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9-Fluorenone Catalyzed Visible Light Oxidation of Hydrazides: An Efficient Route for the Synthesis of *N,N′*-Diacylhydrazines Derivatives

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A visible light-mediated oxidative coupling of hydrazides into corresponding *N,N′*- diacylhydrazines using a commercially available and low-cost metal-free photocatalyst was reported. The versatility of the reaction has been demonstrated across a broad spectrum of functional groups present in hydrazides. Interestingly, the developed methodology was utilized to synthesize symmetrical and unsymmetrical *N,N′*-diacylhydrazines in moderate yields. Density Functional Theory (DFT) calculations, along with control reactions and quenching studies, provide evidence supporting the proposed mechanism, favoring the photoredox pathway. Additionally, NMR and UV-Vis studies confirmed the generation of H_2O_2 in the reaction mixture, which strengthens the proposed mechanism. To our knowledge, this is the first report for the conversion of hydrazides to *N,N′*-diacylhydrazines using *9*-fluorenone as an organic photoredox catalyst.

1. Introduction

N,N′-diacylhydrazine are a well-known class of organic compounds that contain two acyl groups (RCO—) and one hydrazine group (—HN—NH—) in their structure. These are derivatives of hydrazine (N_2H_4) where one or more hydrogen atoms are replaced by acyl groups. Considerable research has been done for the synthesis of *N,N′*-diacylhydrazines due to its applications[1] in pesticides, insecticides, fungicides, and herbicides, anti-tumor agents, anti-inflammatory drugs, and ligands in metal complexes. Also, *N,N′*-diacylhydrazines finds its importance in synthesis of bioactive molecules such as 1,3,4-oxadiazole and 1,3,4-thiadiazoles as a synthon.[2,3]

Vegetables are amongst the second highest earning crops in the world after cereals, making it essential for farmers to protect them from all insect pest damage.[4] Insect pests are the most significant impediment to vegetable production in India and tropical Asia, amongst which lepidopteran (butterflies and moths) and coleopteran (beetles) pests cause significant damage. These insect pests are primarily controlled by the means of nitrogen containing insecticides such as *N,N′*-diacylhydrazines.[5,6]. Some of the commonly used insecticides such as halofenozide (1), KU-10 (2), methoxyfenozide (3) and tebufenozide (4) have an excellent safety profile, which makes them compatible with their use in integrated pest management (IPM) programmes Figure 1. Dibenzoylhydrazine (DBH) analogues are considered to be very specific to lepidopteran insects, although halofenozide controls coleopteran pests. They are non-steroidal ecdysone agonists[7–9] (or, in other words, are potential insect growth regulators which control insects/pests),
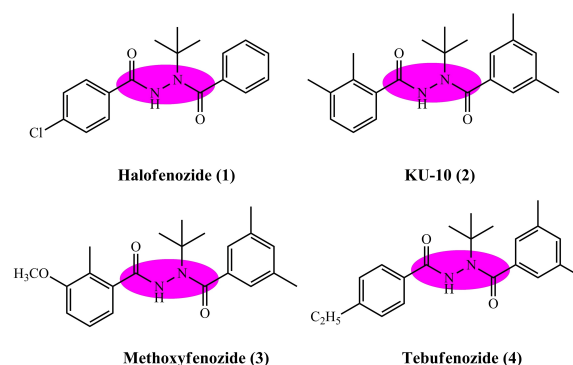

Figure 1. Chemical structures of the DBH compounds having insecticidal activity.

and are used as insecticides because of its unusually high affinity for EcR (Ecdysone receptor) of Lepidopteran insects and Coleopterans. They cause insect larvae to undergo a premature and fatal molt.

Owing to their importance, a surfeit of synthetic methods have been reported to synthesize *N,N′*-diacylhydrazines, with hydrazides as commonly employed principal building blocks. In many cases, the oxidation of hydrazides to *N,N′*-diacylhydrazines have been executed using various oxidizing agents such as lead tetra-acetate, halogens, ammonium acetate, trifluorotoluonylsulphonyl peroxides, benzene selenic acid, polymer-supported periodate ion, diacetoxyiodobenzene, sodium perborate, oxone, copper(II) acetate, Amberlyst A-26, acids such as sulfuric acid, phenylselenic acid and $NaBO_3$ / AcOH. However, all these reported methods use either hazardous and expensive chemicals/ organic solvents or tedious workup procedures. Thus, there continues to be a demand for the development of new, mild, environmentally friendly and facile procedures for the oxidation of hydrazides to *N,N′*-diacylhydrazines.[10–17]

An alternative approach for the oxidative coupling of hydrazides involves the use of visible light-mediated photo-

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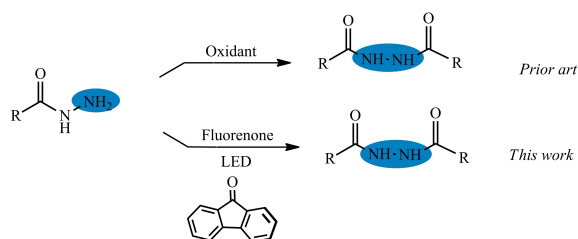**Chemistry Europe**
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redox catalysis (Scheme 1). In recent years, photoredox catalysis[19–24] has been a powerful tool in the development of a variety of synthetic transformations due to milder reaction conditions, eco-friendly and cheaper oxidants. In particular, the oxidative coupling reactions have generated wide interest, mainly because of their broad synthetic utility.[18–22]

With our interest in the development of new strategies using photoredox catalysis and understanding the importance of efficient synthetic route towards N,N'-diacylhydrazines. Herein, we report the oxidation of hydrazides to N,N'-diacylhydrazines in the presence of 9-fluorenone as a photoredox catalyst under metal-, base-, and additive-free conditions using visible light irradiation. This study represents the first report for the conversion of hydrazides to N,N'-diacylhydrazines using 9-fluorenone as a photoredox catalyst.

2. Results and Discussion

2.1 Reaction Optimization

In order to develop the intended protocol, we chose benzoyl hydrazine **1a** as a model substrate for the conversion into N,N'-diacylhydrazines. We studied the reaction for oxidative coupling of benzoyl hydrazine **1a** in presence of 20 mol% of 9-fluorenone as photocatalyst in acetonitrile. The reaction mixture was irradiated with blue LED (455 nm) in an open air for 24 hours as a model reaction (Table 1, entry 1), to our expect-

ations, the reaction resulted in the formation of desired N,N'-diacylhydrazine in 73% yield.

Further, the oxidative coupling of benzoyl hydrazine (1a) was examined utilizing various LEDs (Table 1) as the light source in the presence of 20 mol% of 9-fluorenone. As reported in literature, 9-fluorenone has absorption maxima at around 377 nm, thus, as expected, white and blue LEDs giving desired product 1a in 17 and 73% yields, respectively (Table 1, entries 1,3). However, under green and red LED irradiation, no desired product was formed (Table 1, entry 2 and 4). No reaction in the presence of green and red LEDs attributed to the higher absorption wavelength. Also, in dark, the desired product was not formed, suggesting that the reaction follows a photoredox pathway (Table 1, entry 5). With the promising results from the use of blue LED, we decided to use the same light source for further studies. It is noted that when the reaction is carried out under an argon/ nitrogen atmosphere, it leads to a decrease in the product yield (Table 2, entries 13 and 14). These results also confirm that visible light, photocatalyst, and air are essential for the reaction to undergo the photochemical pathway.

The choice of solvent greatly impacts the outcome of the photochemical reaction because solute-solvent interactions modifies the energies and crossings between electronic states of the chromophores and affect the structures of the photoexcited molecules.

Thus, we studied the influence of solvents like acetonitrile, DMF, DCM, MeOH (Table 2, entries 1–15). After screening various solvents, we concluded that acetonitrile was the most suitable solvent to carry out the oxidation of benzoyl hydrazine (Table 2, entry 11). When solvents like THF, CHCl₃, IPA, and MeOH were employed, we observed lesser yields in the range 2–8% (Table 2, entries 1, 2, 7, 8). Using solvents like DMF, DMSO, Glycerol, and PEG-300, the reaction did not yield any product (Table 2, entries 6, 9, 10, 15).

After light source- and solvent-optimization, the reaction was further screened with various organic photocatalysts using

Scheme 1. Oxidation of hydrazides to N,N'-diacylhydrazines.

Table 1. Effect of the light source in photocatalytic oxidation of hydrazides.

Entry	Light source	Yield (%)
1	White LED	8
2	Blue LED	3
3	Red LED	9
4	Green LED	–
5	Dark	–

[a] Reaction were carried at 0.5 mmol of 1a with 20 mol% of 9-fluorenone in 5 mL MeCN.

Table 2. Screening of solvents for the oxidation of benzoyl hydrazines.

Entry	Solvents	Atmosphere	Yield (%)
1	THF	Air	8
2	CHCl₃	Air	2
3	Toluene	Air	22
4	t-BuOH	Air	2
5	Hexane	Air	24
6	PEG-300	Air	–
7	MeOH	Air	4
8	IPA	Air	4
9	DMF	Air	–
10	DMSO	Air	–
11	MeCN	Air	73
12	Dioxane	Air	4
13	MeCN[a]	Nitrogen	2
14	MeCN[b]	Argon	2
15	Glycerol	Air	–

[a] Reaction conditions: Substrates (0.4 mmol, 1 eq.) in MeCN (4 mL) at room temperature under an air atmosphere accompanied by 1 W blue LEDs for 24 h.

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air as an oxidant. We screened various dyes ranging from rhodamine B to *9*-fluorenone (Table 3) for the model reaction. When 20 mol% *9*-fluorenone catalyst was used, we achieved the *N,N'*-diacylhydrazine (**1b**) with an good yield (Table 3, Entry 16) of 73% within 24 hours, while other photocatalysts gave the expected product with significantly lower yields ranging from 2%–18% (Table 3, entry 1–15). Amongst the
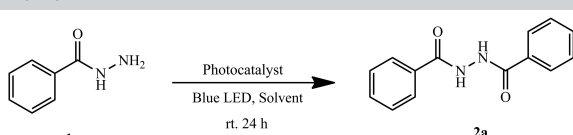
photocatalysts examined (Table 3, entries 6–11), namely eosin B, erythrosine B, and fluorescein, a slight increase in activity was observed under optimized conditions. However, other photo-catalysts such as phenothiazine, anthrone, dicyanobenzene and dicyanonaphthalene yielded no product. (Table 3, entries 4, 5, 12, 13)

With the optimized conditions in our hand, we investigated the scope of this reaction by synthesizing *N,N'*—diacylhydra-zines derivatives using various aromatic and heteroaromatic hydrazides. The oxidative coupling of hydrazides (ortho/para-substitution on EWG or EDG) was carried out using 20 mol% *9*-fluorenone, and the desired *N,N'*-diacylhydrazines derivatives were isolated in good to excellent yields from 8–92% (**2a–j**) (Scheme 2a). Additionally, we tried the reaction between the two different hydrazides, which successfully yielded the desired unsymmetrical diacylhydrazines derivatives in 7–21% yield (**2k–o**). However, **2o** could not be obtained under optimized conditions (Scheme 2b).

After the substrate scope evaluation, control reactions were conducted to prove that the reaction proceeds via a photo-redox pathway (Table 4; entries 3 and 4). When the reaction was performed in the dark (Table 4; entry 3) and in blue LED without a catalyst (Table 4; entry 4), no product was formed. Also, no product was obtained when the reaction was carried out in the absence of light at 50°C (Table 4; entry 5). These control experiments revealed that a catalyst and light source are necessary requirements for the reaction to proceed through a photochemical pathway.

Furthermore, to gain deeper insights into the chemical transformation, mechanistics studies were performed (Table 5, entries 1–6). The use of $CuCl_2$ in the reaction system resulted in a lower yield, which indicates that SET mechanism is involved[19,23] (Table 5, entry 1). The same inference can be drawn with the use of (1,4 Diazabicyclo[2.2.2]octane) DABCO (Table 5, entry 2). The presence of singlet oxygen radicals and superoxide anion was confirmed through additional experi-ments utilizing sodium azide (Table 5, entry 6) and benzoqui-none (Table 5, entry 3) as quenchers in the reaction mechanism. A yield of only 8% obtained with butylated hydroxytoluene (BHT) (Table 5, entry 4), and no product formation with the utilization of singlet oxygen quenching reagent 2,2,6,6-tetrame-thylpiperidine (TEMPO) (Table 5, entry 5), suggested the in-volvement of a radical mechanism. Additionally, under nitrogen atmosphere gave only a 2% yield which clearly indicates the important role of oxygen in facilitating the reaction as an oxidant (Table 5, entry 7). Finally, a reaction with the catalase

Table 3. Optimization of the reaction conditions for the oxidation of benzoyl hydrazines.

Entry	Photocatalysts	Yield (%)
1	Rhodamine B	8
2	Acenaphthenequinone	3
3	Methylene blue	9
4	Phenothiazine	–
5	Anthrone	–
6	Eosin B	2
7	Rose Bengal	4
8	Eosin Y	2
9	Fluorescein	9
10	Erythrosin B	13
11	TiO_2	18
12	Dicyanobenzene	–
13	Dicyanonaphthalene	–
14	Chrysazin	7
15	DDQ	9
16	*9*-Fluorenone	73

Light source : LED (Blue LED, 465 nm); Temperature: RT Dye: 20 mol%; irradiation time 24 h. [a] Under N_2 atmosphere. [b] Under Ar atmosphere.
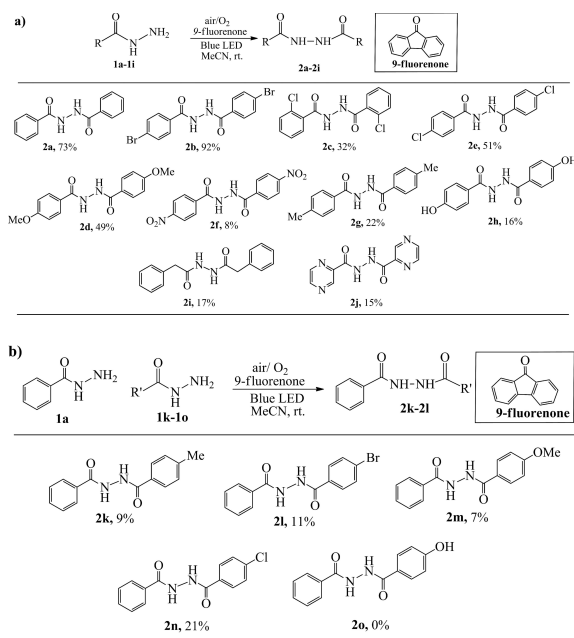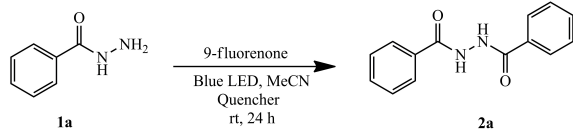

Scheme 2. a) Substrate scope of the symmetrical *N,N'* diacylhydrazines.[a]. Scheme b) Substrate scope of the unsymmetrical *N,N'* diacylhydrazines.[a]

Table 4. Controlled parameters.

Entry	Controlled parameters	Yield (%)
1	Standard conditions	73
2	N_2 atmosphere	2
3	No light	0
4	No catalyst	0
5	50°C	0

[a] Reaction conditions: Substrates (0.4 mmol, 1 eq.) in MeCN (4 mL) at room temperature irradiated under 1 W blue LEDs for 24 h.

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Table 5. Quenching experiments for the oxidation of hydrazides.[a]

Entry	Quencher	Yield (%)	Notes
1	CuCl$_2$	4	Electron Scavenger
2	DABCO	2	Singlet oxygen scavenger
3	Benzoquinone	6	Superoxide radical anion scavenger
45	BHTTEMPO	8	Radical scavengerRadical scavengerSinglet oxygen scavenger
6	NaN$_3$	0	–peroxide radical scavengerHydoxide radical scavenger
7	N$_2$ atmosphere	2	
8	Catalase	2	
9	t-butanol	9	
		45	

[a] Reaction conditions: Substrates (0.4 mmol, 1 eq.), 9-fluorenone (20 mol%), MeCN (4 mL), quenchers, 24 h.

enzyme confirmed the presence of peroxide radical species (Table 5, entry 8). A reaction with H$_2$O$_2$ as an oxidant was attempted leading to a lower yield, which indicated that H$_2$O$_2$ was not responsible for the oxidation of hydrazides. Instead, it suggested the involvement of peroxo species as an intermediate within the reaction system. Using tertiary butanol, the reaction showed a slight decrease in the yield of the product, which ruled out the possibility of the formation of a hydroxyl radical intermediate in the reaction mixture (Table 5, entry 9).

Further investigation of the reaction mechanism was carried out by Stern-Volmer fluorescence quenching studies. These experiments showed a significant decrease in the fluorescence intensity upon increasing the concentration of benzoyl hydrazine, which unveiled that the excited photocatalyst was effectively quenched by the benzoyl hydrazine (Figure 2).

2.2 Computational Studies

To gain insight into the mechanism of photochemical reaction of benzoyl hydrazine 1a to form N,N'-diacylhydrazines 2a. The
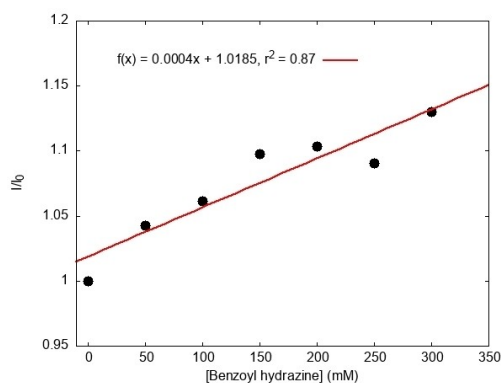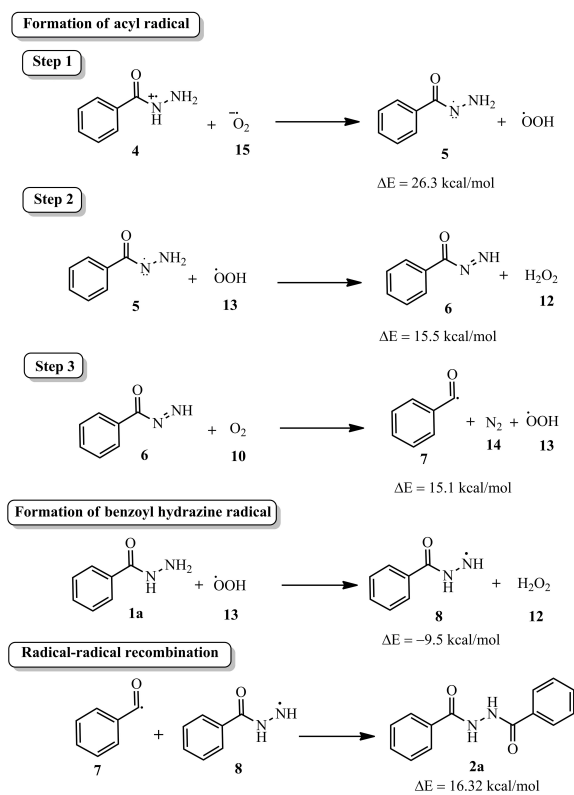
standard reduction potentials of 1a and 9-fluorenone 3 were calculated and found to be −2.34 and −1.34 V vs SHE. The experimental value of standard reduction potential of 9-fluorenone[19] is −1.35 V, thus the calculated value matches with the experiment with a difference of 0.01 V. The thermodynamic quantities calculated in this exercise is tabulated in Table S6 (see supporting information). Since, the reduction potential of 9-fluorenone is relatively positive it undergoes photochemical reduction thereby oxidizing benzoyl hydrazine 1a to 4 as shown in the Scheme 4.

It is proposed that N,N'-diacylhydrazine (2a) is formed through a radical-radical recombination reaction involving acyl and benzoyl hydrazine radicals (Scheme 3). The formation of acyl radicals occurs through a series of consecutive reactions in three steps. (Scheme 3, Step 1 to 3)

In step 1, the radical generated (4) in the photoredox step reacts with the superoxide ion (15) to form intermediate (5) and a hydroperoxyl radical (13) with an energy change of 26.3 kcal/mol. The transition state formed during this step involves the abstraction of a proton from the amide nitrogen.

Step 2 involves the reaction of intermediate (5) with the hydroperoxyl radical (13) to produce N-benzoyldiazene (6) and hydrogen peroxide (12), with an energy barrier of 15.5 kcal/mol. The transition state in this step abstracts one of the protons from the terminal nitrogen of intermediate (6) to form hydrogen peroxide.

Figure 2. Stern-Volmer plot for the oxidation of benzoyl hydrazine.

Scheme 3. Different steps involved for the formation of N,N'-diacylhydrazine.

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In step 3, *N*-benzoyldiazene (6) reacts with atmospheric oxygen (10) to form an acyl radical, diatomic nitrogen, and a hydroperoxyl radical (13), with an energy barrier of 15.1 kcal/mol. The transition state involves the abstraction of a proton on the terminal nitrogen of *N*-benzoyldiazene (6) to form the products. Although the product complex for step 3 could not be optimized, the intrinsic reaction coordinate (IRC) calculated using the transition state suggests the aforementioned products. The product complex obtained at the end of the IRC calculations are provided in the supplementary information (Tables S4 and S5).

Benzoyl hydrazine radicals are generated when radical (1a) reacts with hydroperoxyl radicals (13), with hydrogen peroxide as a byproduct. This reaction proceeds with an energy change of −9.5 kcal/mol. Finally, the radical-radical recombination of the acyl radical (7) and benzoyl hydrazine radicals (8) leads to the formation of *N,N'*-diacylhydrazine (2a), with an energy change of 16.3 kcal/mol.

The DFT study revealed that the reaction proceeds through the formation of hydrogen peroxide. This theoretical finding was experimentally confirmed by observing a peak at $\lambda_{max} =$ 346 nm in the UV-Vis spectra of the reaction mixture.

2.3 Proposed Mechanism

Combining all the mechanistic studies, we proposed a plausible reaction mechanism for the oxidation of benzoyl hydrazine to *N,N'*-diacylhydrazines (Scheme 4). Initially, photocatalyst 3a undergoes excitation upon irradiation of light to 3b*. The excited state photocatalyst 3b* accepts one electron from benzoyl hydrazine, transforming the photocatalyst into radical anion 3c and generation of benzoyl hydrazine radical cation 4. The radical cation 4 subsequently loses a proton molecule to
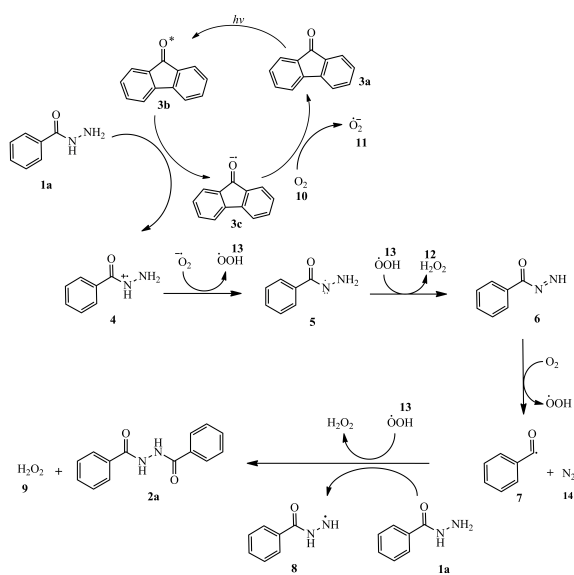
peroxyl radical to give benzoyl hydrazine radical 5. Further, radical 5 reacts with an hydroperoxyl radicals (13) to form intermediate 6. In an important step intermediate 6, in a homolytic fashion, loses a nitrogen molecule to generate acyl radical 7. Acyl radical combines with the benzoyl hydrazine radical 8, which is in turn formed by abstraction of hydrogen radical by hydrogen peroxide radical to give the desired compound *N,N'*-diacylhydrazine 2a. The Mechanism proposes the formation of H_2O_2 and acyl radical, hence we thought of studying them using NMR and trapping agent, respectively. In literature generation of H_2O_2 in the reaction mixture have been reported using UV-Vis spectroscopy and by using NMR spectroscopy. The peak at 8.89 ppm in ^{1}H-NMR and absorption maxima at 346 nm reveals the formation of H_2O_2 in the reaction mixture (see supporting information, Figure 2S). Also, we compared this ^{1}H NMR spectrum with authentic sample of H_2O_2 which validated our theory for the formation of H_2O_2 (see supporting information, Figure S4). Acyl radical was trapped using TEMPO (2,2,6,6-tetramethylpiperidine) and its formation and confimed by using HRMS and LC-MS (see supporting information, Figure S2 and S3).

3. Conclusions

In summary, the first use of *9*-fluorenone as a photoredox catalyst under visible light for the oxidation of benzoyl hydrazides and its derivatives have been presented. The reaction is illustrated by its simplicity and mild reaction conditions; it can be conducted under visible light at room temperature in an open atmosphere and with a less expensive metal-free photocatalyst. A wide range of *N,N'*-diacylhydrazines derivatives was obtained with moderate to good yields in the range of 8-92% under optimal reaction conditions. Also, the present methodology caters to the synthesis of mixed *N,N'*-diacylhydrazines derivatives in moderate yields. DFT, control, and quenching experiments have been found helpful in the establishment of the mechanism of the benzoyl hydrazides oxidation reaction.

Experimental Section

General Procedure for the Synthesis of Hydrazides in Acetonitrile

To a mixture of benzoyl hydrazide (0.4 mmol), *9*-fluorenone (20 mol%) in acetonitrile (4 mL) was added, and the reaction mixture was kept under blue LED with stirring at room temperature for 24 hours to form corresponding *N,N'*-diacylhydrazines (as monitored by TLC). After completion of the reaction, the mixture was extracted with EtOAc, dried over anhydrous Na_2SO_4, and purified by column chromatography to give the desired product.

Computational Methodology

The standard reduction potentials of 1a and *9*-fluorenone 3 were calculated as per the procedure reported elsewhere and absolute potential of SHE is considered as 4.44 V.[23] Briefly, the Born-Haber

Scheme 4. Proposed reaction mechanism for oxidation of benzoyl hydrazine.

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cycle for the reduction of *9*-fluorenone/benzoyl hydrazine is constructed as shown in Figure 3 and the free energy change ΔG° (total) was calculated as per the Equation (1) and from ΔG° (total) the E° is calculated as per Equation (2).

$$\Delta_r G^0 \text{ (total)} = \Delta_r G^0 \text{ (gas)} + \Delta_r G^0 \text{ (solv., } \bar{A}) + \Delta_r G^0 \text{ (solv., A)} \qquad (1)$$

$$E^0 = \frac{-\Delta_r G^0 \text{ (total)}}{nF} \qquad (2)$$

The redox potential was calculated using ωB97XD/6311++G-(3df,3pd) level of theory. Reaction mechanism was investigated using density functional theory (DFT) employing unrestricted M062X/6-31+G(d,p) level of theory in acetonitrile solvent using self-consistent reaction field (SCRF) method, utilizing the polarizable continuum model (PCM) of solvation. All the calculations were performed using Gaussian 16 program.[24] Frequency calculations were conducted for all geometries. Transition states were confirmed when a single imaginary frequency was detected, while the absence of any imaginary frequency indicated geometries with energy minima on the potential energy surface.

Author Contributions

The manuscript was written through contributions of all authors. All authors have helped to draft the manuscript. All authors have read and approved the final manuscript.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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Figure 3. (a) Thermodynamic free energy cycle (Born–Haber) used to calculate the ground-state redox half-reaction potentials.