DIRECT CHEMILUMINESCENCE OF DIOXETANIMINE DERIVED FROM 9-(*N-tert*-BUTYLIMINOMETHYLIDENE)-10-METHYLACRIDAN. COMPARISON OF DIOXETANES BY SCF CALCULATIONS

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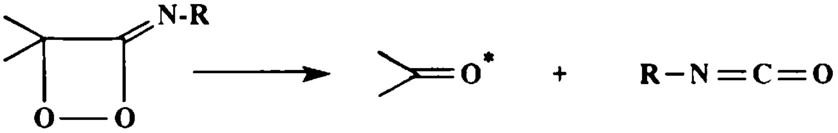
Abstract: Oxidation of a new ketenimine, the title compound, with singlet-oxygen gave a weakly chemiluminescent dioxetanimine, which decomposed into excited *N*-methylacridone and *tert*-butyl isocyanate. The SCF calculations of LUMO energies and total energies of dioxetane derivatives could explain lower efficiency of dioxetanimines in chemiluminescence.

Introduction

Dioxetanimines have been generated as the intermediates in autooxidation of *N*-methyl-9-cyanoacridanide anion (1), base-catalyzed decomposition of α-hydroperoxy nitriles (2), and singlet-oxygen oxidation of ketenimines (3,4). These investigations revealed that thermal decomposition of dioxetanimines gave the excited carbonyl compounds and cyanate ions or isocyanates as the fragments in a similar manner of dioxetanes or dioxetanones (5) as illustrated bellow. In decomposition of dioxetanimines weak indirect chemiluminescence was generally observed in the presence of fluorescent additives but the yields of excited states were generally low (3,4). However, it will be possible to observe direct chemiluminescence of dioxetanimines, if the generated carbonyl compound is highly fluorescent and it can be excited by lower energy. Such a possibility prompted us to explore a new chemiluminescent dioxetanimine.

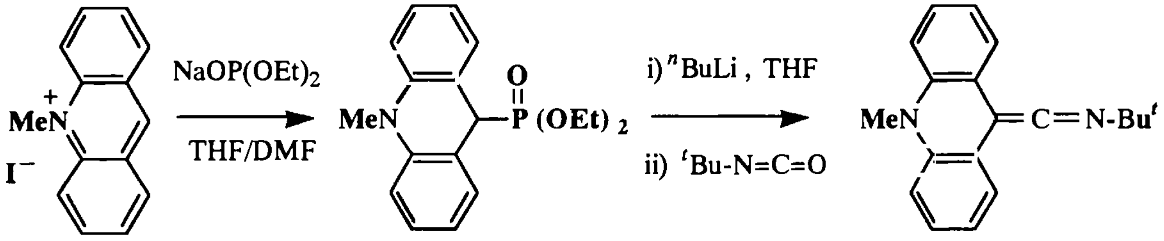


Since dioxetanimines are conveniently prepared by photosensitized oxygenation of ketenimines and the formation of excited *N*-methylacridone (NMA) often gives the good chemiluminescent systems (6), an 9-iminomethyliden-10-methylacridan derivative is a suitable candidate for a precursor of a directly chemiluminescent dioxetanimine. In the present paper we report the preparation of such a new ketenimine, its chemiluminescent oxidation, and some calculations to compare with other dioxetanes.

Results and discussion

Amongst various methods of the preparation of ketenimines (7), the Horner-Wittig reaction of diethyl 10-methyl-9,10-dihydroacridine-9-phosphonate **1**, prepared from 10-methylacridinium iodide and the sodium salt of diethyl phosphite, with *tert*-butyl isocyanate was found to be the most suitable way after some trials. As shown in Scheme 1, the ketenimine **2**. 9-(*N*-*tert*-butyliminomethylidene)-10-methylacridan, was obtained in a 67% yield as a pale-yellow liquid, which showed the characteristic absorption band at 2000 cm^{-1} in ir spectrum but was very sensitive against air and moisture to decompose into NMA. When phenyl isocyanate was employed instead of *tert*-butyl isocyanate, the formation of the ketenimine could not be detected but the trimer of phenyl isocyanate was obtained as the chief product.

Scheme 1

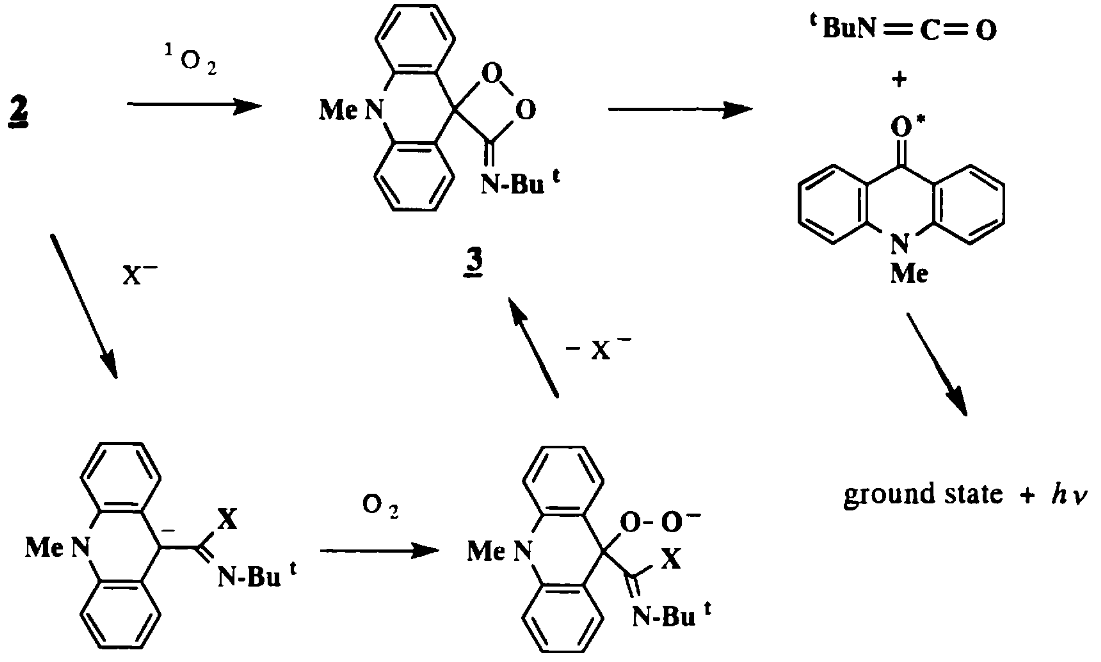


1 **2**

Oxidation of **2** with singlet-oxygen was carried out in dichloromethane at -45 °C in the presence of tetraphenylporphine as a sensitizer. After the oxidation was completed, weak and long lasting pale-blue light emission was observed in the dark as the solution was warmed to ambient temperature. After concentration of the solution the oily residue exhibited an absorption band at 2250 cm^{-1} in ir spectrum assigned to that of *tert*-butyl isocyanate. The separation of the residue gave NMA in a 55% yield. The observation of light emission and detection of both fragment products showed that the corresponding dioxetanimine **3** was formed as a high energy intermediate. Further, oxidation of **2** with triphenyl phosphite-ozone adduct in dichloromethane at -70 °C was performed. When the temperature of the solution reached ca. -30 °C, the solution began to gleam and the emission became stronger upon warming-up. It is known (8) that singlet oxygen is generated by decomposition of triphenyl phosphite-ozone adduct at about -30 °C. Interestingly, chemiluminescence was also observed when **2** was treated with alkaline hydrogen peroxide in aqueous tetrahyrofuran (THF). We could measure an emission spectrum of this chemiluminescent reaction, whose emission at 455 nm was identical with a fluorescence spectrum of NMA (446 nm, THF/water = 3/2). This agreement indicated that the emission was due to the fluorescence of NMA. Autooxidation of 2 in an alkaline solution without hydrogen peroxide also gave chemiluminescence, which suggests that dissolved oxygen would react with the imidate anion to form 3 as described by Janzen et al. (1) in the autooxidation of *N*-methyl-9-cyanoacridanide anion. These chemiluminescent reactions are summarized in Scheme 2.

Although the yield of the excited states has not been measured, the observation of weak direct chemiluminescence shows the fulfillment in energy during decomposition of 3 to form excited NMA in a singlet state. The observed chemiluminescence might be due to a CIEEL (chemically induced electron exchange luminescence) path as pointed out by Singer et al. (9), but no evidence could be obtained at present.

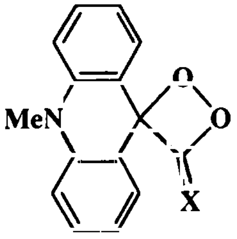
Scheme 2



(X= OOH, OH)

The previous studies on dioxetanimines suggested (3,4) that the yields of singlet and triplet excited states of carbonyl compounds were very low, and that the role of a CIEEL path was not important in contrast to dioxetanones although both dioxetanes contained sp^2 carbons in the four-membered rings. As the CIEEL path involves one electron transfer from an electron donor to LUMOs of dioxetanes (10), the comparison of LUMO energies calculated by the SCF method would inform acceptability of electrons for dioxetanes leading to the CIEEL path. To this end SCF calculations were performed using a STO-3G basis set for the structures 4, 5, and 6 (Table 1). The calculated LUMO energies indicated that 5 could accept an electron most easily and the LUMO energy of 6 was the highest of the three. This agrees with the unimportance of the CIEEL path for the case of dioxetanimines. Similarly, the calculations for the parent compounds 7, 8, and 9 were also carried out (Table 2). The highest LUMO energy was also found for the dioxetanimine. Additionally, differences in the total energies were calculated to be 66 kcal/mol for 7. → 2H_2CO, 84 kcal/mol for 8 → H_2CO + CO_2, and 61 kcal/mol for 9 → H_2CO + HNCO, respectively, which showed that decomposition of 7 was the most exothermic but that of 9 was the least. Although only qualitative comparison can be allowed in these calculations, this result predicts a lower efficiency of dioxetanimines in chemiluminescence than those of dioxetanones and dioxetanes.

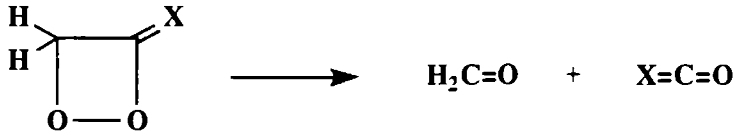
Table 1: LUMO Energies of Dioxetanes with 10-Methylacridanyl Groups Calculated by STO-3G.[a]



	X	LUMO energy
4	H_2	0.2204
5	O	0.2147
6	NBu^t	0.2263

a. All structures were optimized by MM2 and energies are described in atomic unit.

Table 2: LUMO Energies and Difference of Total Energies During Decomposition of Dioxetanes Calculated by 4-31G.[a]



	X	LUMO energy	Total energy	Total energy (H_2CO+XCO)	Energy difference
7	H_2	0.1236	-227.27180	-227.37626	0.10446 (66 kcal/mol)
8	O	0.1080	-300.84134	-300.97476	0.13342 (84 kcal/mol)
9	NH	0.1472	-281.03261	-281.12950	0.09689 (61 kcal/mol)

a. All structures were optimized by MM2 and energies are described in atomic unit except the numbers in the parenthses.

Experimental

IR spectra were recorded on a JASCO IRA-1 spectrometer, ^{1}H NMR spectra on a JOEL PMX-FX 60 (60MHz), and Fluorescence spectra on a HITACHI 650-10.

Preparation of Diethyl 10-Methyl-9,10-dihydroacridine-9-phosphonate **1**:

This phosphonate can be prepared according to Redmore's method (11) but we employed *N*-methylacridinium iodide instead of *in situ* generated *N*-methylacridinium methylsulfate. To a suspension of sodium hydride (60% in oil, 3.40 g, 85 mmol) in THF (100 ml) was added diethyl phosphite (11.74 g, 85 mmol) dropwise under a nitrogen atmosphere. After hydrogen evolution was ceased, this solution was added dropwise to a suspension of acridinium iodide (24.26 g, 2.56 mmol) in dry dimethylformamide (360 ml). To the resulting solution was added chloroform (200 ml) and water (200 ml). The organic layer was separated, washed with brine, and dried over sodium sulfate. Removal of the solvent gave **1** as a pale yellow crystal (6.71 g, 79%) , which was recrystallized from benzene. Thus prepared **1** was identical in spectral data with those reported (11).

Preparation of 9-(N-tert-butyliminomethylidene)-10-methylacridan **2**:

To a solution of the phosphonate **1** (5.00 g, 15.1 mmol) in THF (50 ml) was added dropwise *n*-butyl lithium (1.59 mol/L in hexane, 9.5 ml, 15.1 mmol) at room temperature under a nitrogen atmosphere. After the solution was stirred for 20 min., *tert*-butyl isocyanate (1.72 ml, 15.1 mmol) was added via syringe and the solution was allowed to stand for three days at an ambient temperature. The progress of the reaction was checked by ir spectrum. After the solvent was evaporated, benzene (20 ml) was added to the residue and the insoluble matter was removed by filtration. The filtrate thus obtained was chromatographed (silica gel) using benzene as an eluant and a yellow fraction was concentrated to give the almost pure ketenimine **1** (2.36 g, 57 %). IR : (neat) 2000 cm $^{-1}$ ($\nu_{C=C=N}$), ^{1}H NMR : δ (CCl_4) 1.42 (9H, s), 3.16 (3H, s), 6.44-7.17 (8H, m). This ketenimine was too sensitive against moisture and air to obtain other analytical data.

Photosensitized oxygenation of **2** :

A solution of **2** (1.08 g, 3.9 mmol) and tetraphenylporphine (0.01 g) in dichloromethane (300 ml) was irradiated by a high-pressure Hg arc for 30 min. under an oxygen atmosphere at - 45 °C. During a rise of temperature pale-blue light emission was observed and the emission lasted for ca. 1 hr until the temperature of the solution reached 30 °C. After concentration of the solution, the residue exhibited the characteristic absorption band at 2250 cm^{-1} in ir spectrum and treatment with petroleum ether gave *N*-methylacridone (0.45 g, 55 %), which was identified with the authentic sample.

Acknowledgement. This work was partially supported by a Grant-in-Aid for Scientific Research (No. 06805077) from Ministry of Education, Science and Culture.

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Received January 20, 1995