

The *E*-configuration relative to the C=C bond of compounds **3** was confirmed by the values of vicinal SSC constants in the ^{13}C NMR spectra, for example, for **3a** $^3J_{\text{cis}}^{\text{C(1)O,H(3)}} = 3.7 \text{ Hz} < ^3J_{\text{trans}}^{\text{C(5''),H(3)}} = 10.3 \text{ Hz}$ (cf. to *E*-enamine similar in structure⁴). The downfield shifts of the NH signals in the ^1H NMR spectra prove the presence of a strong intramolecular hydrogen bond. These data and the same set of signals in CDCl_3 and $\text{DMSO}-d_6$ indicate the *Z*-configuration of another C=C bond in compounds **3**.

Diethyl (2*E*,5*Z*)-6-cyano-5-phenyl-2-(1*H*-tetrazol-5-yl)-4-azahepta-2,5-dienoate (**3a**), yield 75%, m.p. 195–198 °C (decomp.). IR (KBr), ν/cm^{-1} : 2210 (CN), 1710, 1690 (C=O). ^1H NMR (400 MHz, $\text{DMSO}-d_6$), δ : 1.09 (t, 3 H, Me); 1.33 (t, 3 H, Me); 4.15 (q, 2 H, CH_2); 4.39 (q, 2 H, CH_2); 7.52 (d, 1 H, 3-H, $^3J_{\text{H(3),NH}} = 12.4 \text{ Hz}$); 7.70–7.60 (m, 5 H, Ph); 13.35 (d, 1 H, NH, $^3J_{\text{NH,H(3)}} = 12.4 \text{ Hz}$). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$), δ : 13.75 (Me); 14.09 (Me); 61.12 (CH_2); 61.71 (CH_2); 84.73 (C(6)); 95.94 (C(2)); 116.15 (CN); 128.84, 129.25, 130.36, 131.42 (Ph); 141.91 (C(3)); 148.5 (C(5'')); 163.66 (C(5)); 163.84 (C(7)); 164.80 (C(1)). High-resolution MS, m/z : M^+ 382.1395, calculated M 382.1389.

Diethyl (2*E*,5*Z*)-5-(4-bromophenyl)-6-cyano-2-(1*H*-tetrazol-5-yl)-2-azahepta-2,5-dienoate (**3b**), yield 77%, m.p. 201–

205 °C (decomp.). IR (KBr), ν/cm^{-1} : 2210 (CN), 1690 br. (C=O). ^1H NMR (200 MHz), δ : in $\text{DMSO}-d_6$: 1.13 (t, 3 H, Me); 1.33 (t, 3 H, Me); 4.20 (q, 2 H, CH_2); 4.40 (q, 2 H, CH_2); 7.48 (d, 1 H, 3-H, $^3J_{\text{H(3),NH}} = 12.4 \text{ Hz}$); 7.62 (d, 2 H, Ph, $J = 8.5 \text{ Hz}$); 7.91 (d, 2 H, Ph, $J = 8.5 \text{ Hz}$); 13.35 (d, 1 H, NH, $^3J_{\text{NH,H(3)}} = 12.4 \text{ Hz}$); 16.08 (br.s, 1 H, $\text{NH}_{\text{tetraz}}$); in CDCl_3 : 1.19 (t, 3 H, Me); 1.39 (t, 3 H, Me); 4.23 (q, 2 H, CH_2); 4.47 (q, 2 H, CH_2); 7.34 (d, 2 H, Ph, $J = 8.5 \text{ Hz}$); 7.67 (d, 1 H, 3-H, $^3J_{\text{H(3),NH}} = 12.0 \text{ Hz}$); 7.75 (d, 2 H, Ph, $J = 8.5 \text{ Hz}$); 13.28 (br.s, 1 H, $\text{NH}_{\text{tetraz}}$); 13.68 (d, 1 H, NH, $^3J_{\text{NH,H(3)}} = 12.0 \text{ Hz}$). High-resolution MS, m/z : M^+ 460.0494, calculated M 460.0495 for $\text{C}_{18}\text{H}_{17}\text{BrN}_6\text{O}_4$.

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Received January 5, 1998;
in revised form March 17, 1998

Chemiluminescence in the reaction of dimethyldioxirane with quaternary ammonium salts

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The reaction of methyl(trifluoromethyl)dioxirane with Bu_4NI (**1**) has been studied previously.¹ It was shown that salt **1** catalyzes the decomposition of dioxirane to give 1,1,1-trifluoroacetone and oxygen. Superoxide-ion is the intermediate of this reaction.

In this work, we have shown for the first time that the reaction of dimethyldioxirane (**2**)² with quaternary ammonium salts $\text{Et}_3(\text{PhCH}_2)\text{NCl}$ (**3**), $\text{Et}_3(\text{PhCH}_2)\text{NBr}$ (**4**), and **1** was accompanied by intense chemiluminescence (CL) in the visible and IR spectral regions. Salts **1**, **3**, and **4** were purified by recrystallization. The reaction was carried out in a temperature-controlled 2 mL-

reactor at 0–33 °C. A 0.02–0.2 *M* solution of a quaternary ammonium salt (0.01–0.1 mmol) in MeCN was placed in the reactor, and a 0.012–0.05 *M* temperature-controlled solution of salt **2** (0.012–0.05 mmol) in an acetone–acetonitrile mixture (1 : 1, v/v). The changes in intensity of chemiluminescence in the visible and IR regions was measured as reported earlier.³ The kinetics of consumption of salt was studied by spectrophotometry.⁴

In the case of salt **3**, the visible CL was of unusual character. Several maxima were observed on the curves of the changes in the CL intensity. The number of

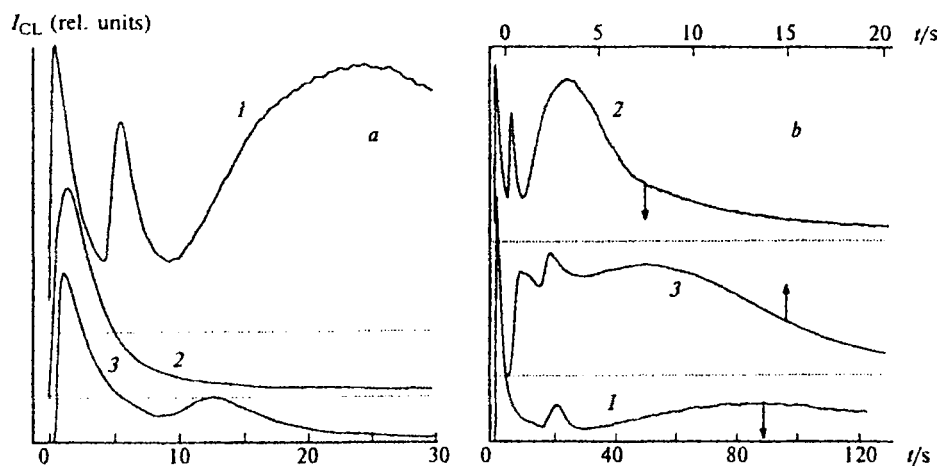


Fig. 1. Intensity versus concentration (a) and temperature (b) dependences of chemiluminescence curves recorded in reaction of dimethyldioxirane with triethylbenzylammonium chloride: a, $T = 14^\circ\text{C}$, $[2] : [3] = 1 : 2$ (1), $1 : 10$ (2); $10 : 1$ (3); b, $[2] : [3] = 1 : 2$, $T = 0^\circ\text{C}$ ($\times 8$ times) (1); 14°C ($\times 2$ times) (2), 33°C (3).

maxima depended on the ratio of the reagent concentrations (Fig. 1, a). An increase in temperature resulted in convergence of the peaks and an increase in CL intensity (see Fig. 1, b). Purging with either oxygen or an inert gas did not significantly affect the shape of the CL curves. The CL spectrum of emission (in the region 400 to 640 nm) determined by boundary light filters, indicated the presence of two maxima at ~ 450 and ~ 550 nm. In addition, a very bright CL was recorded in the IR region 1000 to 1300 nm that quickly attenuated and had two splashes. The attenuation time was satisfactorily consistent with the kinetics of salt consumption at the equimolar ratio of the reagents.

Similarly, CL in the visible and IR regions was found in the reactions of 2 with salts 1 and 4. It is obvious that several luminescence emitters are formed in the reac-

tions studied. Additional investigations are required to identify them.

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Received February 3, 1998