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Novel, Light-Emitting Reaction of (*E*)-2-(Phenylsulfonyl)-3-phenyloxaziridine with Strong Bases

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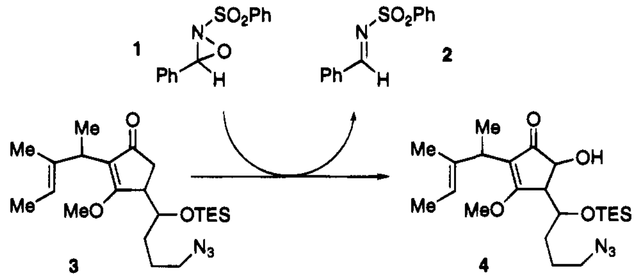
Reactions that emit light visible to the human eye have drawn much attention from the scientific community.[1] In this communication, we report a hitherto unknown chemiluminescence of (*E*)-2-(phenylsulfonyl)-3-phenyloxaziridine, commonly known as Davis' oxaziridine,[2] and its analogs in the presence of strong bases.

Davis' oxaziridine (**1**) is widely used in organic synthesis. One of its important applications is the hydroxylation of enolates, yielding α-hydroxy ketones (Scheme 1).[3] For example, addition of **1** in tetrahydrofuran to a solution of the enolate of **3** in THF under a nitrogen atmosphere yielded the expected α-hydroxy ketone **4** in 75% yield. However, when more than 2 equiv of lithium diisopropylamide (LDA) was used, **1** instantaneously decomposed and no α-hydroxylation of **3** was observed. Interestingly, this process was accompanied by emission of intense yellow light. A brief survey of commercially available strong bases revealed that not only LDA but *tert*-butyllithium, *n*-butyllithium, and potassium hexamethyldisilazanide (KHMDS) also underwent reaction with **1** to yield visible light, whereas methylmagnesium chloride and sodium and lithium hexamethyldisilazanides (NaHMDS and LiHMDS) did not give light emission.

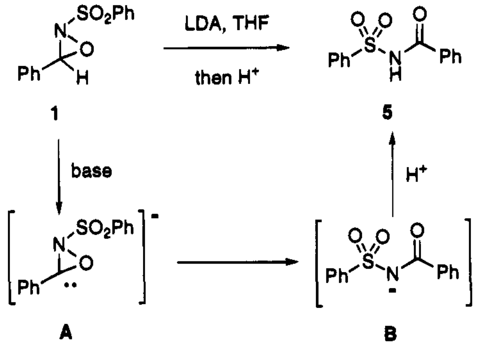
Relevant to this study, Newcomb and Reeder had demonstrated that (*E*)-2-*tert*-butyl-3-phenyloxaziridine reacts with lithium amide bases to yield *N*-*tert*-butylbenzaldimine and *N*-*tert*-butylbenzamide in a competing fashion.[4] In the present case, upon acidic workup of the chemiluminescent reaction at −78 °C, *N*-benzoylbenzenesulfonamide (**5**) was identified as the only isolable product and no *N*-benzylidenebenzenesulfonamide (**2**) was detected[5−7] (Scheme 2). Sulfonamide **2** was not stable under the reaction conditions employed. However, we observed overlapping signals in the ^{1}H-NMR spectra of the crude products resulting from the reactions of **2** or the oxaziridine **1** with LDA.[8] These experiments strongly suggested that **1** also reacted both through proton- and oxygen-transfer processes with LDA.

The light emission from the reaction of **1** with LDA was short-lived and consisted of brief flashes of light upon addition of each drop of base. Using a syringe pump to add LDA at a steady rate (0.5 mL/min) to the solution of **1** (20 mg in 2 mL of THF) in a cuvette, we were able to obtain a rough spectrum of the emitted light (λ_{max} = 520 nm). The quantum yield of this reaction was found to be between 10^{-4} and 10^{-5}.

Scheme 1



Scheme 2



We next searched for the light-emitting species. The *N*-benzoylbenzenesulfonamide (**5**) did not show a fluorescence maximum around 500 nm under a variety of basic and neutral conditions in various solvents including THF, DMSO, and MeOH. We could not exclude the possibility that **5** was generated in some isomeric form otherwise inaccessible through deprotonation and excitation by light.[9] However, the spectrum of light emission correlated well with the emission spectrum of the *N*-benzylidenebenzenesulfonamide (**2**) upon irradiation at 459 nm, strongly suggesting **2** to be the light emitter.

To gain further insight on the chemiluminescence reaction, analogs **6** and **8** were prepared.[10] As expected, **6** exhibited a red shift, with light emission λ_{max} = 570 nm. The chemiluminescence spectrum corresponded to the emission spectra of imine **7**. On the other hand, **8** exhibited a blue shift (λ_{max} = 460 nm). This emission seemed to originate from the naphthalenesulfonamido group. Indeed, fluorescence emission spectra of both the imine **9** and the naphthalenesulfonamide **10** matched the light emission spectrum of **8**. These experiments demonstrated that a process exergonic enough to produce photons at 460 nm occurred.

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(1) (a) Schuster, G. B.; Schmidt, S. P. In *Advances in Physical Organic Chemistry;* Gold, V., Bethell, D., Eds.; Academic Press: London, 1982; Vol. 18, p 187. (b) Nakashima, K.; Imai, K. In *Molecular Luminescence Spectroscopy, Methods and Applications: Part 3*; Schulman, S. G., Ed.; Wiley: New York, 1988; Chapter 1.

(2) For reviews on this subject, see: (a) Davis, F. A.; Sheppard, A. C. *Tetrahedron* **1989**, *45*, 5703. (b) Davis, F. A.; Chen, B.-C. *Chem. Rev.* **1992**, *92*, 919.

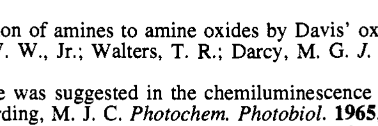
(3) Davis, F. A.; Vishakarma, L. C.; Billmers, J. M.; Finn, J. M. *J. Org. Chem.* **1984**, *49*, 3241.

(4) Newcomb, M.; Reeder, R. A. *J. Org. Chem.* **1980**, *45*, 1489. It was shown that *N*-*tert*-butylbenzamide was formed through simultaneous deprotonation and ring opening of (*E*)-2-*tert*-butyl-3-phenyloxaziridine.

(5) The photochemical rearrangement of **1** into **5** is known: Davis, F. A.; Nadir, U. K. *Tetrahedron Lett.* **1977**, 1721.

(6) The structure of **5** was confirmed by the independent synthesis with modification of the method reported by Wallach: Wallach, O. *Justus Liebigs Ann. Chem.* **1882**, *214*, 193.

(7) Light emission was observed over a wide range of temperatures (-78 °C to room temperature). When the chemiluminescent reaction was run at higher temperatures (0 °C to room temperature), 3-phenyl-1,2-benzisothiazole 1,1-dioxide (i) was isolated as the sole product. Upon treatment with excess LDA at room temperature, **5** yielded i quantitatively. However, this transformation did not seem to be relevant to chemiluminescence. This transformation has been reported recently: Hermann, C. K. F.; Campbell, J. A.; Greenwood, T. D.; Lewis, J. A.; Wolfe, J. F. *J. Org. Chem.* **1992**, *57*, 5328.



(8) The oxidation of amines to amine oxides by Davis' oxaziridines is known: Zajac, W. W., Jr.; Walters, T. R.; Darcy, M. G. *J. Org. Chem.* **1988**, *53*, 5856.

(9) Such a case was suggested in the chemiluminescence of lophines: White, E. H.; Harding, M. J. C. *Photochem. Photobiol.* **1965**, *4*, 1129.

(10) Prepared in the same way as **1**: Davis, F. A.; et al. *J. Am. Chem. Soc.* **1980**, *102*, 2000; *J. Org. Chem.* **1990**, *55*, 1254.

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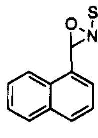

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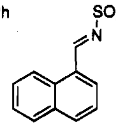

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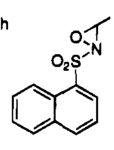

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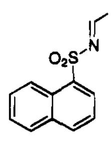

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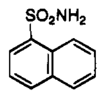

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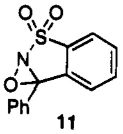
When 9,10-diphenylanthracene (DPA), perylene, or rubrene was added at equimolar amounts, light emissions occurred from the added energy acceptor. DPA and perylene had emission maxima at lower wavelengths than the direct chemiluminescent emission. Furthermore, perylene and rubrene enhanced the quantum yield to 10^{-2} and 10^{-3}, respectively. These results suggested that imine **2** was not the species generated initially at the excited state. Rather, as the imine **2** was formed in the reaction, it was excited through an energy transfer from an initially generated nonfluorescent intermediate. The observation that the reaction of **1** with LiHMDS was not chemiluminescent (*vide supra*), but became chemiluminescent upon addition of perylene, argues that the chemiexcitation step is different from the step generating a light emitter. We suggest that the process generating an intermediate at the excited state involves the proton-transfer reaction. This is consistent with the fact that the oxaziridine **11**[10] bearing no abstractable proton did not emit light either in the presence or in the absence of added energy acceptors.



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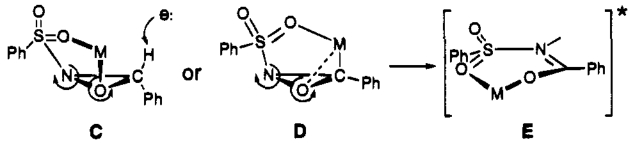
Assuming that the proton transfer is the first step in the light-emitting process, the initial intermediate at the excited state must be the anion **B**, generated through the highly exergonic ring opening of **A**. Marcus theory predicts that, after a certain value of free energy of reaction (ΔG), the free energy of activation (ΔG^*) starts increasing as a reaction becomes more exergonic.[11] Thus, ΔG^* for formation of the excited state of the anion **B** from **A** need not be unfavorable in comparison to ΔG^* for formation of the ground state.

Scheme 3



Furthermore, the ring-opening process of the oxaziridine anion **A** to the anion **B** can be treated as a pericyclic cyclopropyl anion ring opening.[12] The disrotatory ring opening could provide favorable crossing between the ground state surface of oxaziridine anion **A** and the excited state surface of anion **B**. Metal chelation may play an important role for the ring opening to take place in a disrotatory fashion (Scheme 3); a metal chelation such as in **C** or **D** would force the ring opening to be in a thermally forbidden disrotatory mode to avoid the stepwise process from the oxaziridine anion **A** to the chelated anion **E**.

If the suggested explanation is correct, this would represent the first thermal disrotatory ring opening of a cyclopropyl anion which is coupled with light emission. Thus, it would again demonstrate the predictive and explanatory powers of the Woodward–Hoffmann rules and could lead to the rational design of similar chemiluminescent systems.

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