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Photolytic, autocatalyzed decomposition of benzylic dialkoxy disulfides

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ABSTRACT

The dialkoxy disulfide moiety has been shown to go through an intramolecular fragmentation to liberate trappable S_2, and can yield an alkoxy radical under photolytic conditions. We have examined a family of benzylic dialkoxy disulfides ($X–Ph–CH_2–O–S–S–O–CH_2–Ph–X$) under photolytic conditions and observed a correlation of decomposition based upon the substituent. We have been able to show that the decomposition is autocatalyzed and has a parabolic correlation with Swain and Lupton's field constant, $\mathscr{F}$.

Since the initial synthesis of the dialkoxy disulfides in 1895[1], little has been done on this functionality until recently.[2–11] In fact, it was not until 1997 when the actual linear arrangement, –OSSO–, was unambiguously confirmed.[3] Harpp and co-workers have reported the isomeric form, thionosulfite (–OS(=S)O–), however only in cyclic structures.[4] Structural aspects of dialkoxy disulfides that are unusual are its short S–S bond (ca. 1.95 Å)[5] coupled with its greatly enhanced barrier of rotation of ca. 18 kcal/mol.[6] The novelty of this functionality has been illustrated both thermolytically and photolytically. When benzylic[7] or cubylcarbinolic[8] dialkoxy disulfides were heated in the presence of dienes, a pseudo-Diels–Alder reaction was observed yielding cyclic di- and tetra-sulfides; presumably from the liberation of S_2 (Fig. 1). Under photolytic conditions, Lunazzi and Placucci reported that the alkoxy radical was produced which reacted with fullerenes.[9] In addition, it was reported that bis-cubylmethyl-dialkoxy disulfide was converted to bis-cubylmethyl sulfite by ambient light while open to the air.[8] Very recently, dialkoxy disulfides have been incorporated into polymers as a new high energy-storage material.[10] Due to the novelty of this group, we report here the photolytic fragmentation of *para*-substituted benzylic dialkoxy disulfides and examine the effect of electron-withdrawing and electron-donating groups of this functionality.

We initially synthesized seven bis(phenylmethoxy) disulfides with various electronegative groups in the para position based upon past procedures.[11] All were obtained in good to excellent yields, {**1**: bis(benzyloxy) disulfide, BBD; **2**: bis(*p*-methylbenzyloxy) disulfide, BMBD; **3**: bis(*p*-methoxybenzyloxy) disulfide, BMxBD; **4**: bis(*p*-nitrobenzyloxy) disulfide, BNBD; **5**: bis(*p*-chlorobenzyloxy) disulfide, BCBD; **6**: bis(*p*-*t*-butylbenzyloxy) disulfide, BtBBD; **7**: bis(*p*-phenylbenzyloxy) disulfide, BPBD}, with BPBD (**7**) being newly synthesized (Scheme 1).[12] All were successfully purified via column chromatography and stored in the freezer in the dark until use.

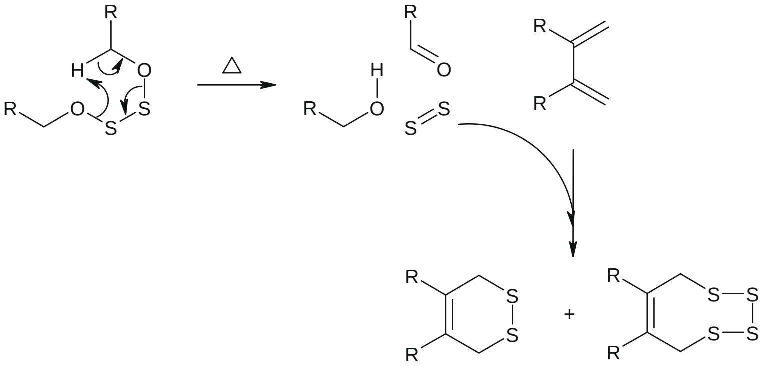

Figure 1. Intramolecular fragmentation and pseudo-Diels–Alder reaction of dialkoxy disulfides.

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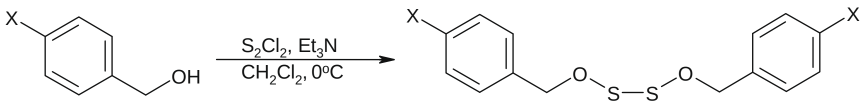


X =	
H,	**1**: BBD
Me,	**2**: BMBD
MeO,	**3**: BMxBD
NO_2,	**4**: BNBD
Cl,	**5**: BCBD
t-Bu,	**6**: BtBBD
Ph,	**7**: BPBD

Scheme 1. Synthesis of library of dialkoxy disulfides.

Each dialkoxy disulfide was dissolved in toluene (0.1 g/10 mL), wrapped in aluminum foil (to prevent light from entering) and argon was bubbled through for 30 min. After this time, a sample was removed and concentrated in vacuo and a ^{1}H NMR performed. This was classified as our starting point.[13] The mixture was then placed in a Srinivasan–Griffin–Rayonet Photochemical Reactor, the wrap was removed, then continually irradiated (350 nm) and maintained at 35 °C while still under an argon atmosphere. At various time intervals, 0.5 ml of the mixture was removed, and ^{1}H NMR was performed. All seven dialkoxy disulfides eventually completely converted to the corresponding alcohol, however, at different rates and all were autocatalyzed. Figure 2 illustrates the photolytic decomposition of both BBD (**1**) and BMxBD (**3**). It is clear that there is an initial lag, presumably due to the stability of the dialkoxy disulfide. However, as time proceeds there is a drastic loss of the dialkoxy disulfide. Lunazzi and Placucci postulated that under photolytic conditions, initially a homolytic cleavage occurs between the disulfide bond and the subsequent R–O–S$^{\cdot}$ would rapidly convert to the alkoxy radical at temperatures above −100 °C.[9] As this in a non-linear rate (hence non-zero order decomposition), the curve suggests that this process is in some way autocatalyzed.[14] Based upon the fact that in all cases a small amount of aldehyde was formed along with quantitative amounts of elemental sulfur, two possible competing mechanisms are proposed here.

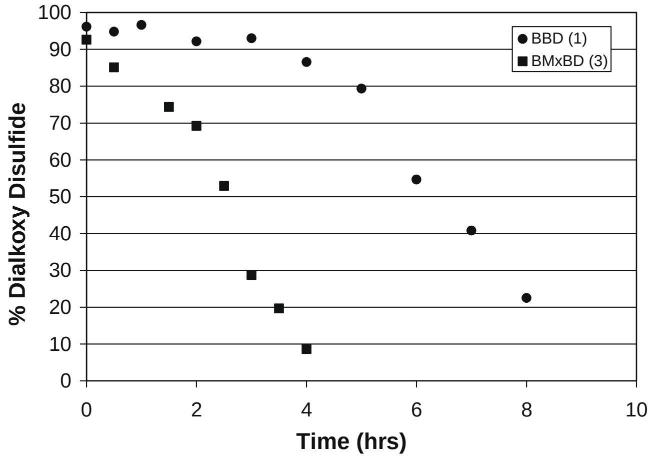
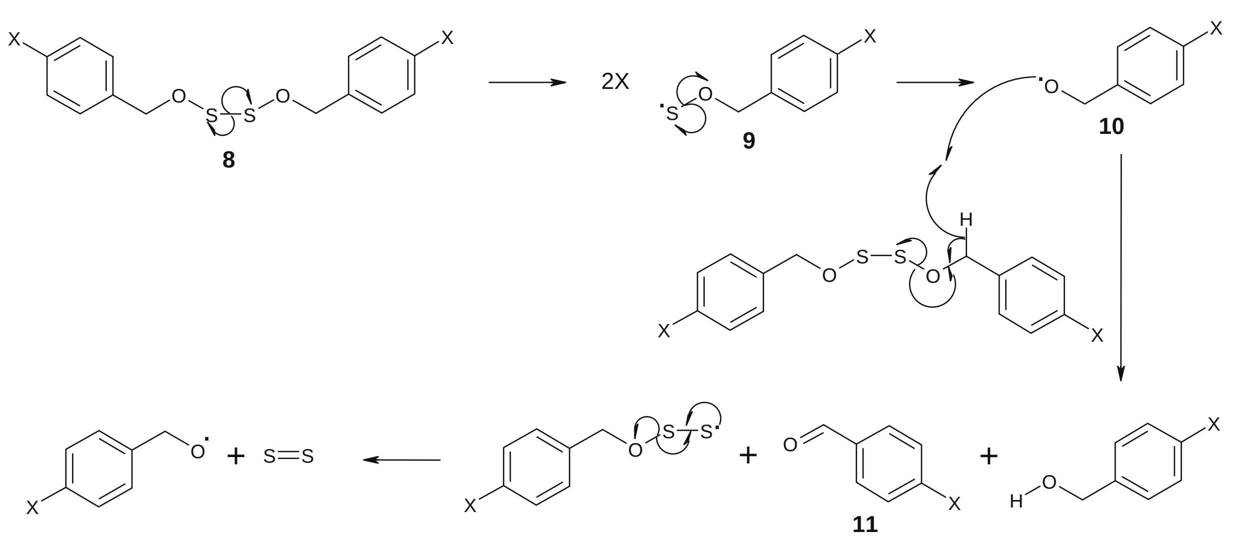


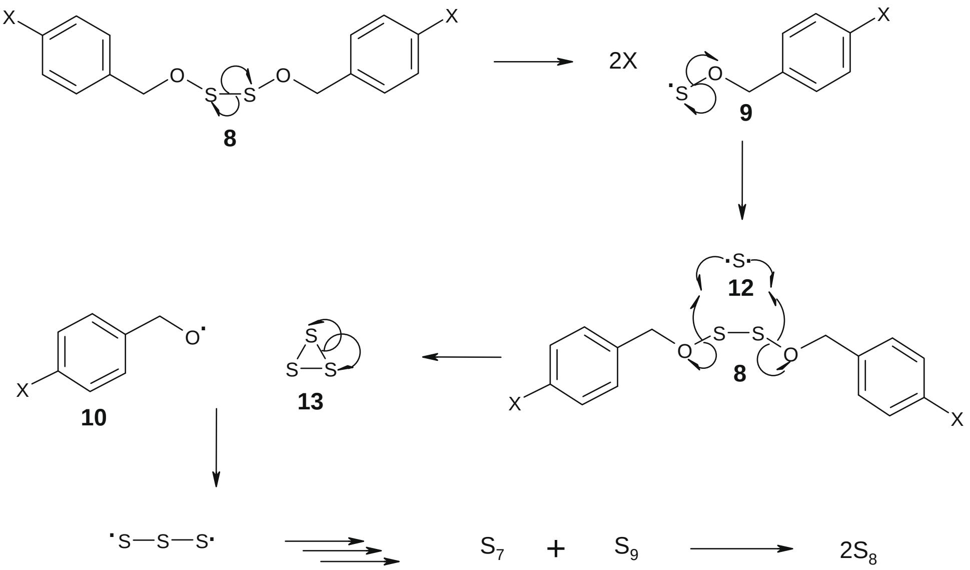
Figure 2. Photolytic decomposition of BBD (**1**) and BMxBD (**3**).

One possible mechanism (Scheme 2) involves the initial homolytic cleavage of the dialkoxy disulfide (**8**) providing **9** which would further cleave to form an alkoxy radical, **10,** as the temperature at which the experiments are done is at 35 °C.[9] This reactive intermediate could abstract a benzylic proton from another starting dialkoxy disulfide, **8**, forming the aldehyde, **11**, and ultimately S_2 and another alkoxy radical. This pathway is reasonable; however, it would indicate that a 1:1 ratio should form between alcohol and aldehyde. As at most there was a 9:1 ratio of alcohol to aldehyde an alternate autocatalyzed pathway is also proposed.

In addition to the alkoxy radical (**10**) that would be formed initially, reactive sulfur (**12**) will also be produced. It is theorized (Scheme 3) that this species could interact with another dialkoxy disulfide (**8**) forming two more alkoxy radicals and S_3 (**13**). This allotrope of sulfur would continue to react until S_8 is formed. Although, both mechanisms are reasonable and possibly compet-



Scheme 2. Possible mechanism I for the photolytic, autocatalyzed decomposition of dialkoxy disulfides.



Scheme 3. Possible mechanism II for the photolytic, autocatalyzed decomposition of dialkoxy disulfides.

ing, the large excess of alcohol formed compared to that of aldehyde suggests that the mechanism II is the predominant pathway.

To compare the rates of autocatalyzed reactions, they are reported as the time to ½ life of the starting dialkoxy disulfides. It is believed that at this time, the rate would be at a maximum that Figure 2 visually illustrates. Table 1 lists the rates for each of the dialkoxy disulfides tested.

It can be seen that there is a great difference in rate based upon which substituent is present. The shortest ½ life for photolytic decay was compound **3** at 2.6 h, whereas the lengthiest was **4**, requiring 28.3 h. This almost 1000% difference in rate based upon substituent present, led us to initially examine Hammett's constant.[15] It was not too surprising there were no direct correlations with σ-values, as there is no conjugation of the substituent and the dialkoxy disulfide. However, we discovered that there was a parabolic correlation with Swain and Lupton's field constant, $\mathscr{F}$.[16] The parabolic relationship gave a curve with an equation of $t_{1/2} = 59.5\mathscr{F}^2 - 49.9\mathscr{F} + 11.1$ with a R^2 value = 0.868. By examining the slope of the curve versus the $\mathscr{F}$-value, we do obtain a linear correlation of $dt_{1/2}/d\mathscr{F} = 119\mathscr{F} - 49.9$. What this suggests is that at high and low field constants the rate of decomposition is slowed. With the methoxy substituent having the fastest rate of decomposition, it is proposed that the strong electron-donating potential of this group possibly stabilizes the radical intermediate through space and bond transmissions. As the electron-donating potential decreases, the stability of the radical intermediate is hindered, thus a slower rate (i.e., **4**, BNBD). In addition, with the *tert*-butyl substituent (**6**, BtBBD), the electron density of this group is remote from the ring, destabilizing any possible radical intermediate. It has been reported that formation of $X–C_6H_4–CH_2^{\cdot}$ has no correlation to Swain and Lupton's resonance constant, $\mathscr{R}$.[16] In addition, studies have shown that substituent effects have been related almost solely to the field constant, $\mathscr{F}$[17,18] (Fig. 3).

Table 1
Half-life for library of dialkoxy disulfides.

Compound #	Substituent	½ life (h)
1	–H	6.3
2	–Me	11.5
3	–OMe	2.6
4	$-NO_2$	28.3
5	–Cl	6.5
6	–*t*-Butyl	23.6
7	–Ph	3.5

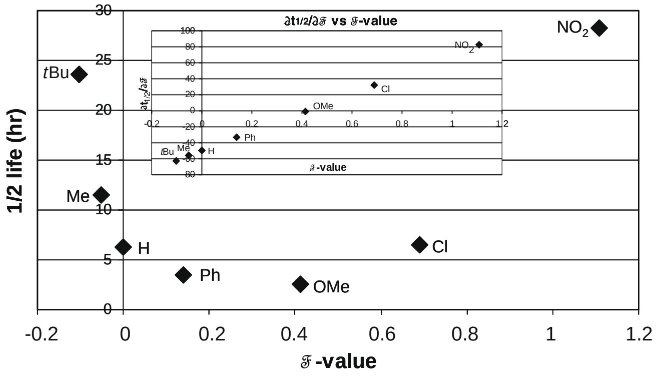


Figure 3. Half-life of photolytic decomposition of the library of dialkoxy disulfides versus Swain and Lupton's field constant, $\mathscr{F}$.

The novelty of dialkoxy disulfides has been illustrated by its thermolytic and photolytic behavior. This moiety can serve as an S_2 as well as an alkoxy donor, respectively. We have examined the photolytic decay of a range of para-substituted bis(benzyloxy) disulfides each of which decomposes at different rates but all autocatalytically. In addition, their rate of decomposition is parabolically correlated to Swain and Lupton's field constant, $\mathscr{F}$. Examination of the currently unknown *ortho*- and *meta*-substituted derivatives of dialkoxy disulfides may provide additional information concerning this pathway.

Acknowledgment

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References and notes

1. Lengfeld, F. *Chem. Ber.* **1895**, *28*, 449.
2. (a) Tardif, S. L.; Harpp, D. N. *J. Org. Chem.* **2000**, *65*, 4791; (b) Cerioni, G.; Plumitallo, A. *Magn. Reson. Chem.* **1998**, *36*, 461; (c) Snyder, J. P.; Nevins, N.; Tardiff, S.; Harpp, D. N. *J. Am. Chem. Soc.* **1997**, *119*, 12685.
3. Lunazzi, L.; Mazzanti, A.; Spagnolo, P.; Degl'Innocenti, A. *J. Org. Chem.* **1997**, *62*, 2263.

4. Zysman-Colman, E.; Abrams, C. B.; Harpp, D. N. *J. Org. Chem.* **2003**, *68*, 7059.
5. Koritsanszky, T.; Buschmann, J.; Luger, P.; Schmidt, H.; Steudel, R. *J. Phys. Chem.* **1994**, *98*, 5416.
6. Borghi, R.; Lunazzi, L.; Placucci, G.; Cerioni, G.; Foresti, E.; Plumitallo, A. *J. Org. Chem.* **1997**, *62*, 4924.
7. Tardif, S. L.; Williams, C. R.; Harpp, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 9067.
8. Priefer, R.; Farrell, P. G.; Harpp, D. N. *Tetrahedron Lett.* **2002**, *43*, 8781.
9. Borghi, R.; Lunazzi, L.; Placucci, G.; Cerioni, G.; Plumitallo, A. *J. Org. Chem.* **1996**, *61*, 3327.
10. Su, Y.-Z.; Dong, W.; Zhang, J.-H.; Song, J.-H.; Zhang, Y.-H.; Gong, K.-C. *Polymer* **2007**, *48*, 165.
11. Zysman-Colman, E.; Harpp, D. N. *J. Org. Chem.* **2005**, *70*, 5964.
12. *Typical experimental procedure:* To a stirred solution of 4-phenylbenzyl alcohol (2.00 g, 0.0109 mol) in CH_2Cl_2 (40 mL) was added Et_3N (1.52 mL, 0.0109 mol) at 0 °C followed by cannulation of a solution of S_2Cl_2 (0.44 mL, 0.0054 mol) in CH_2Cl_2 (20 mL) over 5 min. After stirring at 0 °C for 2 h, the reaction was quenched with water, and the organic layer was separated. The aqueous phase was extracted with CH_2Cl_2 (2 × 10 mL), and the combined organic was washed with dH_2O, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by silica-gel column chromatography with EtOAc/hexanes (10:1) to furnish the pure BPBD, (**7**: 1.98 g, 84.7%) as an off-white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 4.87, 4.98 (ABq, J = 10.8 Hz, 4H), 7.36–7.38 (m, 2H), 7.43 (d, J = 8.0 Hz, 8H), 7.59 (d, J = 7.2 Hz, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 76.5, 127.1, 127.3, 127.5, 128.8, 129.2, 135.5, 140.6, 141.4. Exact mass calculated for $C_{26}H_{22}O_2S_2$ 430.1056, found 430.10611.
13. Due to the thermo instability of some of the dialkoxy disulfides, the typical starting amounts ranged from 92% to 100%.
14. Galajda, M.; Lente, G.; Fabian, I. *J. Am. Chem. Soc.* **2007**, *129*, 7738.
15. McDaniel, D. S.; Brown, H. C. *J. Org. Chem.* **1958**, *23*, 420.
16. Swain, C. G.; Lupton, E. C., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 4328.
17. Nakayama, C.; Wataya, Y.; Meyer, R. B., Jr.; Santi, D. V. *J. Med. Chem.* **1980**, *23*, 962.
18. Chakraborty, K.; Devakumar, C. *J. Agric. Food Chem.* **2006**, *54*, 1868.