HETEROCYCLES, Vol. 63, No. 7, 2004, pp. 1667 - 1672
Received, 2nd April, 2004, Accepted, 27th May, 2004, Published online, 1st June, 2004

CHEMILUMINESCENT AUTOXIDATION OF α-SILYL CARBANIONS DERIVED FROM 9-SILYL-10-METHYLACRIDANES

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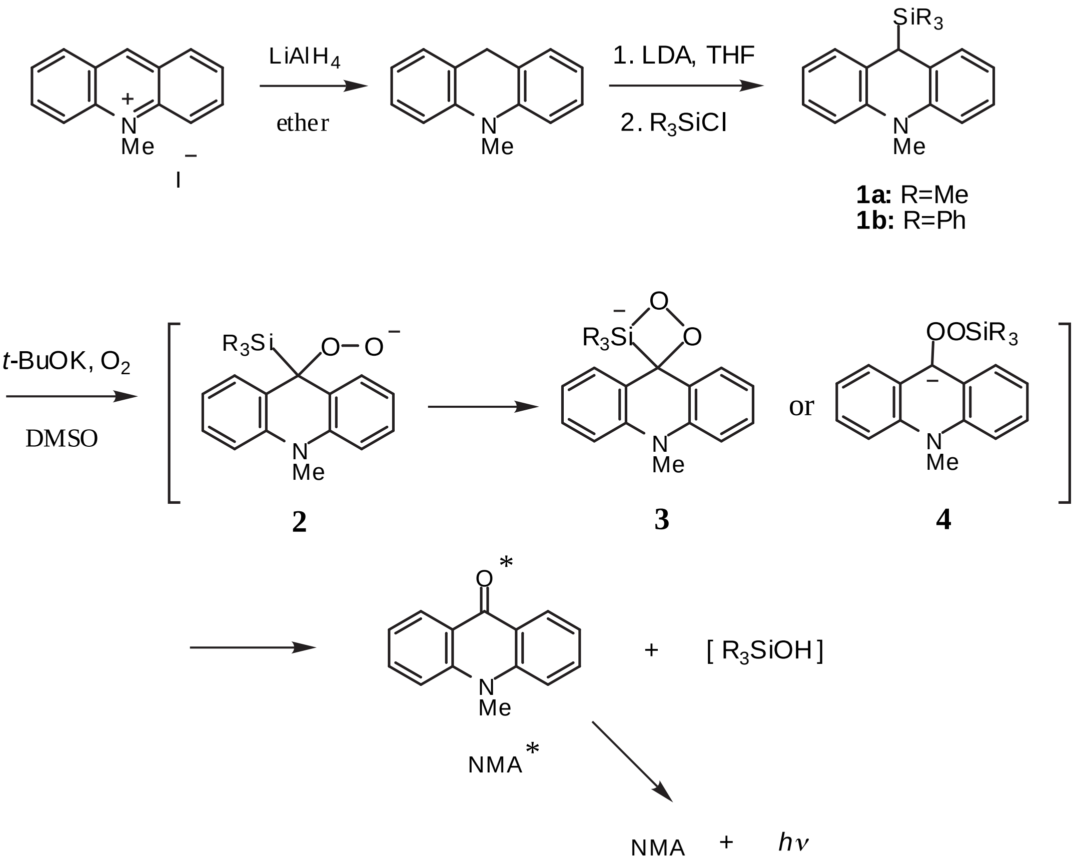
Abstract – The autoxidation of α-silyl carbanions derived from 9-trimethysilyl- and 9-triphenylsilyl-10-methylacridanes (**1a** and **1b**) produced the fluorescent *N*-methylacridone (NMA) accompanied by weak chemiluminescence. Differences in the chemiluminescence quantum yields and the time course of the light emission were detected between the reactions of **1a** and **1b**, which was due to the substituent on the silicon atom. Additionally, the 9-trimethylsilyl-10-methylacridinium salt also underwent a chemiluminescent reaction when reacted with alkaline hydrogen peroxide. It is probable that these chemiluminescent reactions would proceed *via* the Peterson-type reaction and involve the dioxasiletanide-like species during the reaction pathway.

One of the most important features of silicon in organic chemistry is the strong affinity of an oxyanion for the silyl moiety, and such a peculiar chemical property allows for the synthetically versatile reaction called the Peterson reaction; [1] the interaction of α-silyl carbanions with carbonyl compounds producing olefins as the silicon variation of the Wittig-type reactions. On the other hand, the interaction between α-silyl carbanions and molecular oxygen is, to our knowledge, only been slightly investigated, though the autoxidation of α-phosphoryl carbanions is well studied. [2] If the autoxidation of α-silyl carbanions forming the corresponding carbonyl compounds proceeds *via* the Peterson-type reaction, [3] either cyclic or linear peroxides should be involved during the reaction process, which might provide chemiluminescence from the excited fluorescent molecules generated by decomposition of the peroxides. In fact, we have found that the autoxidation of the phosphonate carbanions derived from 9-phosphorylacridanes was chemiluminescent. [4] Therefore, it is of significance to determine the behavior of α-silyl carbanions toward oxygen and whether or not such a reaction is chemiluminescent. In this paper, we report our results of the autoxidation of 9-silyl-10-methylacridanides and related reactions from the viewpoint of chemiluminescence.

The autoxidation of the 9-trimethylsilyl- and 9-triphenylsilyl-10-methylacridanes (**1a**) [5] and (**1b**) [6], prepared by reduction of *N*-methylacridinium iodide followed by silylation of 9-lithio-10-methylacridanide with trimethylchlorosilane or triphenylchlorosilane, was carried out in the presence of potassium *tert*-butoxide (*t*-BuOK) in aerated DMSO to give *N*-methylacridone (NMA) as the sole fluorescent product in 55 and 52 % yield, respectively (Scheme 1). In the reaction of **1b**, triphenylsilanol was isolated in 64% yield along with NMA. [7] These products were those expected from the Peterson-type reaction, namely, an α-silyl carbanion initially reacted with molecular oxygen to give the oxyanion (**2**), and the final products would be formed by the cleavage of the four-membered peroxide, 1,2,3-dioxasiletanide (**3**) generated by a Wittig-type reaction, or a linear silylperoxide (**4**) generated by a Brook-type rearrangement as shown in Scheme 1.



Scheme 1

Of interest is the weak light emission observed when a concentrated solution of **1a** or **1b** was treated with *t*-BuOK in aerated DMSO or DMF. In these reactions, the light emission was very weak, so that the emitter could not be spectroscopically identified. As NMA was the sole fluorescent product of these reactions, it is the most likely candidate for the emitter. The chemiluminescence quantum yields (Φ_{CL}) were estimated to be 5.0 x 10^{-7} and 1.6 x 10^{-6} einstein/mol for the reactions of **1a** and **1b** in aerated DMSO,[8] respectively, by a photon-counting method with a photomultiplier tube compared with the light emission from a luminol chemiluminescence as a standard. These values were very low, but Φ_{CL} for **1b** was by three times greater than for **1a**. The more distinct difference was found in the time course of the light emission as shown in Figure 1. These results show that the light emission from **1b** lasted longer than that from **1a**, namely, the light forming process of **1b** proceeds more slowly but effectively than that of **1a** due to the substituent effect of the silyl groups. A remarkable substituent effect in the Peterson reactions of α-silyl amides and esters was reported, in which a large difference in the geometrical selectivity was detected when the reagents having trimethylsilyl or triphenylsilyl were used in the reaction with aldehydes.[9] The difference both in the electronic factor and in the size of the silyl groups would lead to the different kinetics between the reactions of **1a** and **1b**.

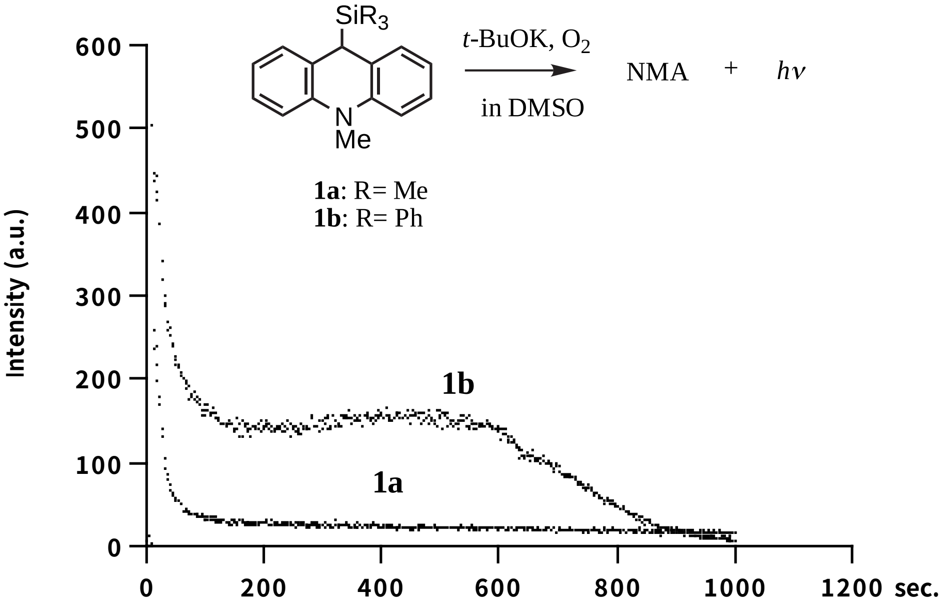
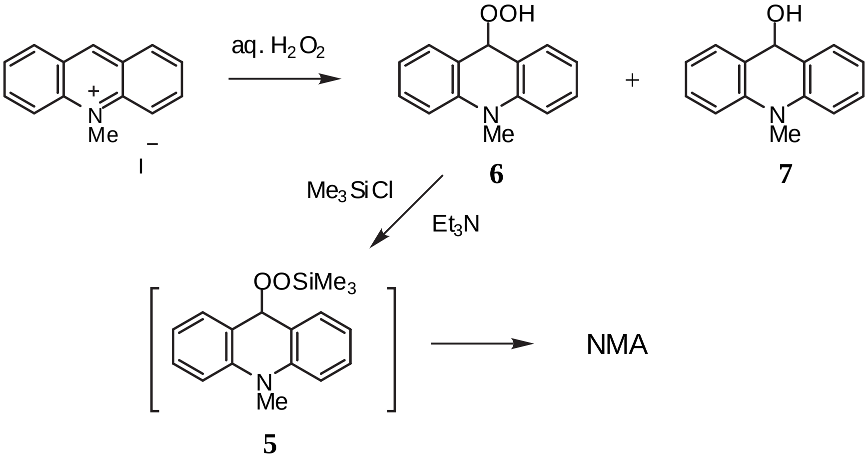


Figure 1 Time course of chemiluminescence reaction of **1a** and **1b.**

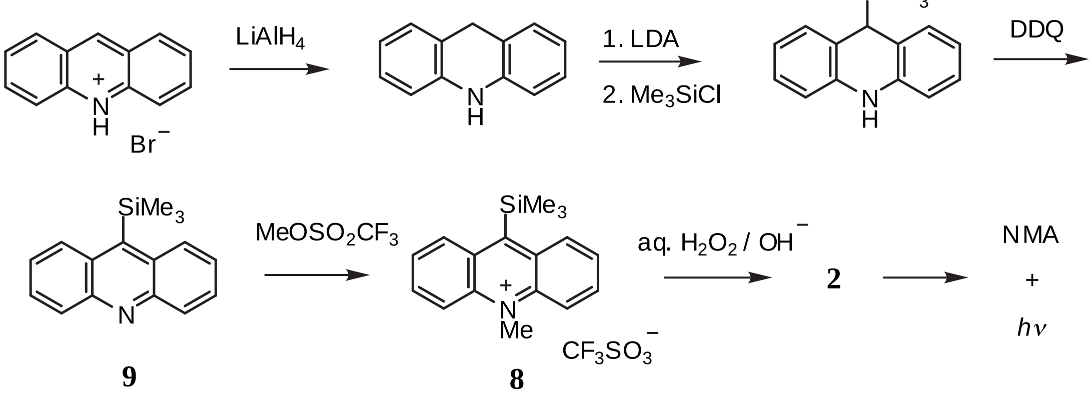
To explore the properties of the silylperoxide (**5**), one of the probable intermediates in the present chemiluminescent autoxidation, its precursor, a hydroperoxide (**6**), was prepared by the reaction of *N*-

methylacridinium iodide and aqueous hydrogen peroxide in methanol as shown in Scheme 2. Thus an inseparable mixture of the hydroperoxide (**6**) and the alcohol (**7**) was obtained in the ratio of 52 : 48, [10] which was subsequently treated with trimethylchlorosilane and triethylamine to give NMA in 12 % yield, while no change in the mixture was found in the absence of trimethylchlorosilane. Therefore, the silylperoxide (**5**) easily decomposes into NMA even under weak basic conditions, but this decomposition reaction was not luminescent.



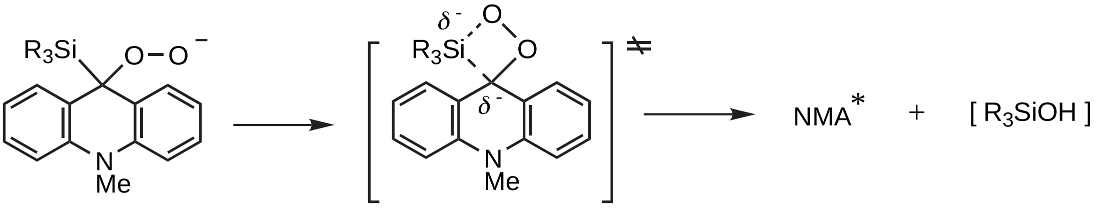
Scheme 2

9-Trimethylsilylacridinium trifluoromethylsulfate (**8**) [11] was prepared by a 4-step synthetic procedure *via* 9-trimethylsilylacridine (**9**) (Scheme 3) and examined for its reaction. A weak and instantaneous light emission was observed with the quantitative formation of NMA, when **8** was treated with alkaline hydrogen peroxide in the dark. The reaction path of this chemiluminescent reaction should be similar to that for the autoxidation of **1**, because the oxyanion (**2**) should also be formed by the attack of the hydroperoxide anion on the 9-carbon of **8**. As the similar reaction of *N*-methylacridinium iodide lacking a silyl group gave no chemiluminescence, the silyl group of **8** plays a crucial role in the light formation process.



Scheme 3

The chemiluminescent reactions presented in this study might proceed *via* two pathways [3] as described in Scheme 1. Although current evidence for specifying the reaction pathway is insufficient, the substituent effect observed in this study seems to suggest the involvement of the 1,2,3-dioxasiletanide-like species, because the difference in the electronic and steric factors of the trimethylsilyl and triphenylsilyl would be large enough to affect the rates of the formation of the four-membered ring. In addition, the cyclic peroxide would be more suitable for the high-energy species producing the excited molecules rather than the linear peroxide. It is also probable that a 1,2,3-oxasiletanide-like species is a transition state (Scheme 4), because it has been proposed that a 1,2-dioxetane is not needed as an intermediate for the chemiluminescence reactions of 9-acridinepercarboxylates, but a transition state could also supply sufficient energy for generation of the excited acridone anion.[12] The Φ_{CL}'s estimated in the present reactions are much lower than those for the chemiluminescent autoxidation of the 9-phosphorylacrydanyl anions, [4] which would be due to an apparently less strained structure of a 1,2,3-dioxasiletanide than that of a phospha-1,2-dioxetane as found when compared with an oxaphosphetane and an oxasiletanide . [13]



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Scheme 4

ACKNOWLEDGEMENTS

This work was partially supported by a Grant-in-Aid for the 21st Century COE program by the Ministry of Education, Culture, Sports, Science, and Technology.

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6. H. Gilman and G. D. Lichtenwalter, *J. Org. Chem.*, 1958, **23**, 1586. Selected data for **1b**: mp 136-138 °C (benzene-hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.53 (s, 3H), 4.36 (s, 1H), 6.51-7.33 (m, 23H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.58, 38.35, 112.23, 120.97, 127.62, 127.97, 128.36, 129.66, 133.34, 135.42, 136.98, 144.09. m/z 453 (M^+). Anal. Calcd for $C_{32}H_{27}NSi$: C, 84.72; H, 6.00; N, 3.09. Found: C, 84.84, H, 5.68; N, 2.95.
7. A solution of **1b** (1.0 g, 3.7 mmol) in THF (50 mL) was bubbled with oxygen gas for 10 min, and *t*-BuOK (0.49 g, 4.4 mmol) was then added to the solution. After being stirred for 2 h at room temperature and under reflux for 1 h in an oxygen atmosphere, the solvent was removed in *vacuo*. The residue was extracted with benzene. The triphenylsilanol was determined by comparison of an authentic sample using liquid chromatography. NMA was isolated by purification using column chromatography (0.24 g, 52 %).
8. A solution (2.0 mL) of **1a** (1.0×10^{-4} M) in DMSO and a solution (1.0 mL) of *t*-BuOK (2.0×10^{-2} M) in *t*-BuOH was mixed in air and the photons immediately generated from the reaction were counted by a photomultiplier tube (R464, Hamamatsu Photonics K.K) in the range of 300-650 nm.
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10. Selected data for the mixture of **3** and **4**: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.50 (s, 1.44H, CH_3 for **4**), 3.53 (s, 1.56H, CH_3 for **3**), 5.56 (s, 0.48H, 9-H for **4**), 6.06 (s, 0.52H, 9-H for **3**). The alcohol (**4**) was independently prepared by the reaction of *N*-acridinium iodide with saturated K_2CO_3 solution.
11. Selected data for **9**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.00 (s, 9H), 7.56 (t, 2H, J = 7.60 Hz), 7.77 (dd, 2H, J = 8.40, 7.60 Hz), 8.01 (d, 2H, J = 8.40 Hz), 8.25 (d, 2H, J = 8.40 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.05, 99.67, 114.80, 125.75, 127.59, 128.64, 131.49, 144.15. Selected data for **7**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02 (s, 9H), 5.09 (s, 3H), 8.22-9.04 (m, 8H).
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