_3) group. With the loss of O^+ ion, the prominent ion peak appears at m / z 191. Then the loss of (-HCN) gives the daughter ion peak at m / z 166. Others ion peaks at m / z 106, 78 appear on fission of the fragment ions.

Under these reaction conditions, benzophenone seems to transfer its energy to α-cyanoamine to form diradical specie on which hydroxide free radical generated in situ by iodide salt, to form hydroxyamino radical which is subsequently attacked by hydroxymethyl radical[7], during photoirradiation the hydroxymethylamino intermediate gets dehydrated to form imidazoline intermediate, bringing the two aromatic C-phenyl and N-phenyl rings in close proximity which on oxidation with loss of H-atom get connected to form fused cyclic imidazolo ring system (Scheme 2).



Scheme 2. Proposed mechanism of 2-oxo-1,2,2a,11-tetrahydrobenzo[3,4-a]quinolines

Table 1 Characterization data of azomethines and N-(α-cyano-α-substitutedphenyl)-methylanilines

Entry	X	Y	M.p. of azomethines (^{0}C)	M.p. of N-(α-cyano-α-substituted phenyl)-methylanilines (^{0}C)
II(a)	H	2-CH_3	63-65	88-90
II(b)	H	3-CH_3	78-80	90-92
II(c)	H	3-Cl	56-58	80-82
II(d)	2-OH	2-CH_3	82-84	123-25
II(e)	2-OH	3-CH_3	79-81	98-100
II(f)	2-OH	3-Cl	95-97	110-12
II(g)	4-OCH_3	2-CH_3	72-74	95-97
II(h)	4-OCH_3	3-CH_3	58-60	70-72
II(i)	4-OCH_3	3-Cl	76-78	93-95

Table 2 Characterization data of 2-oxo-1, 2, 2a, 11-tetrahydrobenzo [3, 4-a] imidazolo [3, 4-a] quinoline

Entry	X	Y	M.p. of benzoimidazolo quinolines (^{0}C)	Reaction time (h)	Yield (%)
II(a)	H	2-CH_3	153-55	35	75
II(b)	H	3-CH_3	232-35	38	74
II(c)	H	3-Cl	128-30	32	73
II(d)	2-OH	2-CH_3	232-34	38	76
II(e)	2-OH	3-CH_3	225-27	40	78
II(f)	2-OH	3-Cl	200-02	35	72
II(g)	4-OCH_3	2-CH_3	137-39	32	71
II(h)	4-OCH_3	3-CH_3	127-29	30	72
II(i)	4-OCH_3	3-Cl	122-25	33	73

CONCLUSION

Moreover the originality of the work lies in using simple reagents which are easily available at convenience. The synthesis of improved yields of substituted benzoimidazoloquinolines with sensitized benzophenone which act as a catalyst in synthesis.

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