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## C–S and C–C Bond Fission in the Thermal Decomposition of a New Dithio-substituted Dioxetane

## Wataru Ando\* and Yoshio Kabe

Department of Chemistry, University of Tsukuba, Sakura-mura, Ibaraki 305, Japan

The dithio-substituted dioxetane, (3), is relatively stable and decomposes to give (5) and (6) by both C–C and C–S bond cleavage.

Sulphur-substituted 1,2-dioxetanes, once believed to be only fleeting intermediates and too unstable to be isolated, have now been prepared by Adam's<sup>1</sup> and Foote's groups.<sup>2</sup> These dioxetanes, (1) and (2), are thermally labile and are derived *via* singlet oxygenation of corresponding 1-alkylthio- and 1,1-bis(alkylthio)-ethylenes. They give only normal C–C bond

cleavage products, though the decomposition of many postulated sulphur-substituted 1,2-dioxetanes is accompanied by the formation of C–S bond cleavage products.<sup>3</sup> After the repeated failure to detect the 1,2-dioxetanes of 1,2bis(alkylthio)ethylenes, which are expected to decompose by both C–C and C–S bond cleavage, we found that the





1,2-dioxetane (3) has a lifelong time in solution and so we could characterize its structure and unique decomposition.

The 1,2-bis(alkylthio)ethylene (4) (m.p. 72-73.5 °C) was synthesized by Krebs' method.<sup>4</sup> The photo-oxygenation at -78 °C of (4) (ca. 0.1 mmol) in CD<sub>2</sub>Cl<sub>2</sub> (ca. 0.5 ml) with polymer-bound Rose Bengal as a sensitizer using a 500 W xenon lamp was monitored by <sup>1</sup>H and <sup>13</sup>C n.m.r. spectroscopy. The irradiation was continued until all the starting material had been consumed as indicated by the disappearance of two characteristic singlet resonances {(4)  $\delta$  6.15 [1H,  $O-CH(-S)_2$ ], 3.25 (3H, OMe)}. The <sup>1</sup>H n.m.r. spectrum of the resulting solution showed no change between -78 and -30 °C; at the higher temperature new low-field singlets at  $\delta$  6.85 and 3.59 were observed. Similar behaviour was observed in the  ${}^{13}Cn.m.r.$  spectrum: the doublet  $[O-CH(-S)_2]$ and quartet (OMe) resonances of (4) were shifted from  $\delta$ 82.9 and 49.5 to 90.0 and 57.9. A more definitive aspect of the <sup>13</sup>C n.m.r. spectrum was that the olefinic carbon resonance of (4) at  $\delta$  133.8 gave way to new upper-field singlet resonance at  $\delta$  124.3, characteristic of the dioxetanyl ring carbon. On warming the solution to room temperature, this spectrum was gradually replaced by a completely different one; the half life was about 45 min. This spectroscopic evidence strongly suggests the 1,2-dioxetane (3), as an unstable intermediate.

In order to assign the <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra of the decomposition products, the photo-oxygenation of (4) (*ca.* 1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (*ca.* 20 ml) with polymer-bound Rose Bengal using a 300 W halogen lamp was carried out at -50 °C for 24 h. The reaction mixture could be separated by column chromatography over silica gel-benzene into two products, (5) (78%) and (6) (17%), the latter is the C-S bond cleavage product of (3). The structures of these products<sup>†</sup> were determined on the basis of i.r., <sup>1</sup>H and <sup>13</sup>C n.m.r., and mass spectra. The <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra of the decomposition products of (3) were completely consistent with the overlapping spectra of (5) and (6), in which the carbonyl resonances of (5) and (6) appeared at  $\delta$  203.4 and 215.1 respectively.

Finally, after the photo-oxygenation was carried out under similar conditions, the suspended polymer-bound Rose Bengal was removed by filtration at ca. -70 °C and the filtrate submitted to chemiluminescence experiments. When samples of the dioxetane (3) were decomposed by rapid warming to room temperature in the dark without any fluorescence or with 9,10-dibromoanthracene, no luminescence was observed. However when a small amount of 9,10-diphenylanthracene was added, stronger luminescence than that obtained with (1) and (2) was observed. This behaviour might indicate that the role of the CIEEL path in the light production of (3) is important.<sup>5</sup>

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<sup>+</sup> Spectroscopic data: Compound (5) (colourless oil) <sup>1</sup>H n.m.r. (CCl<sub>4</sub>, 60 MHz) δ 1.15 (12H, s, CMe<sub>2</sub>), 1.55 (6H, br. s, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 3.55 (3H, s, OMe), 6.55 [1H, s, O-CH(-S)<sub>2</sub>]; <sup>13</sup>C n.m.r. (CDCl<sub>3</sub>, 100 MHz) δ 203.4 (s, C=O), 90.9 [d, O-CH(-S)<sub>2</sub>] 58.2 (q, OMe), 51.4 (s, CMe<sub>2</sub>), 42.7 (t, CH<sub>2</sub>CMe<sub>2</sub>), 23.8 (q, CMe<sub>2</sub>), 22.7 (q, CMe<sub>2</sub>), 17.3 (t, C-CH<sub>2</sub>-C); i.r. (CCl<sub>4</sub>) v 1670 cm<sup>-1</sup>; mass spectrum *m*/z 290 (*M*<sup>+</sup>). Compound (6) (colourless oil) <sup>1</sup>H n.m.r. (CCl<sub>4</sub>, 60 MHz) δ 1.12 (12H, s, CMe<sub>2</sub>), 1.70 (6H, s, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); <sup>13</sup>C n.m.r. (CDCl<sub>3</sub>, 100 MHz) δ 215.1 (s, C=O), 43.5 (s, CMe<sub>2</sub>), 36.8 (t, CH<sub>2</sub>CMe<sub>2</sub>), 24.0 (q, CMe<sub>2</sub>), 19.9 (t, C-CH<sub>2</sub>-C); i.r. (CCl<sub>4</sub>) v 1700 cm<sup>-1</sup>; mass spectrum *m*/z 186 (*M*<sup>+</sup>).