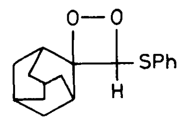
C–S and C–C Bond Fission in the Thermal Decomposition of a New Dithio-substituted Dioxetane

Wataru Ando* and Yoshio Kabe

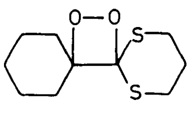
Department of Chemistry, University of Tsukuba, Sakura-mura, Ibaraki 305, Japan

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

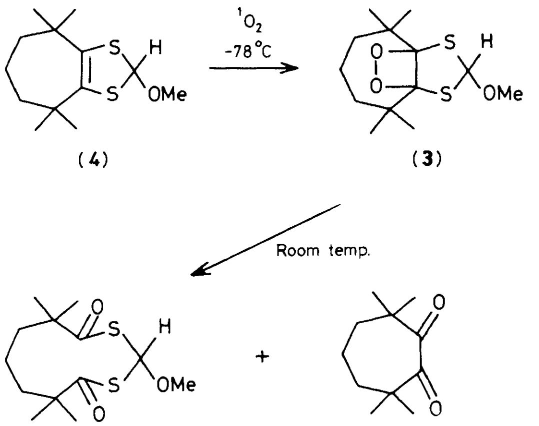
Sulphur-substituted 1,2-dioxetanes, once believed to be only fleeting intermediates and too unstable to be isolated, have now been prepared by Adam's[1] and Foote's groups.[2] These dioxetanes, (**1**) and (**2**), are thermally labile and are derived *via* singlet oxygenation of corresponding 1-alkylthio- 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.[3] After the repeated failure to detect the 1,2-dioxetanes of 1,2-bis(alkylthio)ethylenes, which are expected to decompose by both C–C and C–S bond cleavage, we found that the



(1)



(2)



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.[4] The photo-oxygenation at −78 °C of (**4**) (*ca.* 0.1 mmol) in CD_2Cl_2 (*ca.* 0.5 ml) with polymer-bound Rose Bengal as a sensitizer using a 500 W xenon lamp was monitored by ^1H and ^{13}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**) δ 6.15 [1H, O–CH(–S)$_2$], 3.25 (3H, OMe)}. The ^1H 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 δ 6.85 and 3.59 were observed. Similar behaviour was observed in the ^{13}C n.m.r. spectrum: the doublet [O–CH(–S)$_2$] and quartet (OMe) resonances of (**4**) were shifted from δ 82.9 and 49.5 to 90.0 and 57.9. A more definitive aspect of the ^{13}C n.m.r. spectrum was that the olefinic carbon resonance of (**4**) at δ 133.8 gave way to new upper-field singlet resonance at δ 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 ^1H and ^{13}C n.m.r. spectra of the decomposition products, the photo-oxygenation of (**4**) (*ca.* 1 mmol) in CH_2Cl_2 (*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† were determined on the basis of i.r., ^1H and ^{13}C n.m.r., and mass spectra. The ^1H and ^{13}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 δ 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.[5]

Received, 1st March 1984; Com. 275

References

1 W. Adam, L. A. Arias, and D. Sheutzer, *Tetrahedron Lett.*, 1982, **23**, 2835.
2 G. G. Geller, C. S. Foote, and D. B. Pechman, *Tetrahedron Lett.*, 1983, **24**, 673.
3 W. Ando, *Sulfur Reports*, 1978, **3**, 143; W. Ando and T. Takata, 'Singlet Oxygen,' ed. A. A. Frimer, 1984, vol. 3, ch. 1, CRC Press, in the press and references cited therein.
4 A. Krebs and H. Kimling, *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 509; *Liebigs Ann. Chem.*, 1974, 2074.
5 G. B. Schuster, *Acc. Chem. Res.*, 1979, **12**, 366.

---

† *Spectroscopic data:* Compound (**5**) (colourless oil) ^1H n.m.r. (CCl_4, 60 MHz) δ 1.15 (12H, s, CMe_2), 1.55 (6H, br. s, $CH_2CH_2CH_2$), 3.55 (3H, s, OMe), 6.55 [1H, s, O–CH(–S)$_2$]; ^{13}C n.m.r. ($CDCl_3$, 100 MHz) δ 203.4 (s, C=O), 90.9 [d, O–CH(–S)$_2$] 58.2 (q, OMe), 51.4 (s, CMe_2), 42.7 (t, CH_2CMe_2), 23.8 (q, CMe_2), 22.7 (q, CMe_2), 17.3 (t, C–CH_2–C); i.r. (CCl_4) ν 1670 cm^{-1}; mass spectrum *m/z* 290 (M^+). Compound (**6**) (colourless oil) ^1H n.m.r. (CCl_4, 60 MHz) δ 1.12 (12H, s, CMe_2), 1.70 (6H, s, $CH_2CH_2CH_2$); ^{13}C n.m.r. ($CDCl_3$, 100 MHz) δ 215.1 (s, C=O), 43.5 (s, CMe_2), 36.8 (t, CH_2CMe_2), 24.0 (q, CMe_2), 19.9 (t, C–CH_2–C); i.r. (CCl_4) ν 1700 cm^{-1}; mass spectrum *m/z* 186 (M^+).