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REACTION OF DIBENZOTHIOPHENE SULFONE WITH ALKOXIDES

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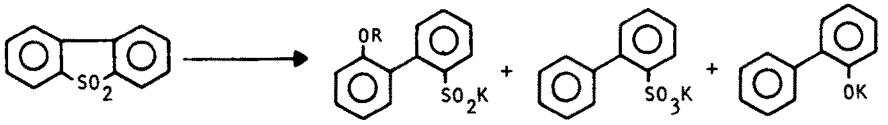
SUMMARY: Cleavage of the C-S bond of dibenzothiophene 5,5-dioxide (**1**) by alkoxide ions proceeds predominantly with carbon-oxygen bond formation, in contrast to the observation of predominant sulfur-oxygen bond formation in the reaction of **1** with hydroxide. The esr spectrum of the radical anion of **1** has been observed in the reacting system.

We recently reported that the reaction of dibenzothiophene 5,5-dioxide, **1**, with KOH yields 20-30% of 2-(2'-hydroxyphenyl)benzenesulfinic acid, **2a**, as well as 2-benzenesulfonic acid, **3**, and 2-phenylphenol, **4**.[1] Previous workers report **3** as the only sulfur-containing product[2,3].



(1)

1

2a, R = K
2b, R = CH_3
2c, R = $(CH_3)_3C$

3

4

In an attempt to delineate the generality of the competition between pathways leading to products such as **2** and **3**, we have studied reactions of **1** with other strong bases and report the results for alkoxides here.

In contrast to the reaction of **1** with hydroxide in which **3** predominates, reaction of **1** with alkoxides affords 2'-substituted 2-phenylbenzenesulfinic acid derivatives **2** as the main products: the 2'-methoxy derivative **2b** from methoxide or the dianion of 2-(2'-hydroxyphenyl)benzenesulfinic acid, **2a**, from t-butoxide (see Table 1). The detection of small amounts of **2c** in the t-butoxide reaction and the known propensity of t-butyl aryl ethers to undergo elimination reactions in the presence of strong base[4], suggests that alkyl aryl ethers **2b** or **2c** are the initial products of the reaction. Two mechanisms for conversion of **1** into **2** come immediately to mind: (1) an elimination-addition (aryne) pathway, equation 2, and (2) an addition-elimination (S_NAr) pathway, equation 3.

TABLE 1. Yield of **2** from Reaction of **1** with Alkoxides, RO^{-a}

Run #	R	Solvent	T, °C	t, hr.	Yield of 2
1	CH_3	m-xylene 18-crown-6	134°	.5	**2b**, 80%
2	CH_3	diglyme	165°	.3	**2b**, 83%
3	CH_3	diglyme	150°	.5	**2b**, 73%[b]
4	t-Bu	mesitylene 18-crown-6	160°	.5	**2a**, 46%[c]
5	t-Bu	diglyme	165°	.5	**2a**, 63%[c]
6	t-Bu	HMPA	155°	24.	**2a**, 70%

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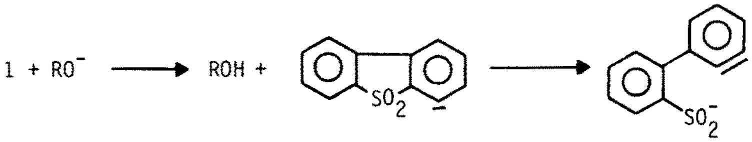
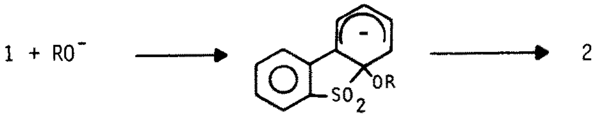
[a] Product yields determined by treating the reaction mixture with CH_3I overnight and analyzing for methyl 2-(2-methoxyphenyl)phenyl sulfone by gas chromatography.

[b] Product yield determined by treating the reaction mixture with CH_3CH_2I overnight and analyzing for ethyl 2-(2-methoxyphenyl)phenyl sulfone by gas chromatrography.

[c] A small amount (less than 2%) of methyl 2-(2-t-butoxyphenyl)phenyl sulfone, derived from **2b**, was detected by gas chromatography.

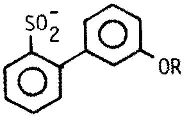


(2)



(3)

The stability of 4-lithiodibenzothiophene-5,5-dioxide[5] and the absence of any aryne involvement in reactions of KOH[6] and sodium piperidide[7] with diphenyl sulfone argue against the aryne mechanism. In addition, if the aryne were generated, it would react with either alkoxide or sulfinate. Attack of alkoxide on the aryne should give, in addition to ortho products **2**, cine-substitution products **5**. However, no meta products were detected. Alternatively, intra-molecular attac by an oxygen atom of the sulfinate anion would lead to sultine **6** which, in the presence of alkoxide should afford **7a-c**. Therefore, demonstration that methyl ether **2b** is the product of reaction of **1** with methoxide and that meta product **5** and sulfinate ester **7b** are absent rules out the aryne mechanism.



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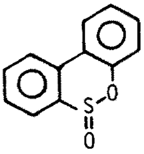

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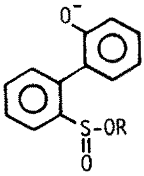

7a, R = K
7b, R = CH_3
7c, R = $(CH_3)_3C$

Ruling out the involvement of arynes has often been considered tantamount to establishing an S_nAr mechanism. However, the recent demonstration of radical and radical ion mechanisms for many reactions traditionally thought to involve purely ionic mechanisms[8,9] and the fact that t-butoxide reacts readily with **1** even though nucleophilic attack at the carbon end of the C-S bond would be sterically and electronically hindered[15], prompted us to look further.

Radical anion **8** is apparently generated under the reaction conditions. Evidence for the presence of **8** during these reactions has been obtained by electron spin resonance with UV-visible spectroscopy. A sealed 5-mm tube containing dibenzothiophene 5,5-dioxide, potassium *t*-butoxide and 18-crown-6 in mesitylene slowly developed a deep purple color. This solution gave an esr signal identical to that reported by Gerdil & Lucken[16] for **8** (see Figure 1). In addition, the ultraviolet-visible spectrum of the deeply violet colored solution showed the presence of a species with a broad absorption maximum centered at 546 nm, and another maximum at 414 nm on the side of the solvent (mesitylene) end absorption. These compare to the band positions of 550 and 425 nm observed by Ito and Matsuda[17] for **8** in a 2-methyltetrahydrofuran glass.

While a number of mechanisms involving **8** can be postulated (see Scheme 1 for one example), all invoke unprecedented reaction pathways for which we have no irrefutable experimental evidence. Of course, it is possible that **8**, though present, is not on the product-yielding reaction coordinate. Therefore, a definitive conclusion that the reaction of **1** with alkoxides proceeds through radical-anions instead of the classic S_NAr mechanism cannot be drawn without additional experimentation. Nevertheless, the observation that the products of the reaction are bifunctional biphenyls such as **2** rather than the expected monofunctional derivatives related to **3**, is novel, has intriguing mechanistic implications, and may be of synthetic utility.

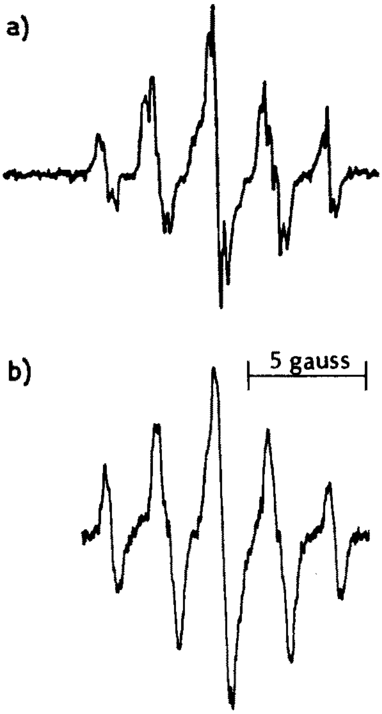

FIGURE 1
ESR SPECTRA OF **8**.
a) **1** + K in DME, Ref. 16
b) **1** + KO*t*-Bu, this work

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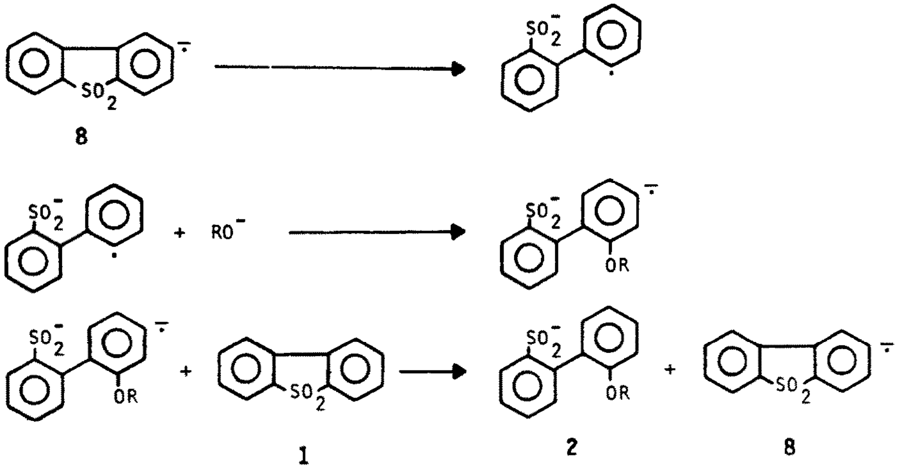

SCHEME 1. POSSIBLE PROPAGATION SEQUENCE FOR A RADICAL CHAIN MECHANISM[18].

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