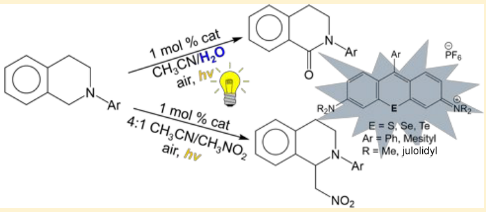
ORGANOMETALLICS
Article
Cite This: *Organometallics* XXXX, XXX, XXX−XXX
pubs.acs.org/Organometallics

Importance of Singlet Oxygen in Photocatalytic Reactions of 2-Aryl-1,2,3,4-tetrahydroisoquinolines Using Chalcogenorosamine Photocatalysts

Jennifer L. Clark,[†] Jackie E. Hill,[†] Irving D. Rettig,[‡] Joshua J. Beres,[†] Roman Ziniuk,[§] Tymish Y. Ohulchanskyy,[§] Theresa M. McCormick,*[‡] and Michael R. Detty*[†]

[†]Department of Chemistry, University at Buffalo, The State University of New York, Buffalo, New York 14260-3000, United States
[‡]Department of Chemistry, Portland State University, Portland, Oregon 97207, United States
[§]Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, College of Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, P.R. China

Supporting Information



ABSTRACT: Aerobic oxidation of 2-aryl-1,2,3,4-tetrahydroisoquinolines was achieved photocatalytically using chalcogenorosamine photocatalysts and LED irradiation. The photocatalytic aza-Henry reaction between these substrates and nitromethane was more efficient with selenorosamine and tellurorosamine photocatalysts than with thiorosamine and rosamine photocatalysts, corresponding to the propensity of the photocatalysts to generate singlet oxygen ($^1O_2$). Appropriately, yields for the photocatalytic aza-Henry reaction were greatly reduced when the reactions were conducted under a nitrogen atmosphere. The 2-aryl-1,2,3,4-tetrahydroisoquinolines were oxidized to the corresponding 2-aryl-3,4-dihydroisoquinolones **13a−13c** with selenorosamine and tellurorosamine photocatalysts in 2% aqueous acetonitrile. Di-2-aryl-1,2,3,4-tetrahydroisoquinolin-1-yl peroxides **14a** and **14b** were shown to be intermediates in this reaction. Thiorosamine photocatalysts, which do generate $^1O_2$ upon irradiation, did not give 2-aryl-3,4-dihydroisoquinolones. These results suggested that the exciplex between $^1O_2$ and the chalcogen atom of the chalcogenorosamines (the corresponding pertelluoxide, perselenoxide, or persulfoxide) and/or the hydrated perchalcogenoxide [hydroxy (perhydroxy)tellurane, -selenane, or -thiane] might be an active oxidant in the formation of **13a−13c**. Computational methods were employed to provide support for the observed photocatalytic reactivity of the tellurorhodamine and selenorhodamine chromophores compared to the thiorosamine chromophores. Δ*G* values were determined for the oxidation and hydration of **10-Te**, **10-Se**, and **10-S** for formation of perchalcogenoxides and hydroxyl(perhydroxy)chalcogenanes, respectively. Calculations indicate formation of the pertelluroxide perselenoxide, and persulfoxide exciplex intermediates are energetically favorable. Hydration of the exciplexes of **10-Te** and **10-Se** have similarly small Δ*G* of −3.49 and 4.51 kcal/mol, respectively. However, a significantly higher Δ*G* value of +22.4 kcal/mol is observed for the hydration of **10-S**, which suggests that this reactive intermediate is not readily formed.

INTRODUCTION

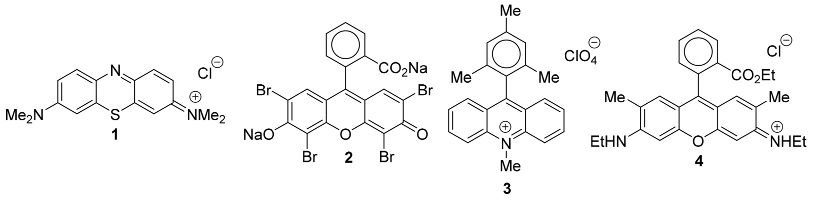
Photocatalysis is a single-electron-transfer process that employs organic dyes or transition-metal complexes along with visible light irradiation.[1] Organic dyes have been utilized to a limited extent in photoredox catalysis, whereas ruthenium(II) and iridium(III) complexes have been extensively studied for over 30 years.[2−7] There are several properties of organic dyes that make them advantageous over transition-metal complexes. Organic dyes are potentially less toxic, more cost-effective, and have improved photophysical properties (increased absorption in the visible region) and high singlet oxygen quantum yields [$\Phi(^1O_2)$], making them a more practical option.[5]

In the past decade, photocatalysis has become of increasing interest as a "green" mode of small molecule activation within organic chemistry.[8] General reactions for alkylations, oxidations, and anti-Markovnikov additions to alkenes have all been developed using photocatalysis.[9−12] Photocatalysts employed to date have various insufficiencies. Titanium dioxide as a photocatalyst can utilize atmospheric oxygen as an oxidant; however, it is only active in the UV region, which drastically reduces light-absorbing efficiency under solar irradiation.[13] Transition-metal-based Ru(II) and Ir(III) polypyridyl complexes have been more extensively studied as photocatalysts and have readily available photophysical and electrochemical properties, although these transition-metal complexes are relatively expensive.[1,6,14]

The structures of several cationic organic dyes that have been used successfully as photocatalysts are shown in Chart 1. The Scaiano group has examined methylene blue (**1**);[4,15,16] the König group studied eosin Y (**2**),[2] and various acridinium salts including the 9-mesityl derivative (**3**) were reported by the Nicewicz and Fukuzumi groups.[11,12] Rhodamine 6G (**4**, Chart 1) and various oxazine, thiazine, and azine dyes have been

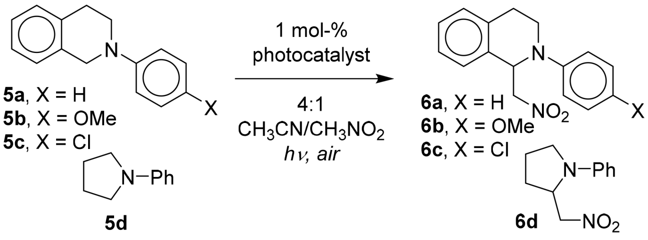
Received: February 25, 2019

Chart 1. Structures of Methylene Blue (1), Eosin Y (2), 9-Mesityl-10-methylacridinium (3), and Rhodamine 6G (4)

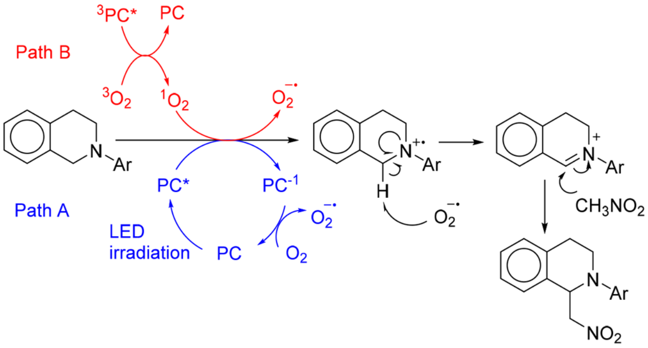


recently compared as photocatalysts for the oxidation of 2-phenyl-1,2,3,4-tetrahydroisoquinoline (**5a**) in the light-mediated aza-Henry reaction with nitromethane to give 1-nitromethyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (**6a**) shown in Scheme 1.[7] Mechanistically, the cationic organic photocatalysts are thought to follow two different pathways (Scheme 2). Path A: the excited photocatalyst can initiate single-electron oxidations via electron transfer from a donor atom of the substrate (N in the case of **5a**) to the excited state of the photocatalyst to give a radical of the photocatalyst and a cation radical of the donor atom.[5,7] Alternatively, in path B, photocatalysts that produce high triplet yields can generate singlet oxygen ($^1O_2$), which oxidizes a donor atom of the substrate to give superoxide ($O_2^{\bullet -}$) as well as the cation radical of the donor atom.[7] In the light-mediated aza-Henry reaction of **5a** with nitromethane,[7] methylene blue (**1**) with $\Phi(^1O_2)$ of 0.52[17] was a superior photocatalyst to rhodamine 6G (**4**) with $\Phi(^1O_2)$ of 0.01.[18]

Scheme 1. Photocatalyzed Aza-Henry Reaction of Amine Substrates Using 1 mol % of Photocatalyst in 4:1 CH_3CN/CH_3NO_2



Scheme 2. Proposed Mechanism for the Aza-Henry Reaction[a]

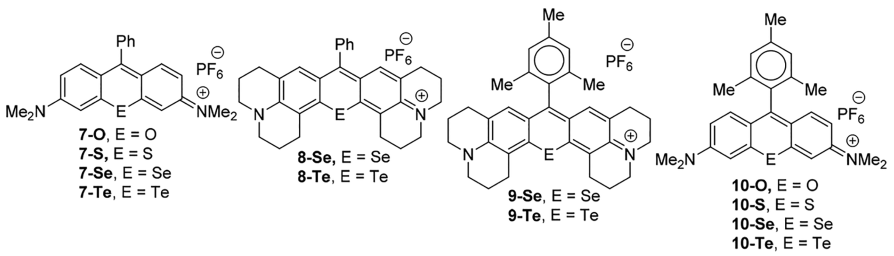


[a] In path A, the radical cation of the isoquinoline is formed by electron transfer from the excited photocatalyst (PC), and in path B, it is formed from electron transfer from singlet oxygen.[5,7]

Chalcogenorosamine dyes **7-E–10-E** (Chart 2) are similar in structure to the organic photocatalysts of Chart 1.[7] Whereas the chalcogenorosamines and structurally related chalcogenorhodamines have not been examined as photocatalysts in synthetic transformations of organic molecules, these molecules have been examined as photosensitizers for photoinduced charge-transfer reactions in dye-sensitized solar cells (DSSCs)[19] and for the generation of hydrogen via the photoreduction of protons.[20] The ability of the seleno- and tellurorosamine/rhodamine analogues to generate $^1O_2$ has been exploited in photodynamic therapy (PDT)[21] and in fluorescence imaging.[22,23]

Whereas dye chromophores incorporating O, S, Se, or Te in the heterocyclic structure generate $^1O_2$, the relative values of $\Phi(^1O_2)$ are very much dependent on the presence of heavy atom(s). The presence of heavy atoms promotes spin–orbit coupling, which scales with nuclear charge, leading to increased rates of singlet–triplet intersystem crossing. Organic dyes incorporating the heavier chalcogen atoms Se or Te have values of $\Phi(^1O_2)$ higher than those of their lighter chalcogen analogues because of this effect.[22,24–27] The Te analogues have $\Phi(^1O_2)$ lower than that of the corresponding Se compounds likely due to reaction of $^1O_2$ with the Te, resulting in lower observed $^1O_2$ phosphorescence.[22b] Furthermore, the exciplex from $^1O_2$ addition to the Te atom can undergo subsequent chemistry with water to produce H_2O_2 and the telluroxide oxidation state (Te(IV)) of the tellurorosamine.[10] The telluroxide, in turn, can function as an oxidant for the conversion of thiols to disulfides in a photocatalytic process.[10] Similar chemistry has also been observed with selenoxides, where addition of hydrogen peroxide generates the corresponding hydroxy(perhydroxy)selenane.[28]

Chart 2. Structures of the Chalcogenorosamines 7-E (E = O, S, Se, Te), 8-E (E = Se, Te), 9-Te, and 10-E (E = O, S, Se, Te)

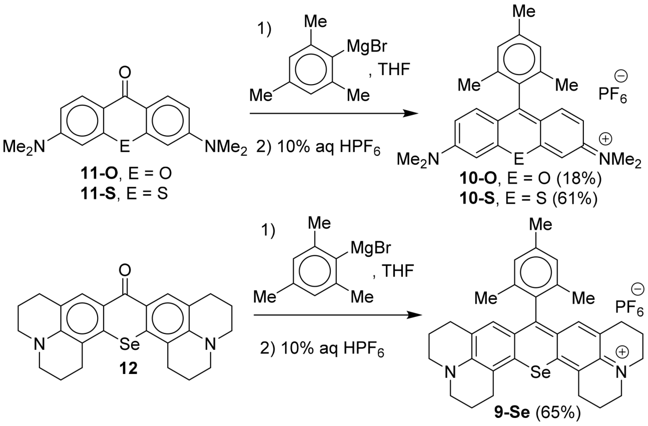


Herein, we compare the chalcogenorosamines **7-E**−**10-E** (Chart 2) as photocatalysts for two reactions of 2-aryl-1,2,3,4-tetrahydroisoquinolines: (1) the aza-Henry reaction with nitromethane to give 1-nitromethyl-2-aryl-1,2,3,4-tetrahydroisoquinolines and (2) the oxidation to the corresponding 2-aryl-3,4-dihydroisoquinolones. The latter reaction is a new photocatalytic reaction, and the importance of the singlet oxygen−photocatalyst exciplex (pertelluroxide, perselenoxide, or persulfoxide) in this process was examined using density functional theory (DFT) calculations. Isoquinolones are of interest due their prevalence in alkaloidal natural products. We have chosen the substrates to allow for direct comparison to previous photocatalytic reactions.[7]

■ RESULTS AND DISCUSSION

Chalcogenorosamine Photosensitizers. The tetramethylchalcogenorosamine **7-E**,[24,25,29] bisjulolidylchalcogenorosamine **8-E**,[22b] and the respective 9-mesityl derivatives **9-Te**[22b] and **10-E** (E = Se, Te)[10,22a] were prepared as previously described. The lighter chalcogen analogues **10-O** and **10-S** and bisjulolidylselenorosamine **9-Se** were prepared as shown in Scheme 3.[22b] Values of absorption maxima (λ_{max}) and extinction coefficients (ε) for **9-Se**, **10-O**, and **10-S** are compiled in Table 1. In order to compare complete sets of photophysical properties among the rosamine series **7-E** and **10-E**, steady-state fluorescence spectra for **10-O** and **10-S** were acquired as were values of $\Phi(^1O_2)$ (Table 1). Emission maxima (λ_{FL}) in MeOH were 572 nm for **10-O** and 598 nm for **10-S**. Quantum yields for fluorescence (Φ_{FL}) in MeOH were 0.74 ± 0.04 for **10-O** and 0.34 ± 0.2 for **10-S**. Values of $\Phi(^1O_2)$ were measured using time-resolved spectroscopy of $^1O_2$ phosphorescence in air-saturated methanol with **7-Se** as a reference [$\Phi(^1O_2) = 0.87$].[25,30−32] Values of $\Phi(^1O_2)$ were 0.03 ± 0.01 for **10-O** and 0.61 ± 0.02 for **10-S**.

Scheme 3. Synthesis of 9-Mesitylrosamine 10-O, 9-Mesitylthiorosamine 10-S, and 9-Mesitylselenorosamine 9-Se



2-Aryl-1,2,3,4-tetrahydroisoquinolines. The 2-aryl-1,2,3,4-tetrahydroisoquinolines used in this study were prepared as shown in Scheme 4.[5] 1,2,3,4-Tetrahydroisoquinoline was coupled to an aryliodide using CuI as catalyst. 2-Phenyl-1,2,3,4-tetrahydroisoquinoline (**5a**) was isolated in 70% yield, the 2-(4-methoxyphenyl) derivative **5b** in 39% yield, and the 2-(4-chlorophenyl) derivative **5c** in 78% yield.

Photocatalyzed Aza-Henry Reaction of 5a. The photocatalyzed aza-Henry reaction of **5** with nitromethane, as shown in Scheme 1, was evaluated using 1 mol % of each of the chalcogenorosamines of Chart 2 and compared to methylene blue (**1**) and rhodamine 6G (**4**) as controls. A 4:1 CH_3CN/CH_3NO_2 solution of **5a** (0.06 M) and photocatalyst (0.0006 M) was irradiated for 3.0 h with a GE 14 W, 850 lm LED light. The % conversion of **5a** to **6a** was determined by ^1H NMR spectroscopy comparing the integral of the 2-nitromethyl methylene protons (δ 4.81 and 4.53) and the 1-methine proton (δ 5.51) of **6a** with the 1-methylene protons (δ 4.42) of **5a**. Values of % conversion are compiled in Table 1 and are the mean of triplicate runs.

Both tetramethyltellurorosamine **7-Te** and 9-phenyl bisjulolidyltellurorosamine **8-Te** bleached rapidly and gave <1% conversion of **5a** to the aza-Henry product **6a**. The three xanthylium core photocatalysts **4** (rhodamine 6G), **7-O**, and **10-O** gave ⩽18% conversion of **5a** to **6a** and were not significantly different from one another (probability value, $p > 0.10$, one-way ANOVA). Photocatalysts **4**, **7-O**, **7-Te**, **8-Te**, and **10-O** were all significantly poorer photocatalysts ($p \leqslant 0.0064$, one-way ANOVA) than the remaining catalysts of Table 1. Selenorosamines **7-Se**, **8-Se**, and **10-Se** and tellurorosamine **10-Te** were the best photocatalysts for conversion of **5a** to **6a** after 3 h, collectively, with ⩾94% conversion of **5a** to **6a**.

Conversions of **5a** to **6a** were also run for 1.0 h with the best performing photocatalysts **7-Se**, **8-Se**, **10-Se**, and **10-Te** in aerated solvent. Values of % conversion are compiled in Table 1 and are the mean of triplicate runs. The 60% conversion with **7-Se** as photocatalyst and 56% conversion with **10-Te** as photocatalyst were not significantly different ($p > 0.10$, one-way ANOVA) from one another. However, the 1 h conversion with both of these catalysts was significantly greater ($p \leqslant 0.03$) than the 1 h conversion with **8-Se** (37%) and **10-Se** (45%), which were not significantly different from one another ($p > 0.07$). However, for all four of these photocatalysts, greater conversions were observed with longer reaction times.

In order to assess the importance of oxygen in the photocatalyzed reactions, the reactions were repeated with several of the photocatalysts following deaeration with N_2 bubbling to remove most of the oxygen from the reaction vessel. Values of % conversion under a N_2 atmosphere with irradiation for 3 h are compiled in Table 1 and are the mean of triplicate runs. In every example, product yields were reduced under a N_2 atmosphere. The non-negligible yields (10−14%) did not increase over time and are attributed to residual oxygen (Table 1).

Preparative Photocatalyzed Aza-Henry Reactions. The survey of chalcogenorosamine photocatalysts suggested that **7-Se** and **10-Te** were perhaps the two most robust and efficient among the photocatalysts compared in Table 1 for the aza-Henry reaction. The aza-Henry reaction was repeated on a 1.0 mmol scale with 1 mol % of photocatalyst (either **7-Se** or **10-Te**), nitromethane, and tetrahydroisoquinoline substrates **5a**, **5b**, and **5c** (Scheme 1 and Table 2). Reactions were followed by thin layer chromatography (TLC) until consumption of starting amine was complete. Following irradiation with the LED light, reaction mixtures were concentrated and the product(s) were isolated via chromatography on SiO_2 eluted with 5% EtOAc in hexanes.

The photocatalyzed aza-Henry reaction of *N*-phenylpyrrolidine (**5d**) with nitromethane and 1 mol % of **7-Se** or **10-Te**

Table 1. Comparison of Photocatalysts for the Photocatalyzed Aza-Henry Reaction of 5a with Nitromethane To Give 6a

photocatalyst	λ_{max}, nm	ε, M^{-1} cm^{-1}	% conversion[a] 3.0 h	N$_2$, 3.0 h	1.0 h	$\Phi(^1O_2)$
1	664[b]	90000[b]	42 ± 3	<1		0.52[c]
4	524[b]	78000[b]	18 ± 3	<1		0.01[d]
7-O	536	108000	18 ± 5	<1		0.08[e]
7-S	557	94400	69 ± 8	9 ± 4		0.21[e]
7-Se	568	117000	94 ± 2	14 ± 2	60 ± 1	0.87[e]
7-Te	601[f]	81000[f]	<1			0.43[g]
8-Se	604[h]	135000[h]	98 ± 1	10 ± 2	37 ± 4	0.68[h]
8-Te	617[h]	144000[h]	<1			0.53[h]
9-Se	604	145000	60 ± 6			
9-Te	617[h]	165000[h]	80 ± 20			
10-O	537	124000	12 ± 4			0.03 ± 0.01
10-S	557	124000	44 ± 7			0.61 ± 0.02
10-Se	568[i]	103000[i]	99.5 ± 0.5	16 ± 2	45 ± 4	0.85[i]
10-Te	600[g]	86000[g]	95 ± 1	14 ± 1	56 ± 3	0.75[g]

[a] Reagents and photocatalyst were dissolved in a 4:1 mixture of MeCN/MeNO$_2$ on a 0.3 mmol scale, and the resulting solution was then irradiated with a GE 14 W, 850 lm LED light with stirring for the indicated time period. Percent conversions were determined by ^{1}H NMR spectroscopy. Values represent the mean of triplicate runs ± 1 SD. [b] From ref 7. [c] From ref 18. [d] From ref 19. [e] From ref 24. [f] From ref 28. [g] From ref 22a. [h] From ref 22b. [i] From ref 10.

Scheme 4. Coupling of Aryliodides to 1,2,3,4-Tetrahydroisoquinoline To Give 2-Aryl-1,2,3,4-tetrahydroisoquinolines 5a, 5b, and 5c

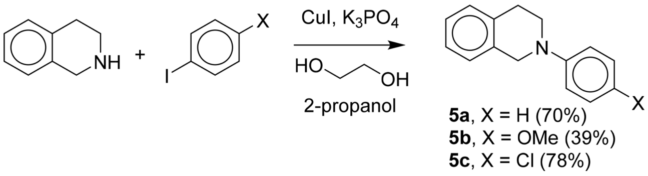


Table 2. Photochemical Aza-Henry Reaction of 1.0 mmol 2-Aryl-1,2,3,4-tetrahydroisoquinolines 5a, 5b, and 5c and *N*-Phenylpyrrolidine 5d in 4:1 CH$_3$CN/CH$_3$NO$_2$ with 1 mol % of Photocatalyst 7-Se or 10-Te and LED Irradiation

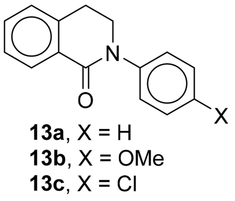
entry	photocatalyst	substrate	$h\nu$, h	product	isolated yield, %
1	**7-Se**	**5a**	11	**6a**	84[a]
2	**10-Te**	**5a**	5	**6a**	85[b]
3	**7-Se**	**5b**	8.5	**6b**	81[c]
4	**10-Te**	**5b**	6.5	**6b**	75[d]
5	**7-Se**	**5c**	5	**6c**	62[e]
6	**10-Te**	**5c**	4	**6c**	85[f]
7	**7-Se**	**5d**	30	**6d**	3
8	**10-Te**	**5d**	30	**6d**	6

[a] Isoquinolone **13a** isolated in 16% yield. [b] Isoquinolone **13a** formed in trace (<2%) amounts. [c] Isoquinolone **13b** isolated in 2% yield. [d] Isoquinolone **13b** formed in trace (<2%) amounts. [e] Isoquinolone **13c** isolated in 17% yield. [f] Isoquinolone **13c** formed in trace (<2%) amounts.

was also examined. The reaction with **5d** was only partially complete with either photocatalyst after 48 h of irradiation with the LED light and is consistent with previous results with this substrate and other organo photocatalysts.[5] Following chromatography on SiO$_2$ eluted with 5% EtOAc/hexanes, the aza-Henry product **6d** was isolated in roughly 3% yield with **7-Se** as the photocatalyst and in roughly 6% yield with **10-Te** as the photocatalyst (Table 2).

2-Aryl-1,2,3,4-tetrahydroisoquinolines also gave various amounts of the corresponding 2-aryl-3,4-dihydroisoquinolones **13a−13c**[33] (Chart 3) as minor products in the photocatalyzed aza-Henry reaction, as compiled in Table 2. These materials were isolated via chromatography on SiO$_2$ eluted with 5% EtOAc in hexanes.

Chart 3. Isoquinolone Products Formed during the Photocatalyzed Aza-Henry Reaction



Oxidation of 1,2,3,4-Tetrahydroisoquinolines to 3,4-Dihydroisoquinolones. There are relatively few methods for oxidizing tetrahydroisoquinolines to the corresponding dihydroisoquinolones, and the most successful example using relay aerobic oxidation required an oxygen atmosphere and Schlenk line techniques and was limited to 0.25 mmol in scale.[33] For most examples of oxidation of benzylic amines to benzylic amides, the amides were isolated as a minor product of the reaction,[34] which is what was observed in the preparative aza-Henry reactions described above to give the dihydroisoquinolones as minor products. We sought conditions to form the dihydroisoquinolones as the major product of photocatalysis. Running the photo-oxidations in pure CH$_3$CN or CH$_2$Cl$_2$ with **7-S**, **7-Se**, **10-S**, **10-Se**, and **10-Te** as photocatalysts gave little if any dihydroisoquinolone. However, addition of 2% water to CH$_3$CN gave photo-oxidation of the tetrahydroisoquinolines to the corresponding dihydroisoquinolones as the major product upon LED irradiation with **7-Se**, **10-Se**, and **10-Te**, indicating that water was a necessary component of the reaction.

Photo-oxidation of **5a**, **5b**, and **5c** was carried out on a 1.0 mmol preparative scale with 1 mol % of chalcogenorosamine photocatalysts **7-S**, **7-Se**, **10-S**, **10-Se**, or **10-Te** using a 4.9:0.1 solution of CH$_3$CN/H$_2$O as solvent under irradiation with an

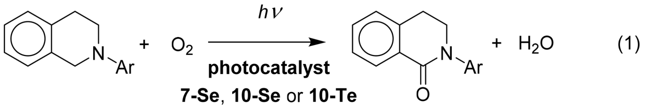
850 lm LED light. The reactions were followed by TLC until the consumption of the starting tetrahydroisoquinoline was complete. Using **7-Se** (entries 2, 3, 7, 11, and 12), **10-Se** (entries 4, 9, 13, and 14), or **10-Te** (entries 5, 10, and 15) as the photocatalyst, the known 2-aryl-3,4-dihydroisoquinolin-1(2*H*)-ones **13a**−**c**[33] were isolated as the major products of reaction, as shown in Table 3. Irradiating 1,2,3,4-tetrahydroisoquinoline **5a** or **5b** for 12 h using thiorosamine photocatalysts **7-S** (entries 1 and 6) and **10-S** (entries 3 and 8) gave essentially unreacted **5a** or **5b** and no isolable amounts of **13a** or **13b** or other products.

Table 3. Photochemical Oxidation of 1.0 mmol 2-Aryl-1,2,3,4-tetrahydroisoquinolines 5a, 5b, and 5c in 4.9:0.1 CH_3CN/H_2O with 1 mol % of Photocatalyst and LED Irradiation

entry	photocatalyst	substrate	$h\nu$, h	product	isolated yield, %
1	**7-S**	**5a**	12	**13a**	<5
2	**7-Se**	**5a**	8	**13a**	58
3	**10-S**	**5a**	12	**13a**	<5
4	**10-Se**	**5a**	8	**13a**	83
5	**10-Te**	**5a**	8	**13a**	63
6	**7-S**	**5a**	12	**13a**	<5
7	**7-Se**	**5b**	13	**13b**	63
8	**10-S**	**5b**	12	**13b**	<5
9	**10-Se**	**5b**	13	**13b**	73
10	**10-Te**	**5b**	8	**13b**	75
11	**7-Se**	**5c**	7.5	**13c**	78[a]
12	**7-Se**	**5c**	36	**13c**	89
13	**10-Se**	**5c**	8	**13c**	70[b]
14	**10-Se**	**5c**	36	**13c**	85
15	**10-Te**	**5c**	3	**13c**	59

[a] Peroxodimer **14a** isolated in 6% yield. [b] Peroxodimer **14a** isolated in 12% yield.

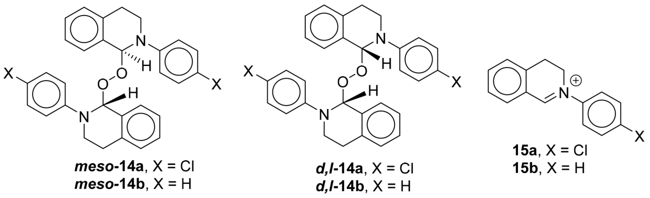
The importance of oxygen in the photocatalysis was demonstrated by reducing the oxygen content of the reaction mixture prior to irradiation. Irradiating 1,2,3,4-tetrahydroisoquinoline **5a** and photocatalyst **7-Se** or **10-Te** in a 4.9:0.1 solution of CH_3CN/H_2O as solvent that had been deaerated with a stream of N_2 gas and then placed under a N_2 atmosphere returned unreacted **5a**. Isoquinolone **13a** was not observed. The photocatalytic conversion of the tetrahydroisoquinolines to the dihydroisoquinolones is summarized in eq 1. Oxygen as it is found in air is the reagent, and water is the byproduct of the photocatalytic oxidation reaction, providing an environmentally benign approach to the synthesis.



(1)

Oxidized Peroxo Intermediate. During the photooxidation of **5c** with photocatalyst **7-Se** in a 4.9:0.1 solution of CH_3CN/H_2O, a white precipitate formed and, when consumption of **5c** was complete, was isolated by filtration. The solid was identified as a mixture of the *meso*- and D,L-diastereomers of the peroxodimer **14a** (Chart 4) primarily through NMR spectral data (Supporting Information) and elemental analysis. The mass spectrum of the white solid gave *m*/*z* 242 as the parent ion with no higher mass peaks, which is consistent with iminium ion **15a** ($C_{15}H_{13}{}^{35}ClN^+$). However, the ^1H NMR spectrum of the mixture of diastereomers of **14a** indicated that the pairs of methylene protons at C3 and C4 were no longer equivalent and geminal coupling was observed. Two singlets were observed in a ratio of 45:55 at δ 6.09 and δ 5.98 for a methine proton at C1, which suggested two compounds were produced in not quite a 1:1 ratio. Combustion analysis was consistent with a dimer of the iminium core perhaps bridged by two oxygen atoms with calculated element percentages for $C_{30}H_{26}Cl_2N_2O_2$ of C, 69.64; H, 5.06; and N, 5.41. Experimentally determined percentages were C, 69.98; H, 4.92; and N, 5.41.

Chart 4. *meso*- and D,L-Diastereomers of Peroxodimers 14a and 14b and the Structure of Iminium Ions 15a and 15b

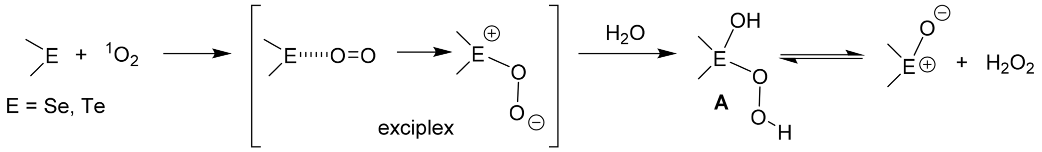


The $^{13}C\{^1H\}$ NMR spectrum of the mixture of diastereomers of **14a** was also consistent with a nearly 1:1 mixture of the *meso*- and D,L-diastereomers. Each diastereomer would have 30 carbons with two identical halves. The symmetry of the 4-chlorophenyl substituent in each would reduce the number of different carbon signals to 26 for each diastereomer, with the mirror plane and C_2 axis reducing the number of unique signals to 13 for each diastereomer or 26 signals in total. The experimental $^{13}C\{^1H\}$ NMR spectrum displayed 21 unique signals for the mixture with the “overlapped” signals observed at δ 136.0, 128.2, 125.7, 115.7, and 42.2. The remaining signals were “paired” with very similar chemical shifts (Supporting Information).

The white precipitate of **14a** began forming when irradiation began and the quantity of precipitate reached a maximum and began declining as irradiation continued. When irradiation was stopped after 4 h (rather than 7.5 h), the white precipitate of **14a** was isolated in 13% yield. After 7.5 h, consumption of **5c** was complete and the precipitate was isolated in 6% yield. The precipitate of **14a** disappeared after 36 h of irradiation, and isoquinolone **13c** was isolated in 89% yield at this point. If the precipitate were returned to a fresh 4.9:0.1 solution of CH_3CN/H_2O (no photocatalyst or **13c**) and LED irradiation continued, isoquinolone **13c** was formed along with other products, which were not identified.

Similar products were observed in the photo-oxidation of **5a** using **7-Se** or **10-Te** as photocatalyst with LED irradiation in 4.9:0.1 CH_3CN/H_2O. The ^1H and $^{13}C\{^1H\}$ NMR spectra for the mixture of the *meso*- and D,L-peroxodimer **14b** were strikingly similar to those for the mixture of the *meso*- and D,L-peroxodimer **14a** (Supporting Information). After 3 h of LED irradiation with photocatalyst **10-Te**, photo-oxidation of 2-phenyl-1,2,3,4-tetrahydroisoquinoline **5a** in 4.9:0.1 CH_3CN/H_2O as solvent was complete—**5a** was no longer observed in the reaction mixture by TLC. At this point, a 9:1 mixture of the *meso*- and D,L-peroxodimer **14b** to the isoquinolone **13a** was formed (Figure S1, Supporting Information). Further LED irradiation for an additional 5 h gave complete disappearance of the *meso*- and D,L-peroxodimer **14b**, and isoquinolone **13a** was isolated in 63% yield from the reaction mixture.

Scheme 5. Formation of Hydroxy(perhydroxy)tellurane (E = Te) or Hydroxy(perhydroxy)selenane (E = Se) Intermediate upon Addition of Water to the Chalcogenide–Singlet Oxygen Exciplex (Pertelluroxide or Perselenoxide Intermediate)



The reaction mixture obtained after 3 h of LED irradiation was purified via chromatography on SiO_2, and a band containing mostly a mixture of *meso*- and D,L-**14b** was isolated as a colorless oil. The mass spectrum of the colorless oil gave *m*/*z* 208 as the parent ion with no higher mass peaks, which is consistent with iminium ion **15b** ($C_{15}H_{14}N^+$). The NMR spectral data for *meso*- and D,L-**14b** was strikingly similar to that of *meso*- and D,L-**14a** (Supporting Information). The ^1H NMR spectrum of the mixture showed that the pairs of methylene protons at C3 and C4 were no longer equivalent, and geminal coupling was observed. Two singlets were observed in a ratio of 45:55 at δ 6.09 and δ 5.98 for a methine proton at C1, which suggested two compounds were produced in not quite a 1:1 ratio. The mixture of *meso*- and D,L-**14b** was not stable and decomposed to many products upon standing overnight under ambient conditions or at −20 °C under a nitrogen atmosphere. Again, for the *meso*- and D,L-**14a**, a total of 26 unique signals would be expected in the carbon NMR, and 21 of the expected 26 signals were observed with the "overlapped" carbons appearing at δ 136.0, 128.2, 127.3, 115.7, and 42.2 (Supporting Information).

Mechanistic Implications with Chalcogenorosamine Photocatalysts. *a. Importance of Singlet Oxygen.* The presence of oxygen and, in particular, the generation of $^1O_2$ appear to be important both for the photochemical aza-Henry reaction and for the photo-oxidation of the tetrahydroisoquinolines to the dihydroisoquinolones. The importance of $^1O_2$ in the aza-Henry reaction has been well-documented, with $^1O_2$ accepting an electron from the donor atom (in this case, the N of the tetrahydroisoquinoline) to generate superoxide ($O_2^{\bullet-}$) as well as the cation radical of the donor atom.[5,7] Alternatively, the excited-state photosensitizer can induce single-electron transfer from the donor atom.

The results compiled in Table 1 show that photocatalysts with higher values of $\Phi(^1O_2)$ give greater conversions of 1,2,3,4-tetrahydroisoquinoline **5a** to aza-Henry product **6a**. The exceptions are tellurorosamine catalysts **7-Te** and **8-Te**, with phenyl substituents in the 9-position that do not shield the 9-position from nucleophilic addition.[35] The selenorosamines **7-Se** and **8-Se** and Se- and Te-containing photocatalysts with a 9-mesityl substituent **9-Se**, **9-Te**, **10-Se**, and **10-Te** have much greater stability and gave higher conversions of **5a** to **6a** than methylene blue (**1**), rhodamine 6G (**4**), rosamines **7-O** and **10-O**, thiorosamines **7-S** and **10-S**, and tellurorosamines **7-Te** and **8-Te**. These results also reflect relative values of $\Phi(^1O_2)$.

When the reaction mixtures were deaerated with a stream of N_2 gas prior to irradiation in the aza-Henry reaction, overall conversion of **5a** to **6a** was greatly reduced (Table 1), indicating the importance of $^1O_2$ in the photocatalyzed aza-Henry reaction with this set of photocatalysts. The absence of formation of isoquinolone **13a** upon photo-oxidation of **5a** with photocatalyst **7-Se** or **10-Te** in deaerated 4.9:0.1 CH_3CN/H_2O also indicates the importance of oxygen and, specifically, $^1O_2$ in the photo-oxidation of the tetrahydroisoquinolines to the dihydroisoquinolones.

b. Importance of Water and the Chalcogenorosamine-$^1O_2$ Exciplex in the Photocatalytic Oxidation to the Dihydroisoquinolones. In the absence of water, the oxidation of tetrahydroisoquinolines to dihydroisoquinolones is not observed with 1 mol % of photocatalyst, LED irradiation, and pure CH_2Cl_2 or CH_3CN as solvent. However, the addition of 2% water to CH_3CN gives oxidation of the tetrahydroisoquinolines to the dihydroisoquinolones with selenorosamine and tellurorosamine photocatalysts as compiled in Table 3. The addition of water to the exciplex between $^1O_2$ and diorganotelluides and diorganoselenides (a pertelluroxide or perselenoxide intermediate) has a rich chemistry, as shown in Scheme 5, to give the corresponding hydroxy(perhydroxy)-tellurane[10] or hydroxy(perhydroxy)selenane[28] (intermediate **A** in Scheme 5). Intermediates **A** can function as an oxidant or they can eliminate H_2O_2 to generate the corresponding selenoxide or telluroxide.[10] The telluroixde can be reduced back to the starting catalyst in a Swern-like oxidation, transforming the 1,2,3,4-tetrahydroisoquinoline to 3,4-dihydroisoquinolone (Supporting Information).

*c. Enigma of the Thiorosamine Photocatalysts **7-S** and **10-S**.* The other interesting feature of the photo-oxidation to the dihydroisoquinolones is that the thiorosamine photocatalysts **7-S** and **10-S** do not give isolable amounts of dihydroisoquinolones as a product of the reaction after 12 h of irradiation in 4.9:0.1 CH_3CN/H_2O. Both of these photocatalysts generate $^1O_2$ upon irradiation with values of $\Phi(^1O_2)$ of 0.21 for **7-S** and 0.61 for **10-S** (Table 1). If $^1O_2$ alone were responsible for oxidation to the tetrahydroisoquinoline to the isoquinolone, one would reasonably expect some oxidation to be observed. Because no oxidation was observed, one might examine the differences in the chalcogenorosamine photocatalysts upon generating $^1O_2$. The other key feature of the photo-oxidation reactions is the necessity of having water as part of the solvent system.

Photocatalysis with the 3-aryl-1,2,3,4-tetrahydroisoquinolines has been shown to proceed through single-electron oxidation of the 3-aryl-1,2,3,4-tetrahydroisoquinoline and subsequent loss of a hydrogen atom to give the corresponding iminium compound (structures **15a** and **15b** in Chart 4, as examples). Both **7-S** and **10-S** are capable of generating the intermediate iminium compound as both of these photocatalysts form product in the aza-Henry reaction (Table 1). However, the hydroxy(perhydroxy)thiane intermediate corresponding to **A** in Scheme 5 has not been implicated in reactions of sulfoxides with hydrogen peroxide.[28]

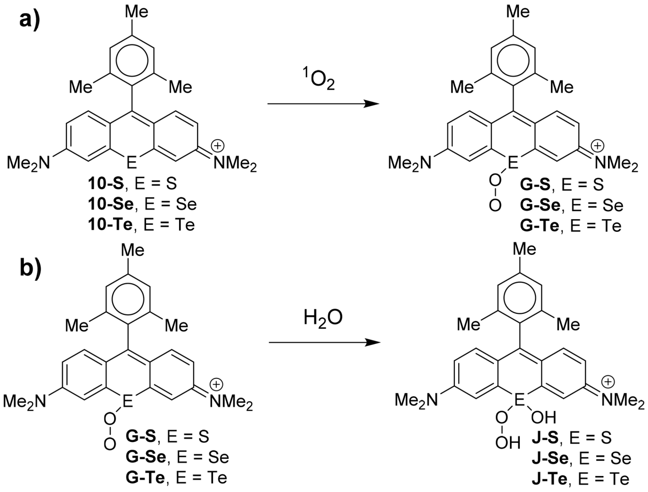
We repeated the photo-oxidation of **5** with thiorosamine **10-S** as the photocatalyst in 4.9:0.1 CH_3CN/H_2O, with 8.8 M aqueous H_2O_2 replacing water to give a 4.9:0.1 CH_3CN/H_2O mixture that was 0.18 M in H_2O_2. After 8 h of irradiation with the LED, tetrahydroisoquinoline **5a** had been consumed and a 1:9 mixture dihydroisoquinolone **13a** and peroxodimers **14b**

DOI: 10.1021/acs.organomet.9b00126

was observed by ^{1}H NMR spectroscopy in the reaction mixture (Figure S2, Supporting Information). These results strongly suggest that either H_2O_2 or the hydroxy(perhydroxy)-chalcogenane intermediate **A** in Scheme 5 is responsible for oxidation of the iminium ion intermediates in the photooxidation of the tetrahydroisoquinolines to the dihydroisoquinolones. As only 1 equiv of H_2O_2 can be produced from each oxidation, the high yields implicate oxidation by intermediate **A** that would regenerate the catalyst. We next examined the energetics of formation of the $^1O_2$-chalcogenorosamine exciplex (the corresponding pertelluroxide, perselenoxide, or persulfoxide intermediate) and its addition product with H_2O.

DFT Calculations. Computational methods were employed to provide support for the observed photocatalytic reactivity of the tellurorhodamine and selenorhodamine chromophores compared to the thiorosamine chromophores. All structures were optimized using the Gaussian09 software package[36] at the B3LYP level of theory.[37−39] The geometries of **10-Se** and **10-S** were optimized using a 6-31+G(d) basis set.[40−42] A split basis set was used for **10-Te** (Lanl2DZ[43−45] for the tellurium atom and 6-31+G(d) for all other atoms).[46] All geometries were optimized in CH_3CN using the SMD solvation model.[47] Energy values were obtained from the frequency calculations of the optimized geometries and used to determine the Gibbs free energies of the reactions (ΔG). ΔG values were determined for the oxidation and hydration of diorganochalchogenides **10-Te**, **10-Se**, and **10-S**, as shown in Scheme 5. The balanced equations used to determine the ΔG values are shown in Scheme 6. All calculated values for ΔG are summarized in Table 4.

Scheme 6. Balanced Equations for (a) Formation of the Exciplex from 10-E via Reaction with $^1O_2$ and (b) Hydration of the Exciplexes To Form the (Perhydroxy)hydroxychalcogen Species



The energy of formation of the $^1O_2$-bound exciplex was explored first to investigate the reactivity of **10-Se** and **10-Te** relative to that of **10-S** as photocatalysts. Although **10-Te** has the lowest energy of formation of **G-Te** at −1.67 kcal/mol, the calculated ΔG values for **G-Se** and **G-S** have small positive values, 2.06 and 3.08 kcal/mol. Thus exciplex formation occurs with minimal change in ΔG for **10-Te**, **10-Se**, and **10-S** and would not explain the difference in reactivity. Hydration of the exciplexes of **10-Te** and **10-Se** have similarly small ΔG, with −3.49 kcal/mol for **G-Te** and 4.51 kcal/mol for **G-Se**. However, a significantly higher ΔG of +22.4 kcal/mol is observed for the hydration of **G-S**, which suggests that the reactive intermediate **J-S** is not readily formed. This is consistent with both the lack of dihydroisoquinolone formation with thiorosamine photocatalysts as well as the requirement of water in the reaction. A summary of the calculated ΔG values for each reaction can be visualized in the reaction coordinate diagram in Figure 1.

Table 4. Calculated ΔG Values for the Formation of G-E and J-E (E = Te, Se, S)

compound	calculated ΔG of formation (kcal/mol)
G-Te	−1.62
G-Se	2.06
G-S	3.08
J-Te	−3.49
J-Se	4.51
J-S	22.35

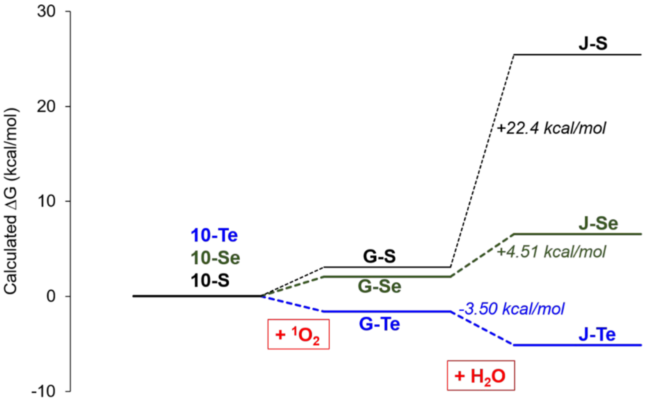


Figure 1. Reaction coordinate diagram of oxidation and hydration of chalchogenorhosamine photocatalysts in Scheme 6. Energies are relative to **10-Te**, **10-Se**, and **10-S** and follow from Scheme 5.

Seferos and co-workers proposed the Te(VI)dioxo intermediate for tellurophene derivatives;[49] however, under the oxidation conditions of this study, this intermediate is unlikely to be observed, although this intermediate can be minimized computationally. Other oxidative addition products, such as a telluradioxirane with a three-membered ring with O_2 and the chalcogen atom as proposed previously,[27] were studied by DFT calculations. However, for **10-Te**, the three-membered ring opened when optimized to the pertelluroxide intermediate proposed in the paper.

■ CONCLUSIONS

The seleno- and tellurorosamines bring very high quantum yields for the generation of singlet oxygen to photocatalysts used in organo photocatalysis. In well-studied reactions, such as the photochemical aza-Henry reaction with 2-aryl-1,2,3,4-tetrahydroisoquinolines,[5−7] the higher values of $\Phi(^1O_2)$ for **7-Se**, **10-Se**, and **10-Te** lead to higher photochemical conversions to product. With other substrates, the transient formation of the chalcogen−singlet oxygen exciplex (the corresponding pertelluroxide or perselenoxide intermediate) can lead to oxidation chemistry not observed with other organic photocatalysts. The oxidation of 2-aryl-1,2,3,4-tetrahydroisoquinolines to 2-aryl-3,4-dihydroisoquinolones proceeds via formation of a peroxo dimer, which is formed from the oxidized photocatalyst.

EXPERIMENTAL SECTION

Preparation of 9-(2,4,6-Trimethylphenyl)bisjulolidylselenorosamine Hexafluorophosphate (9-Se). 2-Bromomesitylene (0.663 g, 0.510 mL, 3.33 mmol) was added to a stirred suspension of magnesium turnings (0.088 g, 3.7 mmol) in dry THF (2 mL) under a dry N_2 atmosphere. The mixture was stirred at ambient temperature for 1 h, and the resulting solution of Grignard reagent was transferred via cannula to a stirred suspension of bisjulolidylselenoxanthone **12**[22b] (0.100 g, 0.222 mmol) in dry THF (7 mL). The resulting solution was heated at reflux for 16 h, cooled to ambient temperature, and then poured into 25 mL of 10% (by weight) aqueous HPF_6. The aqueous mixture was extracted with CH_2Cl_2 (3 × 25 mL), and the combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was recrystallized from 9:1 CH_3CN/diethyl ether to give 0.101 g (65%) of the desired product as a green solid, mp 240−241 °C: ^1H NMR (500 MHz, CD_2Cl_2) δ 7.05 (s, 2 H), 6.95 (s, 2 H), 3.55−3.42 (m, 8 H), 2.86 (t, 4 H, J = 6.0 Hz), 2.63 (t, 4 H, J = 6.0 Hz), 2.43 (s, 3 H), 2.18 (quint, 4 H, J = 5.0 Hz), 1.94 (quint, 4 H, J = 5.0 Hz), 1.81 (s, 6 H); $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2), 161.1, 150.1, 142.5, 140.6, 136.6, 136.0, 134.9, 130.4, 126.9, 120.3, 118.1, 53.1, 52.2, 29.6, 27.8, 22.9, 22.4, 22.2, 21.3; λ_{max} (CH_2Cl_2) 590 nm ($\varepsilon = 1.31 \times 10^5\ M^{-1}\ cm^{-1}$); λ_{max} (CH_3OH) 591 nm ($\varepsilon = 1.55 \times 10^5\ M^{-1}\ cm^{-1}$); HRMS (ESI) m/z 553.2125 (calcd for $C_{34}H_{37}N_2{}^{80}Se^+$: 553.2116). Anal. Calcd for $C_{34}H_{37}N_2Se{\cdot}PF_6$: C, 58.54; H, 5.35; N, 4.02. Found: C, 58.28; H, 5.54; N, 4.03.

Preparation of 3,6-Bis(dimethylamino)-9-(2,4,6-trimethylphenyl)-9*H*-xanthen-9-ylium Hexafluorophosphate (10-O). 2-Bromomesitylene (1.35 mL, 8.85 mmol) was added to a stirred suspension of magnesium turnings (0.13 g, 5.5 mmol) in dry THF (3 mL) under a dry N_2 atmosphere. The mixture was stirred at ambient temperature for 1 h, and the resulting solution of Grignard reagent was transferred via cannula to a stirred suspension of 3,6-bis(dimethylamino)-9*H*-xanthen-9-one[29] (**11-O**, 0.100 g, 0.354 mmol) in dry THF (7 mL). The resulting solution was heated at reflux for 16 h, cooled to ambient temperature, and then poured into 25 mL of 10% (by weight) aqueous HPF_6. After 12 h, the resulting precipitate was collected via filtration and washed with water (5 mL) and diethyl ether (15 mL). The residue was purified by chromatography on SiO_2 eluted with 20% EtOAc/hexanes to remove starting xanthone and then 10% ether/CH_2Cl_2 to collect the product. The product was recrystallized from 9:1 CH_3CN/diethyl ether to give 0.032 g (18%) of the desired product as a green solid, mp 254−255 °C: ^1H NMR (500 MHz, CD_2Cl_2) δ 7.17 (d, 2 H, J = 9.0 Hz), 7.10 (s, 2H), 6.90 (dd, 2 H, J = 2.5, 9.5 Hz), 6.84 (d, 2 H, J = 2.0 Hz), 3.30 (s, 12 H), 2.42 (s, 3 H), 1.90 (s, 6 H); $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2) δ 160.2, 158.3, 158.0, 140.2, 135.9, 131.3, 129.1, 128.6, 114.9, 114.0, 96.9, 41.2, 21.3, 19.8; λ_{max} (MeOH) 537 nm ($\varepsilon = 1.18 \times 10^5\ M^{-1}\ cm^{-1}$); λ_{max} (CH_2Cl_2) 537 nm ($\varepsilon = 1.24 \times 10^5\ M^{-1}\ cm^{-1}$); HRMS (ESI) m/z 385.2265 (calcd for $C_{26}H_{29}N_2O^+$: 385.2274). Anal. Calcd for $C_{26}H_{29}N_2O{\cdot}PF_6$: C, 58.87; H, 5.51; N, 5.28. Found: C, 58.94; H, 5.61; N, 5.28.

Preparation of 3,6-Bis(dimethylamino)-9-(2,4,6-trimethylphenyl)-9*H*-thioxanthen-9-ylium Hexafluorophosphate (10-S). 2-Bromomesitylene (0.77 mL, 5.0 mmol) was dissolved in dry THF (3 mL) under a dry N_2 atmosphere. Magnesium turnings (130 mg, 5.5 mmol) were added, and the resulting mixture was stirred at ambient temperature for 1 h. The resulting solution of Grignard reagent was transferred via cannula to a stirred solution of 3,6-bis(dimethylamino)-9*H*-thioxanthene-9-one[30] (**11-S**, 100 mg, 0.335 mmol) in dry THF (7 mL). The resulting solution was heated at reflux for 16 h, cooled to ambient temperature, and then poured into 25 mL of 10% (by weight) aqueous HPF_6. After 12 h, the resulting precipitate was collected via filtration and washed with water (5 mL) and diethyl ether (15 mL). The CH_3CN-soluble material was filtered through Celite, concentrated, and recrystallized from 9:1 CH_3CN/diethyl ether to give 0.112 g (61%) of **10-S** as a green solid, mp >260 °C: ^1H NMR (500 MHz, CH_2Cl_2) δ 7.34 (d, 2 H, J = 10.0 Hz), 7.11 (d, 2 H, J = 2.0 Hz), 7.10 (s, 2 H), 6.92 (dd, 2 H, J = 2.0, 10.0 Hz), 3.24 (s, 12 H), 2.43 (s, 3H), 1.84 (s, 6 H); $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2) δ 161.6, 154.2, 144.8, 139.8, 136.0, 135.6, 132.0, 129.1, 119.1, 116.2, 105.9, 40.9, 21.3, 19.7; λ_{max} (MeOH) 558 nm ($\varepsilon = 1.03 \times 10^5\ M^{-1}\ cm^{-1}$); λ_{max} (CH_2Cl_2) 557 nm ($\varepsilon = 1.24 \times 10^5\ M^{-1}\ cm^{-1}$); HRMS (ESI) m/z 401.2044 (calcd for $C_{26}H_{29}N_2S^+$: 401.2046); Anal. Calcd for $C_{26}H_{29}N_2S{\cdot}PF_6$: C, 57.14; H, 5.35; N, 5.13. Found: C, 57.41; H, 5.15; N, 5.12.

Photocatalyzed Aza-Henry Reaction of 2-Phenyl-1,2,3,4-tetrahydroisoquinoline (5a). *Comparison of Photocatalysts.* To a 4-dram (15 mL) vial were added 0.063 g (0.30 mmol) of tetrahydroisoquinoline **5a** (0.063 g, 0.30 mmol) and 0.003 mmol (1 mol %) of photocatalyst. The contents were dissolved in 5 mL of a 4:1 mixture of $MeCN/MeNO_2$. The reaction mixture was then irradiated with stirring for 3.0 h with a GE 14 W, 850 lm LED light placed 1 cm from the 4-dram vial. The reaction mixture was concentrated in vacuo, and the % conversion was determined via ^1H NMR spectroscopy comparing the integral of the 2-nitromethyl methylene protons (δ 4.81 and 4.53) and the 2-methine proton (δ 5.51) of **6a** with the 2-methylene protons (δ 4.42) of **5a**. The reactions were run in triplicate, and values reported in Table 1 represent the mean of the three runs ± the standard deviation (SD) for the three runs.

Preparative Conversion of 2-Phenyl-1,2,3,4-tetrahydroisoquinoline (5a) to 1-Nitromethyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (6a). *A. **7-Se** as Photocatalyst.* To a 4-dram vial were added tetrahydroisoquinoline **5a** (0.210 g, 1.00 mmol) and **7-Se** (5.5 mg, 0.010 mmol, 1 mol %). The contents were dissolved in 15 mL of a 4:1 mixture of $MeCN/MeNO_2$. The reaction mixture was then irradiated with stirring for 11.0 h with a GE 14 W, 850 lm LED light placed 1 cm from the 4-dram vial. At the completion of irradiation, the reaction mixture was concentrated in vacuo and the residue was partitioned between a mixture of ether (20 mL) and water (20 mL). The organic phase was separated, and the aqueous layer was further extracted with ether (2 × 10 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated in vacuo. The crude product was purified via chromatography on SiO_2 eluted with 5% EtOAc in hexanes to yield 0.212 g (84%) of **6a**[5] and 0.037 g (16%) of dihydroisoquinolone **13a**.[32]

*B. **10-Te** as Photocatalyst.* The reaction was repeated using photocatalyst **10-Te** (6.0 mg, 0.010 mmol, 1 mol %) with 5 h of irradiation. Products **6a**[5] and **13a**[32] were purified via chromatography on SiO_2 eluted with 5% EtOAc in hexanes to yield 0.22 g (85%) of **6a**[5] and 0.005 g (2%) of dihydroisoquinolone **13a**.[32]

*For **6a**:*[5] colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.08−7.28 (m, 4 H), 6.95 (d, 2 H, J = 7.5 Hz), 6.82 (t, 2 H, J = 7 Hz), 5.52 (t, 1 H, J = 7 Hz), 4.82 (dd, 1 H, J = 7.5, 11.7 Hz), 4.54 (dd, 1 H, J = 6.5, 11.7 Hz), 3.60 (m, 2 H), 3.04 (m, 1 H), 2.75 (m, 1 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 148.3, 135.2, 132.8, 129.5, 129.4, 129.3, 128.0, 126.9, 119.3, 115.0, 78.6, 58.1, 41.9, 26.3.

*For **13a**:*[32] white solid, mp 119−120 °C (lit.[33] mp 119−123 °C); ^1H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, 1 H, J = 7.5 Hz), 7.55−7.35 (m, 7 H), 7.27 (m, 1 H), 4.02 (t, 1 H, J = 6.5 Hz), 3.17 (t, 1 H, J = 6.5 Hz); $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$) δ 164.5, 143.5, 132.4, 130.1, 129.2, 129.0, 127.5, 127.3, 126.5, 125.6, 49.7, 28.9; MS (ESI) m/z 224 (calcd for $C_{15}H_{13}NO+H^+$: 224).

Preparative Conversion of 2-(4-Methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline 5b to 1-Nitromethyl-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (6b).[5] *A. **7-Se** as Photocatalyst.* To a 4-dram vial were added tetrahydroisoquinoline **5b** (0.240 g, 1.00 mmol) and **7-Se** (5.5 mg, 0.010 mmol, 1 mol %). The contents were dissolved in 15 mL of a 4:1 mixture of $MeCN/MeNO_2$. The reaction mixture was then irradiated with stirring for 8.5 h with a GE 14 W, 850 lm LED light placed 1 cm from the 4-dram vial. At the completion of irradiation, the reaction mixture was concentrated in vacuo and treated as described above for the reaction with **5a**. The crude product was purified via chromatography on SiO_2 eluted with 5% EtOAc in hexanes to yield 0.241 g (81%) of **6b**[5] and 0.005 g (2%) of dihydroisoquinolone **13b**.[2]

*B. **10-Te** as Photocatalyst.* The reaction was repeated using photocatalyst **10-Te** (6.0 mg, 0.010 mmol, 1 mol %) with 6.5 h of irradiation. Products **6a**[5] and **13a**[32] were purified via chromatography on SiO_2 eluted with 5% EtOAc in hexanes to yield 0.224 g (75%) of **6b**[5] and 0.003 g (1%) of dihydroisoquinolone **13b**.[32]

*For **6b**:*[5] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08−7.28 (m, 4 H), 6.90 (d, 2 H, *J* = 9 Hz), 6.80 (d, 2 H, *J* = 9 Hz), 5.38 (dd, 1 H, *J* = 6, 8.5 Hz), 4.80 (dd, 1 H, *J* = 8.5, 11.7 Hz), 4.54 (dd, 1 H, *J* = 6, 11.7 Hz), 3.73 (s, 3 H), 3.55 (m, 2 H), 3.00 (m, 1 H), 2.67 (m, 1 H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 153.8, 142.9, 135.3, 132.7, 129.3, 127.7, 126.8, 126.4, 118.6, 114.5, 78.7, 58.7, 55.4, 42.8, 25.6.

*For **13b**:*[32] white solid, mp 116−119 °C (lit.[32] mp 120−121 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, 1 H, *J* = 7.5 Hz), 7.45 (td, 1 H, *J* = 1.6, 7.5 Hz), 7.37 (t, 1 H, *J* = 7.5 Hz), 7.20−7.32 (m, 4 H), 3.94 (t, 1 H, *J* = 6.5 Hz), 3.82 (s, 3 H), 3.13 (t, 1 H, *J* = 6.5 Hz); ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$) δ 164.4, 157.8, 138.3, 136.1, 131.9, 129.8, 128.7, 127.1, 126.9, 126.7, 114.2, 55.5, 49.7, 28.7; MS (ESI) *m*/*z* 254 (calcd for $C_{16}H_{15}NO_2$+H^+: 254).

Preparative Conversion of 2-(4-Chlorophenyl)-1,2,3,4-tetrahydroisoquinoline (5c) to 1-Nitromethyl-2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline (6c). *A. **7-Se** as Photocatalyst.* To a 4-dram vial were added tetrahydroisoquinoline **5c** (0.245 g, 1.00 mmol) and **7-Se** (5.5 mg, 0.010 mmol, 1 mol %). The contents were dissolved in 15 mL of a 4:1 mixture of MeCN/$MeNO_2$. The reaction mixture was then irradiated with stirring for 5.0 h with a GE 14 W, 850 lm LED light placed 1 cm from the 4-dram vial. At the completion of irradiation, the reaction mixture was concentrated in vacuo and treated as described above for **5**. The crude product was purified via chromatography on SiO_2 eluted with 5% EtOAc in hexanes to yield 0.187 g (62%) of **6c**[5] and 0.043 g (17%) of dihydroisoquinolone **13c**.[32]

*B. **10-Te** as Photocatalyst.* The reaction was repeated using photocatalyst **10-Te** (6.0 mg, 0.010 mmol, 1 mol %) with 6.5 h of irradiation. The products **6c**[5] and **13c**[32] were purified via chromatography on SiO_2 eluted with 5% EtOAc in hexanes to yield 0.25 g (85%) of **6c**[5] and 0.005 g (2%) of dihydroisoquinolone **13c**.[32]

*For **6c**:*[5] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26−7.34 (m, 4 H), 6.89 (dd, *J* = 1.5, 6.3 Hz), 5.48 (m, 1 H), 4.84 (ddd, 1 H, *J* = 1.2, 8.4, 12.1 Hz), 4.56 (ddd, 1 H, *J* = 1.5, 5.4, 12.1 Hz), 3.62 (m, 2 H), 3.06 (m, 1 H), 2.78 (m, 1 H).

*For **13c**:*[32] white solid, mp 150−152 °C (lit.[33] mp 150−151.5 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, 1 H, *J* = 7.6 Hz), 7.48 (dt, 1 H, *J* = 1.2, 7.6 Hz), 7.40−7.32 (m, 5 H), 7.24 (d, 1 H, *J* = 9.6 Hz), 3.97 (t, 2 H, *J* = 6.4 Hz), 3.14 (t, 2 H, *J* = 6.4 Hz); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 164.2, 141.5, 138.2, 132.2, 131.5, 129.4, 128.9, 128.7, 127.2, 126.9, 126.5, 49.2, 28.5.

Preparation of 2-(Nitromethyl)-1-phenylpyrrolidine 6d.[5] *A. **7-Se** as Photocatalyst.* To a 4-dram vial equipped with a stir bar were added 1-phenylpyrrolidine **5d** (0.086 mL, 0.60 mmol) and 1 mol % of photocatalyst **7-Se** (5.5 mg, 0.010 mmol, 1 mol %). The contents were dissolved in 5 mL of a 4:1 mixture of MeCN/$MeNO_2$. The reaction mixture was irradiated for 90 h with a GE 14 W, 850 lm LED light. The reaction mixture was then concentrated in vacuo. Product **6d** was purified via chromatography on SiO_2 eluted with 5% EtOAc in hexanes to yield 0.0038 g (3.1% yield) of **6d**.

*B. **10-Te** as Photocatalyst.* The reaction was repeated using photocatalyst **10-Te** (6.0 mg, 0.010 mmol, 1 mol %). The product **6d** was purified via chromatography on SiO_2 eluted with 5% EtOAc in hexanes to yield 0.0075 g (6% yield) of **6d**.

*For **6d**:*[5] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34−7.24 (m, 2H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 8.4 Hz, 2H), 4.68−4.59 (m, 1H), 4.48−4.38 (m, 1H), 4.19 (t, *J* = 10.5 Hz, 1H), 3.51−3.44 (m, 1H), 3.27−3.14 (m, 1H), 2.18−2.04 (m, 1H); ^{13}C{^{1}H} NMR (300 MHz, $CDCl_3$): 145.5, 129.7, 117.3, 111.9, 75.8, 57.4, 48.1, 29.3, 22.8.

Preparation of 3,4-Dihydro-2-phenyl-1(2*H*)-isoquinolinone 13a.[32] *A. **7-Se** as Photocatalyst.* In a 4-dram vial equipped with a stir bar, 2-phenyl-1,2,3,4-tetrahydroisoquinoline **5a** (0.209 g, 1.00 mmol) and **7-Se** (5.5 mg, 0.010 mmol, 1 mol %) were dissolved in 15 mL of a 4.9:0.1 mixture of MeCN/H_2O. The reaction mixture was irradiated with a GE 14 W, 850 lm LED light for 8 h. The crude product was purified via chromatography on SiO_2 eluted with 20% EtOAc/hexanes. Isoquinolone **13a** was recrystallized from dichloromethane/diethyl ether to yield 0.129 g (58% isolated yield) of **13a**.

*B. **10-Te** as Photocatalyst.* The reaction was repeated using photocatalyst **10-Te** (6.0 mg, 0.010 mmol, 1 mol %) with irradiation for 8 h. Isoquinolone **13a** was purified via chromatography on SiO_2 eluted with 5% EtOAc in hexanes to yield 0.141 g (63% isolated yield) of **13a**.

*C. **7-S** as Photocatalyst.* The reaction was repeated using photocatalyst **7-S** (5.2 mg, 0.010 mmol, 1 mol %) with irradiation for 12 h. Unreacted **5a** (0.19 g, 90%) was recovered from the reaction mixture.

*D. **10-S** as Photocatalyst.* The reaction was repeated using photocatalyst **10-S** (5.3 mg, 0.010 mmol, 1 mol %) with irradiation for 12 h. Unreacted **5a** (0.20 g, 95%) was recovered from the reaction mixture.

Preparation of 3,4-Dihydro-2-(4-methoxyphenyl)-1(2*H*)-isoquinolinone 13b.[32] *A. **7-Se** as Photocatalyst.* In a 4-dram vial equipped with a stir bar, **5b** (0.239 g, 1.00 mmol) and **7-Se** (5.5 mg, 0.010 mmol, 1 mol %) were dissolved in 15 mL of a 4.9:0.1 mixture of MeCN/H_2O. The reaction mixture was irradiated with a GE 14 W, 850 lm LED light for 13 h. The crude product was purified via chromatography on SiO_2 eluted with 20% EtOAc/hexanes. Isoquinolone **13b** was recrystallized from dichloromethane/diethyl ether to yield 0.098 g (41% isolated yield) of **13b**.

*B. **10-Te** as Photocatalyst.* The reaction was repeated using photocatalyst **10-Te** (6.0 mg, 0.010 mmol, 1 mol %) with irradiation for 8 h. Isoquinolone **13b** was purified via chromatography on SiO_2 eluted with 5% EtOAc in hexanes to yield 0.18 g (75% isolated yield) of **13b**.

Preparation of 3,4-Dihydro-2-(4-chlorophenyl)-1(2*H*)-isoquinolinone 13c[32] Using 7-Se as Photocatalyst. In a 4-dram vial equipped with a stir bar, **5b** (0.244 g, 1.00 mmol) and **7-Se** (5.5 mg, 0.010 mmol, 1 mol %) were dissolved in 15 mL of a 4.9:0.1 mixture of MeCN/H_2O. The reaction mixture was irradiated with a GE 14 W, 850 lm LED light for 7.5 h. The white precipitate was collected by filtration, and the filtrate was then concentrated in vacuo. The crude product was purified via chromatography on SiO_2 eluted with 20% EtOAc/hexanes. Isoquinolone **13c** was recrystallized from dichloromethane/diethyl ether to yield 0.121 g (78% isolated yield) of **13c**. The white precipitate was isolated in 0.031 g (6%) yield and was identified as a mixture of D,L- and *meso*-diastereomers of the peroxodimer **14a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32−7.06 (m, 12 H), 6.82 (t, 4 H, *J* = 7.4 Hz), 6.09 (s, 1 H, one diastereomer), 5.98 (s, 1H, one diastereomer), 3.59−3.46 (m, 1H), 3.42−3.18 (m, 3H), 2.88−2.69 (m, 4H); ^{13}C{^{1}H} NMR (300 MHz, $CDCl_3$) δ 146.8, 146.7, 136.0, 131.91, 131.88, 128.5, 128.4, 128.36, 128.33, 128.2, 127.4, 127.3, 125.7, 123.6, 123.5, 115.7, 90.2, 90.0, 42.2, 27.50, 27.46; MS (ESI) *m*/*z* 242 (calcd for $C_{15}H_{13}{}^{35}ClN^+$ 242; calcd for $C_{30}H_{26}{}^{35}Cl_2N_2O_2$+$H^+$ 517). Anal. Calcd for $C_{30}H_{26}Cl_2N_2O_2$: C, 69.64; H, 5.06; N, 5.41. Found: C, 69.98; H, 4.92; N, 5.41. Organic peroxide species are potentially explosive and care should be taken handing these compounds.

Photo-oxidation of 5a with Photocatalyst 10-S in 4.9:0.1 CH_3CN/8.8 M H_2O_2. In a 4-dram vial equipped with a stir bar, 2-phenyl-1,2,3,4-tetrahydroisoquinoline **5a** (0.209 g, 1.00 mmol) and **10-S** (5.3 mg, 0.010 mmol, 1 mol %) were dissolved in 15 mL of a 4.9:0.1 mixture of MeCN/8.8 M H_2O_2 (final concentration of H_2O_2 of 0.18 M). The reaction mixture was irradiated with a GE 14 W, 850 lm LED light for 8 h and the reaction mixture was concentrated in vacuo.

Quantum Yields for Fluorescence and Singlet Oxygen Generation. Optical absorption measurements were performed using PerkinElmer Lambda 900 UV−vis-NIR spectrophotometer. A Fluorolog-3 spectrofluorimeter equipped with iHR320 spectrometer for infrared range (Horiba) was employed to obtain fluorescence spectra. Absorption for all the measured samples was matched at the wavelength of excitation (532 nm) before spectra acquisition.

To quantify singlet oxygen generation, singlet oxygen phosphorescence emission was detected by the thermoelectrically cooled NIR-

PMT unit (Hamamatsu H10330B-75) attached to the output of the iHR320 spectrometer that was set to 1270 nm. Singlet oxygen decay under pulsed excitation was directly recorded on the Tektronix oscilloscope (TDS 3034C Digital Phosphor oscilloscope) coupled to the NIR-PMT unit. A second harmonic (532 nm) from nanosecond pulsed Q-switched Nd:YAG laser (LS-2137 from Lotis TII) lasing at the SH with repetition rate of 10 Hz was used as an excitation source.

Data Analysis and Statistics. Statistical significance was assessed using one-way ANOVA and a posthoc multiple pairwise comparison using the Tukey test with a significance level of 0.05. The Student's t test was used for pairwise comparisons of independent samples. All t tests were two-sided, and p values less than 0.05 were considered significant.

Computational Details. Calculations were done with Gaussian09[36] input files, and results were visualized using GaussView05.[48] All structures were optimized using the B3LYP[37−39] level of theory with the 6-31+G(d)[40−42] basis set for all light atoms and LanL2DZ[43−45] for Te. Energy values were obtained from the free energy from the frequency calculations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.9b00126.

> Text and figures giving general methods, experimental data for the synthesis of **5a**, **5b**, and **5c**, NMR spectral data (^{1}H and ^{13}C{^{1}H} NMR) for all noncommercial compounds, and ^{1}H NMR spectral data for the mixture of products from irradiation of **5a** and **10-Te** in 4.9:0.1 CH_3CN/H_2O and from **5** and **10-S** in 4.9.1 CH_3CN/8.8 M H_2O_2 (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: t.m.mccormick@pdx.edu.
*E-mail: mdetty@buffalo.edu.

ORCID

Tymish Y. Ohulchanskyy: 0000-0002-7051-6534
Theresa M. McCormick: 0000-0003-1745-2911
Michael R. Detty: 0000-0002-8815-1481

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported in part by the National Science Foundation (CHE-1800599 to T.M.M. and CHE-1800288 to M.R.D.). T.M.M. also thanks Portland State University for financial support.

■ REFERENCES

(1) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. Visible light photoredox catalysis with transition metal complexes: applications in organic synthesis. *Chem. Rev.* **2013**, *113*, 5322−5363.

(2) Hari, D. P.; König, B. Synthetic applications of eosin Y in photoredox catalysis. *Chem. Commun.* **2014**, *50*, 6688−6699.

(3) Romero, N. A.; Margrey, K. A.; Tay, N. E.; Nicewicz, D. A. Site-selective arene C-H amination via photoredox catalysis. *Science* **2015**, *349*, 1326−1330.

(4) Pitre, S. P.; McTiernan, C. D.; Ismaili, H.; Scaiano, J. C. Metal-Free Photocatalytic Radical Trifluoromethylation Utilizing Methylene Blue and Visible Light Irradiation. *ACS Catal.* **2014**, *4*, 2530−2535.

(5) Condie, A. G.; González-Gómez, J. C.; Stephenson, C. R. Visible-light photoredox catalysis: aza-Henry reactions via C-H functionalization. *J. Am. Chem. Soc.* **2010**, *132*, 1464−1465.

(6) Narayanam, J. M. R.; Stephenson, C. R. J. Visible light photoredox catalysis: applications in organic synthesis. *Chem. Soc. Rev.* **2011**, *40*, 102−113.

(7) Pitre, S. P.; McTiernan, C. D.; Scaiano, J. C. Library of Cationic Organic Dyes for Visible-Light-Driven Photoredox Transformations. *ACS Omega* **2016**, *1*, 66−76.

(8) Pan, Y.; Kee, C. W.; Chen, L.; Tan, C.-H. Dehydrogenative coupling reactions catalysed by Rose Bengal using visible light irradiation. *Green Chem.* **2011**, *13*, 2682−2685.

(9) Oba, M.; Tanaka, K.; Nishiyama, K.; Ando, W. Aerobic Oxidation of Thiols to Disulfides Catalyzed by Diaryl Tellurides under Photosensitized Conditions. *J. Org. Chem.* **2011**, *76*, 4173−4177.

(10) Lutkus, L. V.; Irving, H. E.; Davies, K. S.; Hill, J. E.; Lohman, J. E.; Eskew, M. W.; Detty, M. R.; McCormick, T. M. Photocatalytic Aerobic Thiol Oxidation with a Self-Sensitized Tellurorhodamine Chromophore. *Organometallics* **2017**, *36*, 2588−2596.

(11) (a) Romero, N. A.; Nicewicz, D. A. J. Mechanistic Insight into the Photoredox Catalysis of Anti-Markovnikov Alkene Hydrofunctionalization Reactions. *J. Am. Chem. Soc.* **2014**, *136*, 17024−17035. (b) Margrey, K. A.; Nicewicz, D. A. A General Approach to Catalytic Alkene Anti-Markovnikov Hydrofunctionalization Reactions via Acridinium Photoredox Catalysis. *Acc. Chem. Res.* **2016**, *49*, 1997−2006.

(12) (a) Fukuzumi, S.; Kotani, H.; Ohkubo, K.; Ogo, S.; Tkachenko, N. V.; Lemmetyinen, H. Electron-Transfer State of 9-Mesityl-10-methylacridinium Ion with a Much Longer Lifetime and Higher Energy Than That of the Natural Photosynthetic Reaction Center. *J. Am. Chem. Soc.* **2004**, *126*, 1600−1601. (b) Kotani, H.; Ohkubo, K.; Fukuzumi, S. Photocatalytic Oxygenation of Anthracenes and Olefins with Dioxygen via Selective Radical Coupling Using 9-Mesityl-10-methylacridinium Ion as an Effective Electron-Transfer Photocatalyst. *J. Am. Chem. Soc.* **2004**, *126*, 15999−16006.

(13) Lang, X.; Ma, W.; Chen, C.; Ji, H.; Zhao, J. Selective Aerobic Oxidation Mediated by TiO_2 Photocatalysis. *Acc. Chem. Res.* **2014**, *47*, 355−363.

(14) Schultz, D. M.; Yoon, T. P. Solar synthesis: prospects in visible light photocatalysis. *Science* **2014**, *343*, 1239176.

(15) Pitre, S. P.; McTiernan, C. D.; Ismaili, H.; Scaiano, J. C. Mechanistic Insights and Kinetic Analysis for the Oxidative Hydroxylation of Arylboronic Acids by Visible Light Photoredox Catalysis: A Metal-Free Alternative. *J. Am. Chem. Soc.* **2013**, *135*, 13286−13289.

(16) Pitre, S. P.; McTiernan, C. D.; Scaiano, J. C. Understanding the Kinetics and Spectroscopy of Photoredox Catalysis and Transition-Metal-Free Alternatives. *Acc. Chem. Res.* **2016**, *49*, 1320−1330.

(17) Redmond, R. W.; Gamlin, J. N. A compilation of singlet oxygen yields from biologically relevant molecules. *Photochem. Photobiol.* **1999**, *70*, 391−475.

(18) Stracke, F.; Heupel, M.; Thiel, E. Singlet molecular oxygen photosensitized by Rhodamine dyes: correlation with photophysical properties of the sensitizers. *J. Photochem. Photobiol., A* **1999**, *126*, 51−58.

(19) (a) Mann, J. R.; Gannon, M. K.; Fitzgibbons, T. C.; Detty, M. R.; Watson, D. F. Optimizing the Photocurrent Efficiency of Dye-Sensitized Solar Cells through the Controlled Aggregation of Chalcogenoxanthylium Dyes on Nanocrystalline Titania Films. *J. Phys. Chem. C* **2008**, *112*, 13057−13061. (b) Mulhern, K. R.; Detty, M. R.; Watson, D. F. Aggregation-Induced Increase of the Quantum Yield of Electron Injection from Chalcogenorhodamine Dyes to TiO_2. *J. Phys. Chem. C* **2011**, *115*, 6010−6018. (c) Mulhern, K. R.; Orchard, A.; Watson, D. F.; Detty, M. R. Influence of Surface-Attachment Functionality on the Aggregation, Persistence, and Electron-Transfer Reactivity of Chalcogenorhodamine Dyes on TiO_2. *Langmuir* **2012**, *28*, 7071−7082. (d) Kryman, M. W.; Nasca, J. N.; Watson, D. F.; Detty, M. R. Selenorhodamine Dye-Sensitized Solar Cells: Influence

of Structure and Surface-Anchoring Mode on Aggregation, Persistence, and Photoelectrochemical Performance. *Langmuir* **2016**, *32*, 1521−1532.

(20) (a) McCormick, T. M.; Calitree, B. D.; Orchard, A.; Kraut, N. D.; Bright, F. V.; Detty, M. R.; Eisenberg, R. Reductive Side of Water Splitting in Artificial Photosynthesis: New Homogeneous Photosystems of Great Activity and Mechanistic Insight. *J. Am. Chem. Soc.* **2010**, *132*, 15480−15483. (b) Sabatini, R. P.; Eckenhoff, W. T.; Orchard, A.; Liwosz, K. R.; Detty, M. R.; Watson, D. F.; McCamant, D. W.; Eisenberg, R. From Seconds to Femtoseconds: Solar Hydrogen Production and Transient Absorption of Chalcogenorhodamine Dyes. *J. Am. Chem. Soc.* **2014**, *136*, 7740−7750.

(21) (a) McIver, Z. A.; Kryman, M. W.; Choi, Y.; Coe, B. N.; Schamerhorn, G. A.; Linder, M. K.; Davies, K. S.; Hill, J. E.; Sawada, G. A.; Grayson, J. M.; Detty, M. R. Selective photodepletion of malignant T cells in extracorporeal photopheresis with selenorhodamine photosensitizers. *Bioorg. Med. Chem.* **2016**, *24*, 3918−3931. (b) Kryman, M. W.; Davies, K. S.; Linder, M. K.; Ohulchanskyy, T. Y.; Detty, M. R. Seleno-rhodamine photosensitizers with the Texas-red core for photodynamic therapy of cancer cells. *Bioorg. Med. Chem.* **2015**, *23*, 4501−4507. (c) Hill, J. E.; Linder, M. K.; Davies, K. S.; Sawada, G. A.; Morgan, J.; Ohulchanskyy, T. Y.; Detty, M. R. Selenorhodamine Photosensitizers for Photodynamic Therapy of P-Glycoprotein-Expressing Cancer Cells. *J. Med. Chem.* **2014**, *57*, 8622−8634. (d) Wagner, S. J.; Skripchenko, A.; Donnelly, D. J.; Ramaswamy, K.; Detty, M. R. Chalcogenoxanthylium photosensitizers for the photodynamic purging of blood-borne viral and bacterial pathogens. *Bioorg. Med. Chem.* **2005**, *13*, 5927−5935.

(22) (a) Kryman, M. W.; Schamerhorn, G. A.; Yung, K.; Sathyamoorthy, B.; Sukumaran, D. K.; Ohulchanskyy, T. Y.; Benedict, J. B.; Detty, M. R. Organotellurium Fluorescence Probes for Redox Reactions: 9-Aryl-3,6-diaminotelluroxanthylium Dyes and Their Telluroxides. *Organometallics* **2013**, *32*, 4321−4333. (b) Kryman, M. W.; Schamerhorn, G. A.; Hill, J. E.; Calitree, B. D.; Davies, K. S.; Linder, M. K.; Ohulchanskyy, T. Y.; Detty, M. R. Synthesis and Properties of Heavy Chalcogen Analogues of the Texas Reds and Related Rhodamines. *Organometallics* **2014**, *33*, 2628−2640.

(23) Koide, Y.; Kawaguchi, M.; Urano, Y.; Hanaoka, K.; Komatsu, T.; Abo, M.; Terai, T.; Nagano, T. A reversible near-infrared fluorescence probe for reactive oxygen species based on Te−rhodamine. *Chem. Commun.* **2012**, *48*, 3091−3093.

(24) Detty, M. R.; Prasad, P. N.; Donnelly, D. J.; Ohulchanskyy, T.; Gibson, S. L.; Hilf, R. Synthesis, properties, and photodynamic properties in vitro of heavy-chalcogen analogues of tetramethylrosamine. *Bioorg. Med. Chem.* **2004**, *12*, 2537−2544.

(25) Ohulchanskyy, T.; Donnelly, D. J.; Detty, M. R.; Prasad, P. N. Heteroatom Substitution Induced Changes in Excited-State Photophysics and Singlet Oxygen Generation in Chalcogenoxanthylium Dyes: Effect of Sulfur and Selenium Substitutions. *J. Phys. Chem. B* **2004**, *108*, 8668−8672.

(26) Detty, M. R.; Merkel, P. B.; Hilf, R.; Gibson, S. L.; Powers, S. K. Chalcogenapyrylium dyes as photochemotherapeutic agents. 2. Tumor uptake, mitochondrial targeting, and singlet-oxygen-induced inhibition of cytochrome c oxidase. *J. Med. Chem.* **1990**, *33*, 1108−1116.

(27) Detty, M. R.; Merkel, P. B. Chalcogenapyrylium dyes as potential photochemotherapeutic agents. Solution studies of heavy atom effects on triplet yields, quantum efficiencies of singlet oxygen generation, rates of reaction with singlet oxygen, and emission quantum yields. *J. Am. Chem. Soc.* **1990**, *112*, 3845−3855.

(28) Nascimento, V.; Alberto, E. E.; Tondo, D. W.; Dambrowski, D.; Detty, M. R.; Nome, F.; Braga, A. L. GPx-Like Activity of Selenides and Selenoxides: Experimental Evidence for the Involvement of Hydroxy Perhydroxy Selenane as the Active Species. *J. Am. Chem. Soc.* **2012**, *134*, 138−141.

(29) Calitree, B. D.; Donnelly, D. J.; Holt, J. J.; Gannon, M. K., II; Nygren, C.; Sukumaran, D. K.; Autschbach, J.; Detty, M. R. Tellurium Analogues of Rosamine and Rhodamine Dyes: Synthesis, Structure, ^{125}Te NMR, and Heteroatom Contributions to Excitation Energies. *Organometallics* **2007**, *26*, 6248−6257.

(30) Khan, A. U.; Kasha, M. Direct spectroscopic observation of singlet oxygen emission at 1268 nm excited by sensitizing dyes of biological interest in liquid solution. *Proc. Natl. Acad. Sci. U. S. A.* **1979**, *76*, 6047−6049.

(31) Del Valle, D. J.; Donnelly, D. J.; Holt, J. J.; Detty, M. R. 2,7-Bis-N,N-dimethylaminochalcogenoxanthen-9-ones via Electrophilic Cyclization with Phosphorus Oxychloride. *Organometallics* **2005**, *24*, 3807−3810.

(32) Ohulchanskyy, T. Y.; Roy, I.; Goswami, L. N.; Chen, Y.; Bergey, E. J.; Pandey, R. K.; Oseroff, A. R.; Prasad, P. N. Organically Modified Silica Nanoparticles with Covalently Incorporated Photosensitizer for Photodynamic Therapy of Cancer. *Nano Lett.* **2007**, *7*, 2835−2842.

(33) Liu, Y.; Wang, C.; Xue, D.; Xiao, M.; Liu, J.; Li, C.; Xiao, J. Reactions Catalysed by a Binuclear Copper Complex: Relay Aerobic Oxidation of N-Aryl Tetrahydroisoquinolines to Dihydroisoquinolones with a Vitamin B1 Analogue. *Chem. - Eur. J.* **2017**, *23*, 3062−3066.

(34) (a) Ratnikov, M. O.; Xu, X.; Doyle, M. P. Mechanistic Investigation of Oxidative Mannich Reaction with tert-Butyl Hydroperoxide. The Role of Transition Metal Salt. *J. Am. Chem. Soc.* **2013**, *135*, 9475−9479. (b) Han, W.; Mayer, P.; Ofial, A. R. Iron-Catalyzed Oxidative Mono- and Bis-Phosphonation of N,N-Dialkylanilines. *Adv. Synth. Catal.* **2010**, *352*, 1667−1676. (c) Liu, P.; Zhou, C. Y.; Xiang, S.; Che, C. M. Highly efficient oxidative carbon−carbon coupling with SBA-15-support iron terpyridine catalyst. *Chem. Commun.* **2010**, *46*, 2739−2741. (d) Soule, J.-F.; Miyamura, H.; Kobayashi, S. Selective imine formation from alcohols and amines catalyzed by polymer incarcerated gold/palladium alloy nanoparticles with molecular oxygen as an oxidant. *Chem. Commun.* **2013**, *49*, 355−357. (e) Kohls, P.; Jadhav, D.; Pandey, G.; Reiser, O. Visible light photoredox catalysis: generation and addition of N-aryltetrahydroisoquinoline-derived α-amino radicals to Michael acceptors. *Org. Lett.* **2012**, *14*, 672−675.

(35) Earlier studies demonstrated that the 9-position of these tellurorosamines can undergo intramolecular addition of oxygen when the Te atom is oxidized to the telluroxide oxidation state, which would effectively destroy the chromophore of the photocatalyst and lead to reduced photocatalytic turnover numbers. Replacing the 9-phenyl substituent with a 9-mesityl substituent sterically shields the 9-position of the tellurorosamine from the intramolecular addition and gives much greater stability to the oxidized tellurorosamine (ref 22).

(36) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V; Cioslowski, J.; Fox, D. J. *Gaussian 09*, revision E.01; Gaussian Inc.: Wallingford, CT, 2009.

(37) Becke, A. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(38) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785−789.

(39) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. Results obtained with the correlation energy density functionals of becke and Lee, Yang and Parr. *Chem. Phys. Lett.* **1989**, *157*, 200−206.

(40) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. Molecular orbital theory of the electronic structure of organic compounds. V. Molecular theory of bond separation. *J. Am. Chem. Soc.* **1970**, *92*, 4796−4801.

(41) Ditchfield, R.; Hehre, W. J.; Pople, J. A. Self-Consistent Molecular-Orbital Methods. IX. An Extended Gaussian-Type Basis for Molecular-Orbital Studies of Organic Molecules. *J. Chem. Phys.* **1971**, *54*, 724−728.

(42) Hariharan, P. C.; Pople, J. A. The influence of polarization functions on molecular orbital hydrogenation energies. *Theor. Chim. Acta.* **1973**, *28*, 213−222.

(43) Hay, P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. *J. Chem. Phys.* **1985**, *82*, 270−283.

(44) Hay, P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. *J. Chem. Phys.* **1985**, *82*, 299−310.

(45) Wadt, W. R.; Hay, P. J. Ab initio effective core potentials for molecular calculations. Potentials for main group elements Na to Bi. *J. Chem. Phys.* **1985**, *82*, 284−298.

(46) Kryman, M. W.; McCormick, T. M.; Detty, M. R. Longer-Wavelength-Absorbing, Extended Chalcogenorhodamine Dyes. *Organometallics* **2016**, *35*, 1944−1955.

(47) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. *J. Phys. Chem. B* **2009**, *113*, 6378−6396.

(48) Dennington, R.; Keith, T.; Millam, J. *GaussView*, Semichem Inc.: Shawnee Mission, KS, 2009.

(49) Carrera, E. I.; Seferos, D. S. Ring Opening of π-Delocalized 2,5-Diphenyltellurophene by Chemical or Self-Sensitized Aerobic Photooxidation. *Organometallics* **2017**, *36*, 2612−2621.

DOI: 10.1021/acs.organomet.9b00126
Organometallics XXXX, XXX, XXX−XXX