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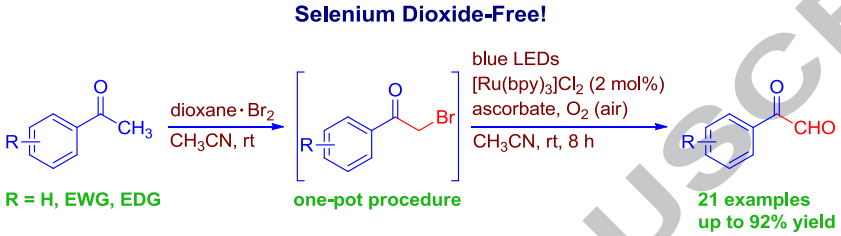

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ABSTRACT

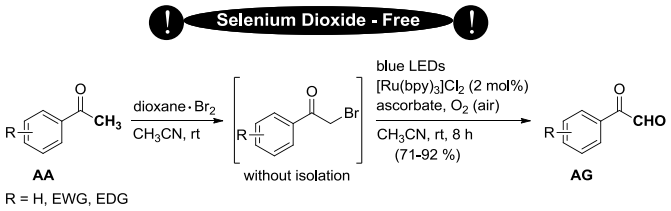
A novel visible-light (blue LEDs: $h\nu$ = 425±15 nm) photocatalyzed one-pot method for the synthesis of electronically diverse aryl glyoxals in good to excellent yields from acetoarylones and green regents such as air, vitamin C and dioxane dibromide has been described. In addition, an application of the current methodology has been demonstrated for the oxidation of monoamine oxidase-B inhibitors, i.e., 1-(4-((4-fluorobenzyl)oxy)phenyl)ethanone and 1-(3-((4-chlorobenzyl)oxy)phenyl)ethanone. This finding may serves as a valuable alternative to the traditional acetoarylones oxidation reactions conducted using selenium dioxide a harmful and unselective reagent known to simultaneously oxidize allylic, benzylic, -CH_3 and so on.

1. Introduction

The aryl glyoxals[1] are very important dielectrophilic precursors that have been used in organic synthesis for the construction of natural products and heterocyclic compounds including hydantoins, imidazoles, oxadiazoles and thiophenodiones[2]. Moreover, they have been used in medicinal chemistry as drugs to modify amino acids and arginines[3]. The aryl glyoxals were first successfully prepared by thermal decomposition of the sulfite derivative of the oxime[4], i.e., $C_6H_5C(O)CH(NOSO_2H)$. However, this method is seldom used due to poor atom economy and difficulties associated with the product purification from sulfamic acid a byproduct. In last 60 years, aryl glyoxals in bulk have been prepared from acetoarylones by oxidation using selenium dioxide (SeO_2) in aqueous solutions[5,6]. Despite the fact that oxidation performed in aqueous medium, but it suffers with several drawbacks such as requires more than stoichiometric amounts of SeO_2, unselective, low product yield (30-70%), needs inert atmosphere, toxic, involves an exhaustive work-up, large amount of metal waste produced, occurs only at elevated temperatures and so on. Hence, the development of environmentally friendly, operationally simple, mild and efficient methodology for the synthesis of glyoxals is very desirable and remains a challenging task for exploration.

Since the seminal works from the research groups of MacMillan[7], Stephenson[8], Yoon[9] and others[10], visible light (400-700 nm) induced organic synthesis[11] has appeared as a promising strategy to access various building blocks, natural products and drugs[12]. Significant energy efficiency, simple reaction setup, environmental friendly, mild reaction conditions and good to excellent yields are some important characteristics of this class of reactions. Using a visible light photoredox catalysis[13] and 9,10-dihydro-10-methylacridine as both electron and proton sources, two decades ago, Fukuzumi's group[14] have reported a mild protocol for the reductive dehalogenation of arylacyl bromides into corresponding acetoarylones. Subsequently, several research groups were utilized Hantzsch esters[15], alkyl amines[16], allyl stannanes, etc[17]., as reductive quenchers for arylacyl radicals to synthesize alkyl aryl ketones under visible-light photocatalyzed conditions. Based on these reports, we hypothesized that reaction between arylacyl radicals and molecular oxygen (O_2) would provide aryl glycols under mild and green conditions. Moreover, we intended to synthesize arylacyl bromides *in situ* from acetoarylones; so that aryl glycols perhaps obtained in one-pot procedure known to minimize time and chemical waste.

In continuation of our studies on the visible-light photoredox catalysis[18], herein we describe a novel one-pot method for the synthesis of aryl/heteroaryl glyoxals from acetoarylones under visible-light (blue LEDs: $h\nu$ = 425±15 nm) photocatalyzed conditions, cf. Scheme 1. In addition, we account an application of this methodology for the oxidation of monoamine oxidase-B inhibitors[19], i.e., 1-(4-((4-fluorobenzyl)oxy)phenyl)ethanone and 1-(3-((4-chlorobenzyl)oxy)phenyl)ethanone into their glyoxal derivatives. Indeed, all reactions proceeded under ambient conditions and pure products were obtained readily by recrystallization or filtration through short pad silica gel column chromatography. To the best of our knowledge, oxidation of aryl/heteroaryl methyl ketones to aryl/heteroaryl glyoxals via visible-light initiated protocol has not yet been reported in the literature.

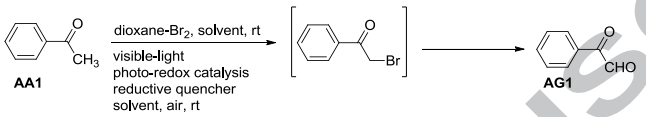


Scheme 1. A selenium dioxide-free one-pot oxidation of aryl/heteroaryl methyl ketones to their corresponding glyoxals under visible-light photocatalysed conditions reported in this work.

Results and Discussion

Dioxane dibromide (**DDB**)[20], a solid brominating agent, has been successfully used for the selective mono-bromination of polycyclic-aromatic hydrocarbons[21], alkylarylketones[22], coumarins[23], etc[24]., at room temperature. Thus, we preferred **DDB** for the conversion of acetoarylones into arylacyl bromides. Nevertheless, initially, an optimization study was carried out with a model reaction between acetophenone (**AA1**, 1.0 equiv.,) and **DDB** (1.1 equiv.,) to examine whether it gives only the α-monobrominated product, i.e., phenacyl bromide. Several

Table 1. Selected results of screening the optimal conditions for the photocatalytic one-pot oxidation of acetophenone (**AA1**) to phenyl glyxoal (**AG1**) at ambient conditions[a]



Entry	Solvent [b]	Photo-redox catalyst	Reductive quencher	Time (h)	Yield (%) [c]
1	CH_3CN	$[Ru(bpy)_3]Cl_2$	Et_3N	36	17[d]
2	CH_3CN	$[Ru(bpy)_3]Cl_2$	Et_3N	36	26
3	CH_3CN	$[Ru(bpy)_3]Cl_2$	Et_3N	36	14[e]
4	CH_3CN	$[Ru(bpy)_3]Cl_2$	Et_3N	36	<10[f]
5	CH_3CN	$[Ru(bpy)_3]Cl_2$	Et_3N	36	0[g,h]
6	CH_3CN	$[Ru(bpy)_3]Cl_2$	sodium ascorbate	18	91
7	CH_3CN	$[Ru(bpy)_3]Cl_2$	Diisopropylethylamine	20	16
8	CH_3CN	$[Ru(bpy)_3]Cl_2$	Triphenylamine	20	11
9	CH_3CN	$[Ru(bpy)_3]Cl_2$	ammonium oxalate	20	38
10	glyme	$[Ru(bpy)_3]Cl_2$	sodium ascorbate	18	22
11	DMF	$[Ru(bpy)_3]Cl_2$	sodium ascorbate	18	88
12	$C_2H_4Cl_2$	$[Ru(bpy)_3]Cl_2$	sodium ascorbate	18	24
13	CH_3CN	$[fac\text{-}Ir(ppy)_3]$	sodium ascorbate	18	47
14	CH_3CN	Eosin Y	sodium ascorbate	18	36
15	CH_3CN	$[Ru(bpy)_3]Cl_2$	sodium ascorbate	8	92[i]
16	CH_3CN	$[Ru(bpy)_3]Cl_2$	sodium ascorbate	8	90[j]
17	CH_3CN	$[Ru(bpy)_3]Cl_2$	sodium ascorbate	8	94[k]
18	CH_3CN	Nil	sodium ascorbate	8	0[h]
19	CH_3CN	$[Ru(bpy)_3]Cl_2$	sodium ascorbate	7	93[i,l]
20	CH_3CN	$[Ru(bpy)_3]Cl_2$	sodium ascorbate	8	<5[i,m]
21	CH_3CN	$[Ru(bpy)_3]Cl_2$	sodium ascorbate	8	<5[i,n]

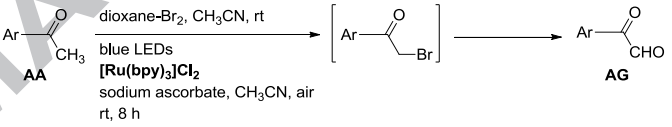
[a] Unless stated otherwise all reactions were performed in a Schlenk tube with 1.1 mmol of **DDB**, 1.0 mmol of **AA1**, 3.0 mmol of reductive quencher and 1mol% photo-redox catalyst in dry solvent under air with the irradiation of a 5W blue LEDs ($h\nu$ = 425±15 nm).
[b] Solvents were rigorously purified following the methods described in reference [25]
[c] Isolated yields.
[d] a household fluorescent lamp used.
[e] 5W green LEDs used.
[f] 15W ambient lamp used.
[g] no irradiation source used.
[h] phenacyl bromide isolated in quantitative yield.
[i] 2% $[Ru(bpy)_3]Cl_2$ used.
[j] 3% $[Ru(bpy)_3]Cl_2$ used.
[k] 5% $[Ru(bpy)_3]Cl_2$ used.
[l] Reaction performed under O_2 atmosphere using a balloon
[m] Reaction performed under Ar atmosphere
[n] Reaction performed under N_2 atmosphere

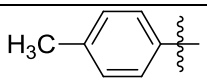
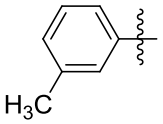
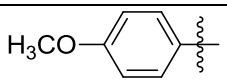
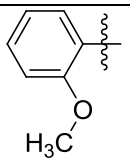
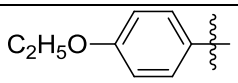
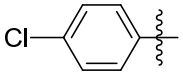
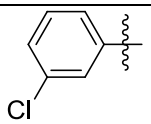
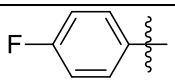
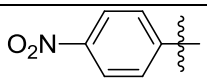
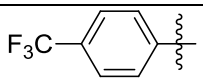
solvents including hexane, toluene, acetonitrile, dichloromethane, carbon tetrachloride, dioxane, N,N-dimethyl formamide, ethanol and water were investigated. The best results were achieved using aprotic polar solvents like acetonitrile, N,N-dimethyl formamide and dioxane. When acetonitrile was used as a reaction medium, TLC analysis suggested the formation of single product. The structure of the isolated product (yield 96%) was confirmed by NMR and elemental analysis (Electronic Supporting Information, ESI) in comparison with known compound from literature data.[20] Results suggest that the phenacyl bromide has been formed exclusively.

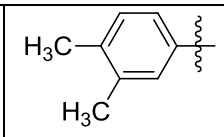
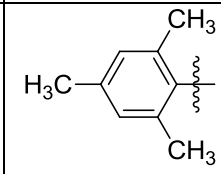
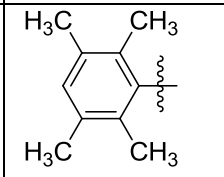
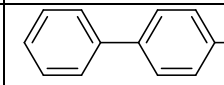
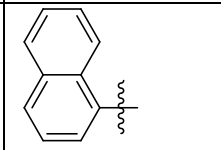
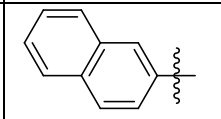
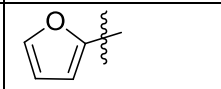
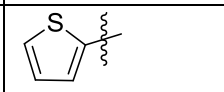
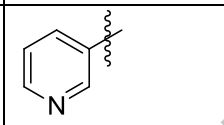
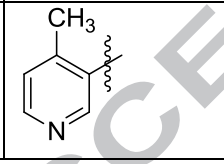
Next, the reaction conditions for one-pot synthesis (Scheme 1) of aryl glyoxals from acetoarylones under photoredox catalyzed conditions were optimized. Irradiation of solution of acetophenone (**AA1**, 1.0 equiv.) in acetonitrile containing **DDB** (1.1 equiv.), $[Ru(bpy)_3]Cl_2$ (1.0 mol%) and triethylamine (3.0 equiv.) under an open air atmosphere (without air bubbling) at room temperature with a household fluorescent lamp for 36 h afforded the desired phenylglyoxal (**AG1**) in 17% yield (Table 1, Entry 1). Encouraged by this initial result, a series of trial experiments were performed to optimize the influences of radiation source, solvents, catalyst and its quantity, reductive quencher and atmosphere on the reaction shown in Scheme 1. Interestingly, the yield of **AG1** enhanced to 26% when the reaction was performed with 5W blue light-emitting diodes (LEDs, $h\nu$ = 425±15 nm, Table 1 and Entry 2). In contrast, the reaction did not proceed satisfactorily when the reaction was irradiated with either 5W green LEDs or ambient lights (Table 1, Entries 3 and 4) or in the absence of light irradiation (Table 1 and Entry 5). We then went on to study the effect of reductive quencher on the reaction (Scheme 1): a better yield of **AG1** was obtained when sodium ascorbate was used (Table 1 and Entry 6). Nevertheless, other quenchers including diisopropylethylamine, triphenylamine and oxalates afforded moderate yield of **AG1** (Table 1 and Entries 7-9). Afterwards, the influence of solvents (Table 1 and Entries 10-12) such as glyme, dimethylformamide, dichloroethane, heptane and diethyl ether on the formation of **AG1** was investigated. The investigation revealed that DMF or CH_3CN was the most effective medium to promote the reaction with 88-91% yield (Table 1, Entries 6 and 11). A maximum yield of **AG1** in DMF or CH_3CN was may be due to the greater solubility of both the catalyst and reductive quencher in that medium. Nevertheless, CH_3CN was used throughout the synthesis due to easy handling and removal from the product. We then studied the effect of other photocatalysts such as [*fac*-$Ir(ppy)_3$] and eosin Y, but none of them gave better results than $[Ru(bpy)_3]Cl_2$. The influence of quantity of catalyst on the product yield was also investigated. An increase in the catalyst amount from 1 mol% to 2 mol%, the reaction time was obviously shortened (18 h to 8 h) with 92% yield of **AG1** (Table 1 and Entry 15). Further increase in catalyst amount had profound effect on neither in reaction time nor in yield of the desired product (Table 1, Entries 16 and 17). However, no product was observed in the absence of catalyst $[Ru(bpy)_3]Cl_2$ (Table 1 and Entry 18). Subsequently, we investigated the influence of atmosphere on the reaction. Under open-air atmosphere or O_2 (balloon), an excellent yield of **AG1** was obtained (Table 1 and Entry 19), whereas in oxygen-free conditions product was detected in negligible quantities (Table 1, Entries 20 and 21). Thus, the combinations of 1.1 equiv. of **DDB**, 2 mol% of $[Ru(bpy)_3]Cl_2$, 3 equiv. of sodium ascorbate and 5W blue LEDs in CH_3CN at room temperature for 8 h are the optimal conditions for one-pot synthesis of aryl glyoxals from acetoarylones as described in Scheme 1.

With the optimized reaction conditions in hand, we further explored the scope of this protocol (Scheme 1) for synthesis of electronically diverse aryl glyoxals (**AG1-AG21**) from corresponding acetoarylones. To our delight, the electronic properties of the acetoarylones had little effect on this transformation (Table 2). For examples, acetoarylones substituted by electron-donating (CH_3, OCH_3, and OC_2H_5) and electron-withdrawing substituents (F, Cl, NO_2 and CF_3) were effectively oxidized into the desired aryl glyoxals in good yields, cf. Table 2. More importantly, electron rich furan (**AA18**), thiophene (**AA19**) and polycyclic aromatic hydrocarbons (**AA15-AA17**) as well as 3-acetyl-4-methylpyridine (**AA21**) were well tolerated, leading to desire glyoxals in good yield (Table 2 and ESI). Moreover, to access the feasibility of applying this method on a preparative scale, we carried out the oxidation of **AA4** on a 100 mmol scale. As expected, the reaction proceeded smoothly; similar to the case in a smaller scale, and the expected 4-methoxyphenyl glyxoal was obtained in 91% yield.

Table 2. Visible-light-mediated one-pot oxidation of acetoarylones into aryl glyoxals under optimized reaction conditions.[a]

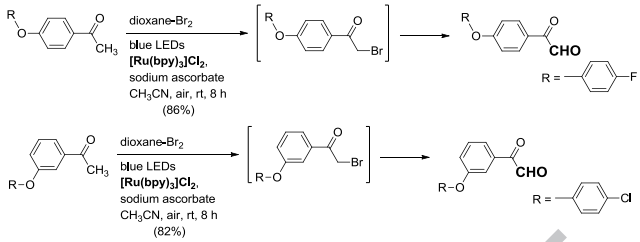


Entry	Ar	Substrate	Product	Yield (%)[b]
1		**AA2**	**AG2**	91
2		**AA3**	**AG3**	89
3		**AA4**	**AG4**	91
4		**AA5**	**AG5**	86
5		**AA6**	**AG6**	91
6		**AA7**	**AG7**	88
7		**AA8**	**AG8**	90
8		**AA9**	**AG9**	84
9		**AA10**	**AG10**	85
10		**AA11**	**AG11**	87

11		**AA12**	**AG12**	92
12		**AA13**	**AG13**	87
13		**AA14**	**AG14**	86
14		**AA15**	**AG15**	89
15		**AA16**	**AG16**	83
16		**AA17**	**AG17**	86
17		**AA18**	**AG18**	89
18		**AA19**	**AG19**	91
19		**AA20**	**AG20**	87
20		**AA21**	**AG21**	83

[a] Reaction conditions: 1.1 mmol of **DDB**, 1.0 mmol of **AA**, 3.0 mmol of sodium ascorbate, 2mol% of $[Ru(bpy)_3]Cl_2$, dry CH_3CN and 5W blue LEDs (hν = 425±15 nm) irradiation under open air atmosphere. [b] Isolated yield.

Finally, to show the applicability of the developed one-pot process, we aimed to oxidize monoamine oxidase-B inhibitors[19] such as 1-(4-((4-fluorobenzyl)oxy)phenyl)ethanone and 1-(3-((4-chlorobenzyl)oxy)phenyl)ethanone (Scheme 2) under standard conditions described in Table 1. In both cases, the reactions were complete within 8 h affording the desired products in 86% and 82% yields. Thus, a mild and efficient one-pot method described here offers a domain for synthesis of highly functionalized- as well as electron rich glyoxals (Table 2, Scheme 2 and ESI) that cannot be accessed via traditional SeO_2 mediated reactions known to simultaneously oxidize allylic, benzylic, -CH_3, and so on.[20]



Scheme 2. Oxidation of 1-(4-((4-fluorobenzyl)oxy)phenyl)ethanone (top) and 1-(3-((4-chlorobenzyl)oxy)phenyl)ethanone (bottom) to their glyoxal derivatives.

Conclusions

In summary, we have developed a novel and operationally simple method for the direct oxidation of acetoarylones including monoamine oxidase-B inhibitors such as 1-(4-((4-fluorobenzyl)oxy)phenyl)ethanone and 1-(3-((4-chlorobenzyl)oxy)phenyl)ethanone into corresponding glyoxals using dioxane dibromide, blue LEDs, ascorbate, 2 mol% $[Ru(bpy)_3]Cl_2$, and O_2 (air) as valuable reagents. A broad tolerance of aromatic rings, one-pot consolidated procedure, large-scale synthesis, easy isolation of the products and good yield are principal advantages of this procedure. Further work is progress in our laboratory to investigate the mechanism and scope of this protocol for the oxidation of dialkylketones and other derivatives.

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Supplementary Data

General synthetic procedure, experimental characterization data and copies of NMR spectra for selected products prepared by the method described here. This material is available free of charge via the Internet.

References and notes

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- In situ produced aryl diazonium salts have been employed as a source of aryl radicals
- 1% $[Ru(bpy)_3]Cl_2$ used as a photo-redox catalyst.
- Complete conversion with up to 94% yield was noticed.