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A 3-Azacyclopropanespiro-1,2-dioxetane via Singlet Oxygenation of a Methyleneaziridine

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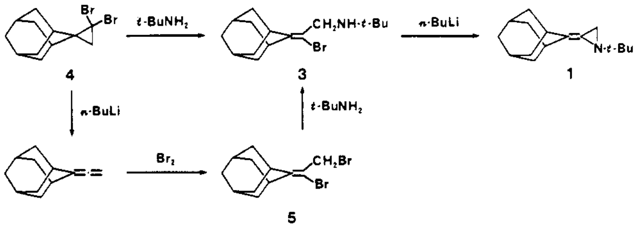
The first three-membered ring substituted spiro-1,2-dioxetane (2) has been synthesized and characterized through the singlet oxygenation of methyleneaziridine 1. Thermodynamic properties of the decomposition of 2 are as follows: $k_{20\,°\mathrm{C}} = 11.5\ \mathrm{s}^{-1}$; $E_a = 18.3$ kcal/mol; $\Delta H^{*} = 17.9$ kcal/mol; $\Delta S^{*} = 7.5$ eu. The chemical properties of this novel dioxetane are compared to those of dioxetanes 11 and 12, dioxetanimine 9, and dioxetanone 10.

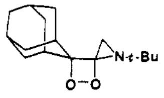
The synthesis of stable 1,2-dioxetanes has been abundantly documented and extensively utilized for the mechanistic exploration of chemienergized electronic excitation.[1] The considerably less stable dioxetanones (α-peroxy lactones), which are an interesting class of high-energy compounds because of similarity to the postulated reaction intermediates in bioluminescence,[1d,e,2] produce electronic excitation through chemically initiated electron-exchange luminescence (CIEEL).[3] The thermal stability of 1,2-dioxetanes is affected by substituents on the dioxetane ring.[4] Work on the synthesis and characterization of dioxetanimines through the singlet oxygenation of ketene imines has only recently been reported.[5] In the course of our search for new chemiluminescence systems,[6] we have now synthesized and characterized 3-(*N-tert*-butyl-azacyclopropane)spiro-4-adamantane-spiro-1,2-dioxetane 2 through the photooxygenation of 1-*tert*-butyl-2-adamantylideneaziridine 1 as the first three-membered ring substituted spiro-1,2-dioxetane.

1 was synthesized by treatment of 3 with an excess of *n*-butyllithium in tetrahydrofuran effecting dehydrobromination[7] as shown in Scheme I.

Photooxygenation of 1 (0.4 M) for 1 h in deuteriochloroform at 15 °C with methylene blue (MB) as sensitizer using two 500-W tungsten–halogen lamps led to formation of adamantanone (6) quantitatively as an isolable product. That singlet oxygen is the oxidizing species was shown by the fact that 1 is stable under the reaction conditions in the absence of the sensitizer and light, and 1,4-diazabicyclooctane, a singlet oxygen quencher,[8] inhibited the reaction. Direct ^{1}H (100 MHz) and ^{13}C NMR (100 MHz) and IR analyses of the reaction mixture indicated the presence of α-lactam 7;[9] singlet proton resonances at δ 1.27 (9 H) and 2.65 (2 H), ^{13}C resonance at δ 162.3,[10] and a carbonyl band at 1850 cm^{-1}.[9,11] α-Lactam 7 was not trapped by methanol;[9] however it was successfully converted to the corresponding oxaziridine 8[12] (27% conversion yield) by oxidation with *m*-chloroperbenzoic acid (*m*-CPBA) in the presence of sodium carbonate.[13] Furthermore, ^{1}H and ^{13}C NMR monitoring of the reaction mixture at low temperature (−74 °C) confirmed the presence of a thermally labile product (2), which exhibited ^{13}C resonances at δ 86.8 and 94.3 consistent with the chemical shifts of dioxetane ring carbons.[1a] Warming up to −50 °C resulted in decrease of the dioxetane peaks ($\tau_{1/2} = 20$ min) and increase of the α-lactam signal.

Scheme I





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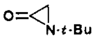

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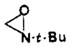

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On flash distillation of a CH_2Cl_2 solution at bath temperature below −40 °C and at 0.01 mmHg, 2 was codistilled with the solvent showing that a monomeric material was on hand, however, extensive decomposition into 6 and 7 occurred during distillation. Isolation of 2 in pure form was not attained in view of its inherent explosive nature, but codistilled 2 rapidly liberated iodine from an aqueous alcohol solution of potassium iodide.

The reaction of 1,2-dioxetanes with triphenylphosphine, affording the corresponding phosphorane derivatives is characteristic of 1,2-dioxetanes.[14] However, 2 did not react

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Table I. Comparison of the Chemical Properties of 1,2-Dioxetanes 2 and 9–12

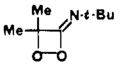
	$k_{20\,°C}$, s^{-1}	E_a, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$^3\Phi/^1\Phi$	CIEEL
2	11.5	18	18	8	66	no
9[a]	6	18	17	3	650	no
10[b]	2×10^{-4}	22	22	0	60	yes
11[c]	3×10^{-7}	28	27	4	120	no
12[d]	5×10^{-2}	17	16	−10		yes[e]

[a] Reference 5a. [b] Reference 29 [c] Reference 30. [d] Reference 31. [e] Intramolecular electron-transfer process.

with triphenylphosphine at all unexpectedly.[15] Although no direct chemiluminescence could be observed in the decomposition of **2**, in the presence of 9,10-dibromoanthracene (DBA) as a fluorescer, moderate chemiluminescence was detected. The experimental and spectroscopic results clearly establish the proposed structure **2** for the singlet oxygenation product of **1**.

The reaction enthalpy, ΔH of **2** to **6** and **7** was estimated by Benson's method[17] as −88 kcal/mol.[18] Thermodynamic parameters[1c] of the decomposition of **2** were determined by following the decrease of peak intensities at δ 86.8 and 94.3:[22] $E_a = 18.3 \pm 2$ kcal/mol; $\log A = 14.7$; $\Delta H^{\ddagger} = 17.9 \pm 2$ kcal/mol; $\Delta S^{\ddagger} = 7.5 \pm 10$ eu. Since the sum of the reaction enthalpy (ΔH) and the activation energy (E_a) for the conversion $\mathbf{2} \rightarrow \mathbf{6} + \mathbf{7}$ was estimated to be ~106 kcal/mol, both singlet ($E_S = 84$ kcal/mol) and triplet ($E_T = 78$ kcal/mol of acetone[5a]) excited states of **6** are energetically accessible from the transition state. A careful product analysis confirmed the formation of *N-tert*-butyl imine (16% yield),[23] supporting the likelihood that electronically excited **7**[24] was also generated from the decomposition of **2** as a minor process. It is well-known that imine is a characteristic compound arising from photochemical decarbonylation of α-lactams.[26] Thermal decomposition of **7** in the reaction mixture did not give *N-tert*-butyl imine appreciably.

In view of the thermal instability and very inefficient chemiluminescence of **2**, it was difficult to estimate quantitatively the yields of singlet and triplet excitation.[27] However, our qualitative observations reveal that the excitation yields are much lower (ca. 100-fold) than those observed for the dioxetanimine **9**. The relative intensities of chemiluminescence in the decomposition of **2** were approximately 1, 1, and 2 for perylene, 9,10-diphenylanthracene, and DBA as fluorescers, respectively. This result ruled out a CIEEL mechanism in the light production from **2** (Table I).[3,5a]



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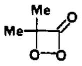

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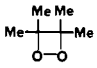

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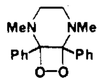

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In summary, **2** was found to be stable at −74 °C, decomposing to **6** and **7**. Although the quantum yields of triplet and singlet, $^3\Phi$, and $^1\Phi$, are very low, the properties of high triplet/singlet ratio[28] and no CIEEL process for decomposition of **2** are similar to those of **9** and **11** rather than to those of **10**. Thermodynamic parameters of the decomposition of **2** resemble those of **9** and **12**, in which a diradical mechanism[5c] and an intramolecular electron-transfer processes from a nitrogen atom to the peroxide σ^* orbital[31] are proposed, respectively. Since the ionization potential of aziridines is much higher than that of amines (e.g., IP (eV) = 9.52 for parent aziridine, 8.36 for dimethylamine, 9.61 for diethyl ether),[32] however, an intramolecular electron-transfer mechanism may not operate in the decomposition of **2**. These observations indicate that the thermal instability of **2** would probably be attributed to the sp^2 character of the spiro carbon of cyclopropane ring and/or its strain effect.

Experimental Section

IR spectra were recorded with a Hitachi 260-50 spectrometer, ^1H NMR spectra with a Varian EM 360A spectrometer, and ^{13}C NMR spectra with a JEOL JNM JX-400 spectrometer (tetramethylsilane as an internal standard). GLC analysis was performed with a Hitachi 164 gas chromatograph with a FID detector. Cyclic voltammograms of substrate **1** were obtained on 0.1 M n-Bu_4NClO_4/CH_3CN solution (vs SCE; scan rate, 200 mV/s; Hokuto Denko Ltd., potentiostat/galvanostat Model HZ-301). The light source was two 500-W tungsten–halogen lamps. Irradiations were carried out in Pyrex tubes in a water bath while oxygen was passed through them.

Reagent grade solvents were used for the experiments in tetrahydrofuran, chloroform, and methylene chloride. Tetrahydrofuran was refluxed over lithium aluminum hydride and distilled before use. Chloroform and methylene chloride were refluxed over calcium chloride and distilled before use. Deuteriated solvents for spectroscopy were used as received. MB (Kanto Chemical) and perylene (Nakarai Chemical) were used as received. 9,10-Dibromo- and 9,10-diphenylanthracene were used after purification by recrystallization. Polymer-bound Rose Bengal (Ⓟ-RB) was prepared by the literature method.[33]

1-Adamantylidene-1-bromo-2-(*tert*-butylamino)ethane (3). Method A.[34] A mixture of 1,1-dibromoadamantylidenecyclo-

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(15) No reaction may be due to steric inhibition of nucleophilic attack on the peroxide oxygen by phosphine, as is the case in that the reaction of thermally stable adamantylideneadamantane dioxetane[16] with triphenylphosphine does not take place at room temperature.

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propane (**4**)[7b] (5.4 g, 16.7 mmol) and *tert*-butylamine (30 mL) was heated under an atmosphere of argon at 135 °C for 7 days in sealed tubes. The cooled mixture was diluted with ether. Removal of the solvent gave an oily residue, which was purified on a silica gel column (benzene/ether) to afford **3** (4.1 g, 78%): IR (neat) 1635 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.55 (s, 2 H), 2.84–3.31 (m, 2 H), 1.36–2.10 (m 13 H), 1.14 (s, 9 H); MS, *m/e* 313, 311.

Method B.[35] 1-Adamantylidene-1-dibromoethane (**5**)[7b] derived from **4** (1.4 g, 4.4 mmol) was slowly added to an etheral solution containing *tert*-butylamine (2.1 g, 29 mmol). The mixture was allowed to stand at room temperature for 24 h with vigorous stirring after addition and then refluxed for 20 h. The precipitated amine hydrobromide was filtered off, and the etheral filtrate was dried (Na$_2$SO$_4$). Removal of the solvent under reduced pressure gave a crude product that was purified on a silica gel column, eluting with chloroform and ether, to afford **3** (0.8 g, 58%).

2-Adamantylidene-*N*-*tert*-butylaziridine (1). To a stirred solution of *tert*-butylamine (4.0 g, 12.9 mmol) in anhydrous tetrahydrofuran (30 mL) under a nitrogen atmosphere, a solution of butyllithium (28.4 mmol) in hexane was slowly added at −78 °C. The temperature was kept below −70 °C. After addition was complete, stirring was continued for 45 min at −78 °C. Upon slow warming to room temperature, stirring was continued for 1 h. The solution was poured onto ice (30 g), and the mixture was extracted with ether (3 × 50 mL). The extract was washed with saturated sodium chloride solution (50 mL), dried with Na$_2$SO$_4$, and evaporated. The residue was purified by bulb-to-bulb distillation (100 °C (10^{-2} mmHg)) to afford **1** (2.5 g, 84%): colorless oil; IR 1795 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.76 (br s, 1 H), 2.57 (br s, 1 H), 1.60–2.10 (m, 14 H), 1.07 (s, 9 H); ^{13}C NMR (CDCl$_3$) δ 117.95 (s), 113.78 (s), 54.37 (s), 39.39 (t), 38.51 (t), 37.40 (t), 35,46 (d), 34.52 (d), 28.59 (d), 27.07 (q), 22.60 (t); MS, *m/e* 231 (M$^+$); exact mass calcd for C$_{16}$H$_{25}$N$_1$ 231.1989, found 231.1993. Oxidation potential (vs SCE) of **1** is 0.91 V.

Photooxygenation of 1. In a typical experiment, **1** (50 mg, 0.22 mmol) was dissolved in deuteriochloroform with MB (0.02 mmol) as sensitizer. After this solution was photooxygenated for 1 h at 15 °C. ^{1}H and ^{13}C NMR spectra of the reaction mixture showed the resonances at δ 1.27 (s), 2.65 (s) and 162.3, respectively, for α-lactam **7** and 1.6–2.2 (m) and 2.58 (br s) for adamantanone. *tert*-Butylimine (16% yield) was analyzed by GLC (4 mm × 3 m glass column, 10% SF-96; column temperature, 40 °C). After separation by silica gel column chromatography eluting with benzene and chloroform, adamantanone was obtained quantitatively as a sole isolable product.

IR analysis of the reaction mixture was carried out as follows. Ⓟ-RB was used as sensitizer. After irradiation of the solution of **1**, Ⓟ-RB was filtered off. The residual solution was analyzed by IR; carbonyl bands for α-lactam **7** at 1850 cm^{-1} and for **6** at 1710 cm^{-1}.

Photooxygenation of **1** in the presence of several additives was also carried out in the same manner.

Low-Temperature NMR Measurement. **1** (135 mg, 0.58 mmol) was dissolved in 0.5 mL of deuteriomethylene chloride with Ⓟ-RB as sensitizer. The photooxygenation was carried out at −78 °C. After irradiation, the reaction mixture was stored at −130 °C (*n*-pentane/liquid N$_2$) as a sample for variable low-temperature NMR measurement. At −74 °C, ^{1}H and ^{13}C NMR spectra of the reaction mixture showed the resonances at δ 1.17 (s) and 86.8 (s), 94.3 (s), respectively for the dioxetane **2**.

Oxidation of 7 with *m*-CPBA in the Presence of Sodium Carbonate. **1** (30 mg, 0.13 mmol) was dissolved in 0.5 mL of deuteriochloroform with MB as sensitizer and the solution was photooxygenated. After confirmation of formation of **7** (28%) by ^{1}H NMR measurement, a methylene chloride solution of *m*-CPBA in the presence of sodium carbonate was added to the photooxygenated solution and left to stand for 1 h at 0 °C.[12] The yield (27%) of oxaziridine **8** compared to an authentic sample was determined by GLC (4 mm × 3 mm glass column, 20%-PEG-20M; column temperature, 50 °C).

Flash Distillation of 2. **1** (200 mg, 0.87 mmol) was dissolved in 0.5 mL of methylene chloride with Ⓟ-RB as sensitizer, and the solution was photooxygenated at −78 °C. Flash distillation of the reaction mixture was carried out at −40 °C by using a vacuum line (10^{-2} mmHg). To the distillate was added aqueous ethanol solution of potassium iodide. Absorption spectra of iodine (λ_{max} = 360 nm) was obtained. ^{13}C NMR measurement of the distillate, however, failed.

Reaction of Dioxetane 2 with Triphenylphosphine. **1** (100 mg, 0.43 mmol) was dissolved in deuteriomethylene chloride with Ⓟ-RB as sensitizer. After this solution was photooxygenated at −78 °C, triphenylphosphine (0.43 mmol) was added to the reaction mixture and kept to stand for 1 h under a nitrogen flow. In ^{13}C and ^{31}P NMR analyses at both −78 and 35 °C, none of the corresponding adduct was detected.

Chemiluminescence Analysis. Chemiluminescence was detected through a quartz window by a photomultiplier (Hamamatsu TV Ind., Model R878) with the chemiluminescence analyzer Model OX-70 (Tohoku Denshi Co., Sendai, Japan). For quantitative chemiluminescence measurement, a sample solution of **2** (7 × 10^{-2} M) was prepared by photooxygenation of **1** in CH$_2$Cl$_2$, using Ⓟ-RB as sensitizer, followed by filtration at −78 °C. To the solution of **2** thus prepared was added an equal volume of the stock solution (7 × 10^{-4} M) of each fluorescer in CH$_2$Cl$_2$, and the chemiluminescence was measured at −40 °C.

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