Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron Letters 48 (2007) 491–496
Tetrahedron Letters

Chemiluminescence in anisotropic microenvironment: splitting of chemiluminescence efficiency for charge-transfer-induced decomposition of optically active bicyclic dioxetanes bearing a 2-hydroxy-1,1′-binaphthyl-4-yl moiety under chiral recognition

Masakatsu Matsumoto,* Hidetoshi Maeda, Naoyuki Hoshiya,
Nobuko Watanabe and Hisako K. Ijuin

Department of Chemistry, Kanagawa University, Tsuchiya, Hiratsuka, Kanagawa 259-1293, Japan

Received 10 October 2006; revised 2 November 2006; accepted 2 November 2006
Available online 30 November 2006

Abstract—Four optical isomers of dioxetane **2** bearing a 2-hydroxy-1,1′-binaphthyl-4-yl moiety decomposed with accompanying emission of light on treatment with three base systems. The chemiluminescence efficiencies of all isomers were practically the same for tetrabutylammonium fluoride (TBAF) in DMSO system, whereas they split into two diastereomer-groups for 18-crown-6 ether complex of *t*-BuOK in benzene–THF system. For the base system using *t*-BuOK complex of optically active crown ether, (*Ra*,*Ra*)-**7** or (*Sa*,*Sa*)-**7**, the chemiluminescence efficiencies split further into four. The shape of chemiluminescence spectrum, maximum wavelength, and the rate of decomposition were also different between each of the four stereoisomers.

It has very recently been reported that optically active diaoxetanes **1** bearing a 2-hydroxy-1,1′-binaphthyl-5-yl group display intramolecular charge-transfer-induced chemiluminescence (CTICL)[1–4] in the coordination sphere of an optically active crown ether complex, where the features of coordination based on the chiral recognition were reflected in their spectra of chemiluminescence.[5] In the course of our further investigation of CTICL in optically anisotropic environment, we synthesized four optically active dioxetanes **2** bearing a 2-hydroxy-1,1′-binaphthyl-4-yl group, in the expectation that the dioxetane ring of **2** would be affected sterically much more by the coordination sphere than the case of **1**, since it lies near the oxido anion to be coordinated. Thus, we found that chemiluminescent decomposition of **2** caused an unusual splitting of chemiluminescence efficiency under chiral recognition as well as under diastereomeric recognition, in addition to the spectral change under chiral recognition (Fig. 1).

Four optical isomers of dioxetane **2** were synthesized by the singlet oxygenation of dihydrofurans substituted with an atropisomeric 2-hydroxy-1,1′-binaphthyl-4-yl group, (*Ra*)-**3** and (*Sa*)-**3**, which were prepared through resolution of an optically active (1*S*)-(+)-camphorsulfonate **4**: X-ray single crystallographic analysis of diastereomer (*Sa*,1*S*)-**4** was successfully achieved as illustrated in Figure 2.[6] Thus, (*Ra*)-**3** afforded a diastereomeric mixture of dioxetanes, (*Ra*,1*R*,5*R*)-**2** and (*Ra*,1*S*,5*S*)-**2** while (*Sa*)-**3** gave a mixture of (*Sa*,1*S*,5*S*)-**2** and (*Sa*,1*R*,5*R*)-**2** exclusively. Usual column chromatography on silica gel was successful for the isolation of these isomers to give (*Ra*,1*R*,5*R*)-**2** ($[\alpha]_D^{25}$ −26.1 in 1,4-dioxane), (*Ra*,1*S*,5*S*)-**2** ($[\alpha]_D^{25}$ 139.2 in 1,4-dioxane), (*Sa*,1*S*,5*S*)-**2** ($[\alpha]_D^{25}$ 26.2 in 1,4-dioxane), and (*Sa*,1*R*,5*R*)-**2** ($[\alpha]_D^{25}$ −140.5 in 1,4-dioxane) in 35–50% yields. The structures of these dioxetanes were determined by ^{1}H NMR, ^{13}C NMR, IR, Mass, and HR mass spectral analysis.[7,8] Stereochemistry of these optically active dioxetanes was determined on the basis of X-ray single crystallographic analysis of (*Ra*,1*S*,5*S*)-**2**, the ORTEP view of which is illustrated in Figure 2.[6] The thus-obtained optically active dioxetanes **2** were quite stable thermally in the dark, though they decomposed into optically active keto esters **5** exclusively in hot xylene; both (*Ra*,1*R*,5*R*)-**2** and (*Ra*,1*S*,5*S*)-**2**

Keywords: Dioxetane; Chemiluminescence; Binaphthyl; Crown ether.

* Corresponding author. Tel.: +81 463 59 4111; fax: +81 463 58 9684; e-mail: matsumo-chem@kanagawa-u.ac.jp

0040-4039/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2006.11.049

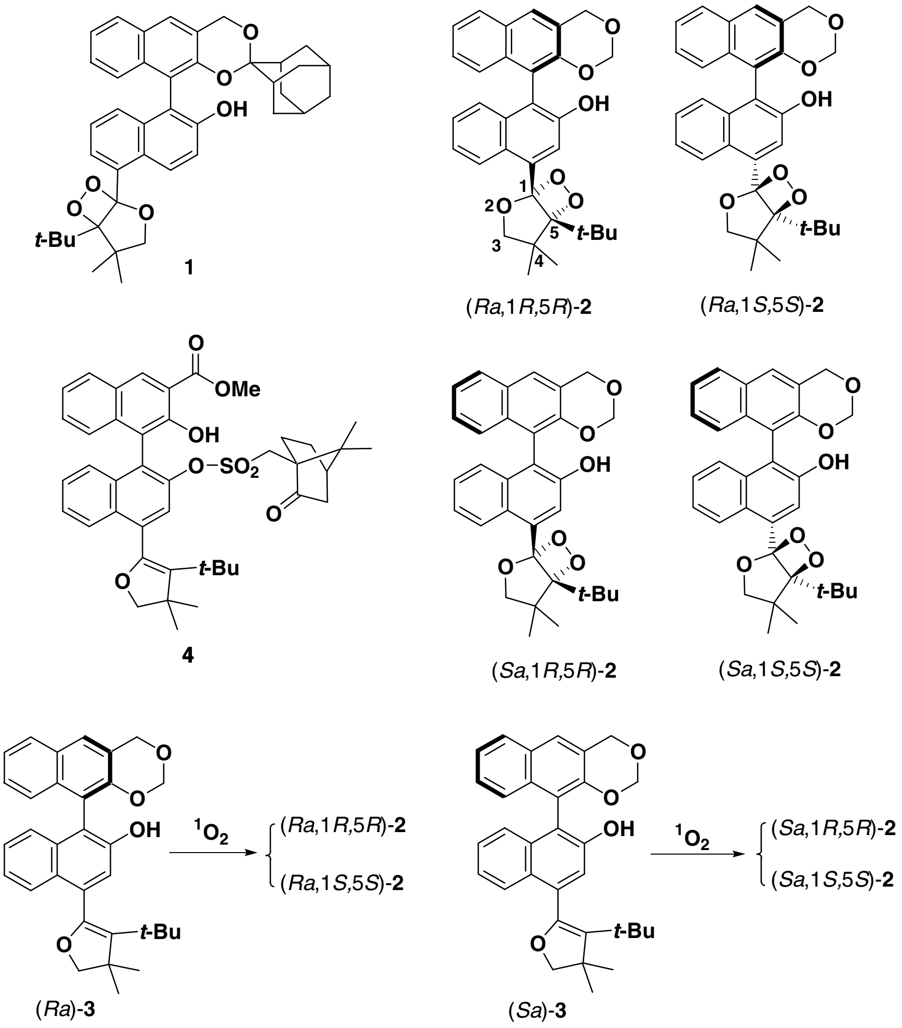

Figure 1.

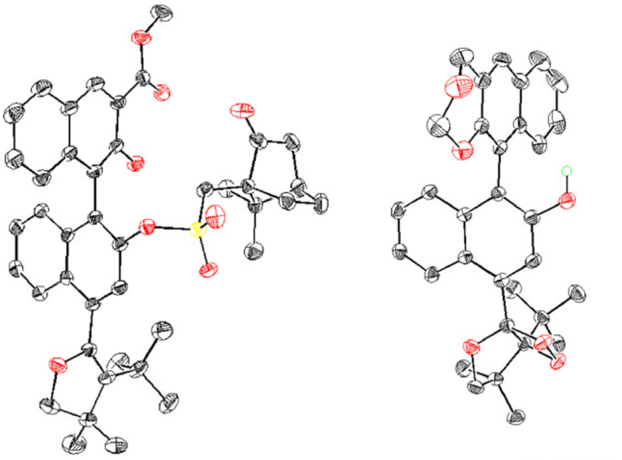
(*Sa*,1*S*)-**4** (*Ra*,1*S*,5*S*)-**2**

Figure 2. ORTEP views of (*Sa*,1*S*)-**4** and (*Ra*,1*S*,5*S*)-**2**.

yielded (*Ra*)-**5**, while both (*Sa*,1*S*,5*S*)-**2** and (*Sa*,1*R*,5*R*)-**2** afforded (*Sa*)-**5** (Scheme 1).

First of all, CTICL decomposition of four optical isomers of dioxetane **2** was examined in a completely homogeneous system. When dioxetane (*Ra*,1*R*,5*R*)-**2** was treated with a large excess of tetrabutylammonium fluoride (TBAF) in DMSO at 25 °C, it decomposed rapidly into a naphthoxide anion of keto ester (*Ra*)-**6** to afford yellow light with maximum wavelength $\lambda_{\max}^{\mathrm{CTICL}} = 525$ nm, chemiluminescence efficiency $\Phi^{\mathrm{CTICL}} = 1.9 \times 10^{-2}$, and CTICL-decomposition rate $k^{\mathrm{CTICL}} = 1.7 \times 10^{-2}\ \mathrm{s}^{-1}$.[9,10] Similar treatment of its enantiomeric dioxetane (*Sa*,1*S*,5*S*)-**2** with TBAF also gave light with the same chemiluminescence properties as those for (*Ra*,1*R*, 5*R*)-**2**. On the other hand, their *meso*-diastereomers, (*Ra*,1*S*,5*S*)-**2** and (*Sa*,1*R*,5*R*)-**2**, also afforded yellow light ($\lambda_{\max}^{\mathrm{CTICL}} = 525$ nm) with Φ^{CTICL}s the same substantially as in the case of *dl*-isomers, though k^{CTICL}s were ca 1/2 of those for *dl*-isomers, (*Ra*,1*R*,5*R*)-**2** and (*Sa*,1*S*,5*S*)-**2**. These results are summarized in Table 1.

Next, we examined CTICL of dioxetanes **2** by the use of 18-crown-6 ether complex with *t*-BuOK, $[\mathrm{K} \subset (18\mathrm{C}6)]^{+}t\text{-BuO}^{-}$, in benzene (PhH)–tetrahydrofuran (THF) (1:1), which provided a sterically anisotropic though not optically active microenvironment on the coordination of **2**. When stereoisomeric dioxetanes **2** were individually treated with a large excess of