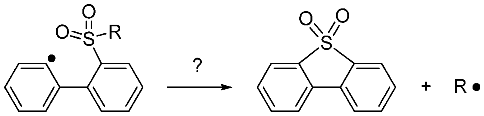
Is There a Homolytic Substitution Chemistry (S_H2) of Sulfones?

David Crich,* Thomas K. Hutton, and Krishnakumar Ranganathan

Department of Chemistry, University of Illinois at Chicago, 845 West Taylor Street,
Chicago, Illinois 60607-7061

dcrich@uic.edu

Received May 18, 2005



A series of 2-alkylsulfonyl-2′-biphenyl radicals, in which the alkyl group is primary, secondary, or tertiary, were generated and the products of their reactions investigated. Dibenzothiophene *S*,*S*-dioxide was not identified among the products, which arose mainly from intramolecular hydrogen abstraction from the alkyl group or addition to the solvent, benzene. On this basis, it is concluded that homolytic substitution at sulfonyl sulfur, if possible at all, is too slow to take precedence over a number of competing decomposition pathways. Previous literature results suggesting the possibility of intramolecular homolytic substitution at sulfonyl sulfur may be explained by alternative processes.

Introduction

Bimolecular homolytic substitution (S_H2) at sulfur(II) with displacement of a carbon radical is a well-known phenomenon, albeit a relatively slow one.[1] When rendered intramolecular the process is much more efficient, as first demonstrated by Kampmeier and co-workers on photolysis of the aryl iodides **1** and **2**.[2] Related systems, based on **1** and **2**, may be incorporated into radical chain reactions where they provide convenient sources of acyl and alkyl radicals,[3] as demonstrated by applications in synthetic and mechanistic studies involving complex carbohydrates, nucleotides, and other natural products.[4,5] Vinyl radicals generated in the course of chain reactions have also been shown to undergo efficient intramolecular homolytic substitution at sulfur.[6] In each of the systems, an initial aryl, vinyl, or alkyl radical is generated either by halogen abstraction with a stannyl or silyl radical, by reduction of a diazonium salt, or by radical addition to an alkyne setting the stage for a cyclization reaction involving S_H2 at sulfur with cleavage of the exocyclic bond and expulsion of an alkyl or aryl radical. In his pioneering study, Kampmeier demonstrated that intramolecular homolytic substitution also takes place at sulfur(IV) in sulfoxides in substrates such as **3**.[2b] Beckwith and Boate later showed the sulfoxide reaction is not only considerably faster than that of the corresponding sulfide but also that it takes place with clean inversion of configuration at sulfur.[7] Sulfone **4**, on the other hand, was reported by Kampmeier not to take part in intramolecular homolytic

---

[1] (a) Ingold, K. U.; Roberts, B. P. *Free Radical Substitution Reactions: Bimolecular Homolytic Substitutions at Saturated Multivalent Atoms*; Wiley: New York, 1971. (b) Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, pp 162−310. (c) Beckwith, A. L. J. *Chem. Soc. Rev.* **1993**, 143. (d) Crich, D. In *Organosulfur Chemistry: Synthetic Aspects*; Page, P., Ed.; Academic Press: London, 1995; Vol. 1, p 49. (e) Schiesser, C. H.; Wild, L. M. *Tetrahedron* **1996**, *52*, 13265. (f) Walton, J. C. *Acc. Chem. Res.* **1998**, *31*, 99. (g) Schiesser, C. H.; Wild, L. M. *J. Org. Chem.* **1999**, *64*, 1131.

[2] (a) Kampmeier, J. A.; Evans, T. R. *J. Am. Chem. Soc.* **1966**, *88*, 4096. (b) Kampmeier, J. A.; Jordan, R. B.; Liu, M. S.; Yamanaka, H.; Bishop, D. J. In *Organic Free Radicals*; Pryor, W. A., Ed.; ACS Symposium Series No. 69; American Chemical Society: Washington, DC, 1978; p 275.

[3] (a) Tada, M.; Matsumoto, M.; Nukamura, T. *Chem. Lett.* **1988**, 199. (b) Crich, D.; Yao, Q. *J. Org. Chem.* **1996**, *61*, 3566. (c) Crich, D.; Hao, X. *J. Org. Chem.* **1997**, *62*, 5982. (d) Ooi, T.; Furuya, M.; Sakai, D.; Maruoka, K. *Adv. Synth. Catal.* **2001**, *343*, 166.

[4] (a) Beckwith, A. L. J.; Boate, D. R. *J. Org. Chem.* **1988**, *53*, 9. (b) Crich, D.; Hwang, J.-T.; Yuan, H. *J. Org. Chem.* **1996**, *61*, 6189. (c) Crich, D.; Yao, Q. *Tetrahedron* **1998**, *54*, 305. (d) De Boeck, B.; Pattenden, G. *Tetrahedron Lett.* **1998**, 6975. (e) Bashir, N.; Murphy, J. A. *Chem. Commun.* **2000**, 627. (f) Harrowven, D. C.; Hannam, J. C.; Lucas, M. C.; Newman, N. A.; Howes, P. D. *Tetrahedron Lett.* **2000**, *41*, 9345. (g) Crich, D.; Suk, D.-H.; Hao, X. *Tetrahedron* **2002**, *58*, 5789. (h) Benati, L.; Leardini, R.; Minozzi, M.; Nanni, D.; Spagnolo, P.; Strazzari, S.; Zanardi, G. *Org. Lett.* **2002**, *4*, 3079. (i) Crich, D.; Yao, Q. *Org. Lett.* **2003**, *5*, 2189. (j) Crich, D.; Yao, Q. *J. Am. Chem. Soc.* **2004**, *126*, 8232.

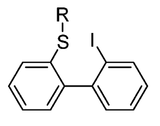
[5] For kinetic studies see ref 4a and: (a) Franz, J. A.; Roberts, D. H.; Ferris, K. F. *J. Org. Chem.* **1987**, *52*, 2256. (a) Beckwith, A. L. J.; Duggan, S. A. M. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1509.

[6] (a) Ooi, T.; Furuya, M.; Sakai, D.; Hokke, Y.; Maruoka, K. *Synlett* **2001**, 541. (b) Benati, L.; Calestani, G.; Leardini, R.; Minozzi, M.; Nanni, D.; Spagnolo, P.; Strazzari, S. *Org. Lett.* **2003**, *5*, 1313. (c) Benati, L.; Leardini, R.; Minozzi, M.; Nanni, D.; Scialpi, R.; Spagnolo, P.; Zanardi, G. *Synlett* **2004**, 987.

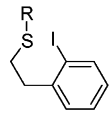
[7] Beckwith, A. L. J.; Boate, D. R. *J. Chem. Soc., Chem. Commun.* **1986**, 189.

10.1021/jo050990c CCC: $30.25

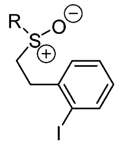
substitution at sulfur, with dehalogenation being the only observed reaction on photolysis in cyclohexane.[2b]



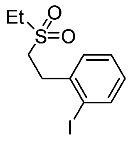
1



2



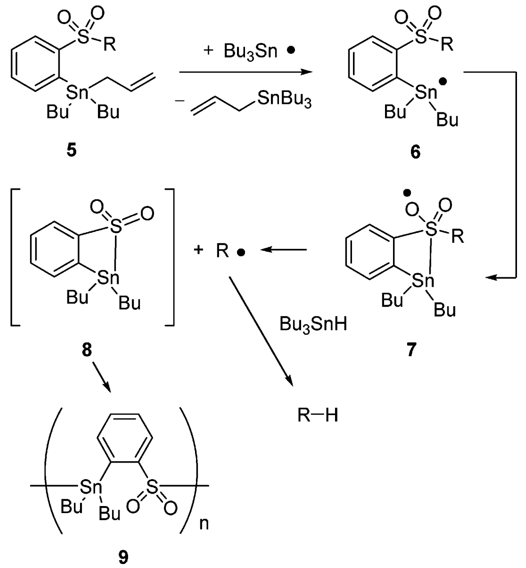
3



4

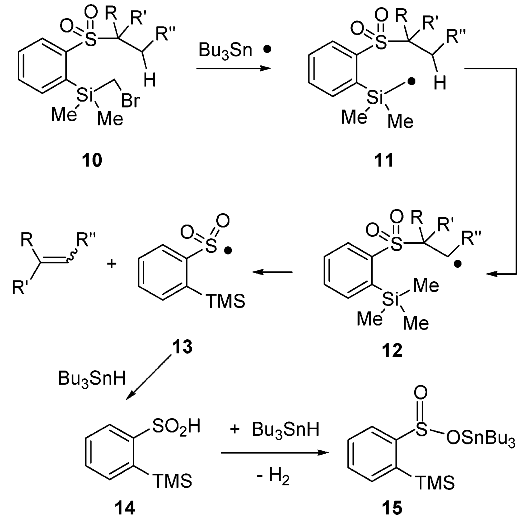
No further reports on homolytic substitution at sulfur in sulfones appeared[8] until the publication of two provocative articles from Van Dort and Fuchs in 1997.[9] The first of these describes a very interesting process in which *o*-allylstannyl-substituted aryl alkyl sulfones **5** undergo homolytic cleavage of the alkyl group with release of a polymeric stannyl sulfinate **9**.[9a] The reaction was considered to proceed by homolytic displacement of the stannyl radical from the allylstannane **5** followed by homolytic substitution at sulfonyl sulfur with displacement of the alkyl radical. The hypothetical four-membered stannyl sulfone **8** generated as a byproduct in this cyclization then undergoes polymerization to form the observed byproduct **9** (Scheme 1).

SCHEME 1. Mechanism for the Release of Alkyl Radicals from Sulfones 5 According to Van Dort and Fuchs

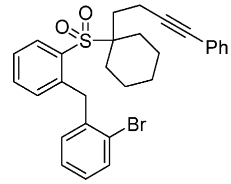


The second paper of the two reports an interesting dichotomy.[9b] A series of silylmethyl radicals **11**, generated by bromine abstraction from the silylmethyl bromides **10** with a stannyl radical, abstract a hydrogen atom from a position β to a sulfone through an eight-membered cyclic transition state leading to a β-sulfonyl radical **12**. As is typical for such radicals, elimination of the sulfonyl radical ensues leading, after chain transfer, to the *o*-trimethylsilylbenzenesulfinic acid **14** which ultimately consumes a further equivalent of the stannane to give a stannyl sulfinate **15** (Scheme 2). All sulfones employed in this study were tertiary allylic, thereby excluding the otherwise preferential hydrogen abstraction from the α-position of the sulfone through a seven-membered cyclic transition state.

SCHEME 2. Intramolecular Hydrogen Abstraction β to a Sulfonyl Group



Identical chemistry is reported for a second system **16** albeit with hydrogen atom abstraction by an aryl radical, via a nine-membered cyclic transition state.[9b]



16

The dichotomy arises when a secondary radical, closely related to **11**, but generated by addition of tris(trimethylsilyl radical) to an allylsilane, undergoes apparent intramolecular homolytic substitution at sulfonyl sulfur, rather than hydrogen atom abstraction, with release of an alkyl radical and formation of a silacyclic sulfone (Scheme 3).[9b] By way of explanation, Van Dort and Fuchs postulate that the difference in reactivity between radical **11** (Scheme 2) and radical **18** (Scheme 3) may result from the additional stability afforded to radical **18** by the presence of two β-silyl groups.

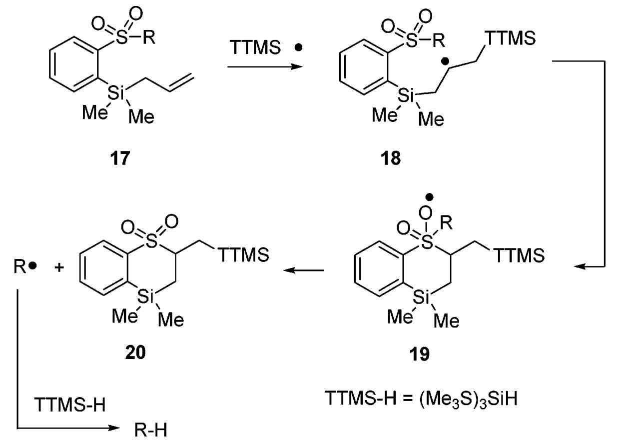
Intrigued by these seemingly contradictory results, and prompted by the need to identify a new radical precursor in our laboratory, we set out to conduct a further investigation into the possibility of homolytic substitution at sulfur in sulfones on which we now report.

---

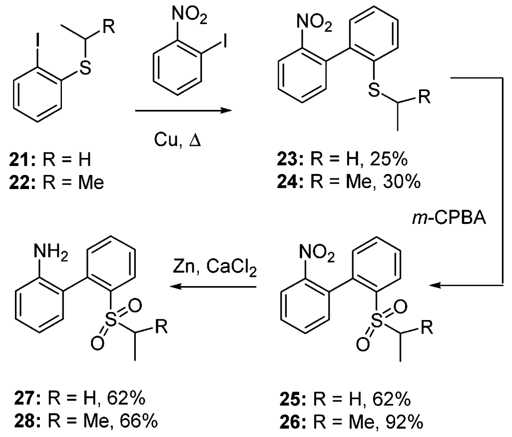
(8) Reviews on the free radical chemistry of sulfones and sulfonyl radicals do not mention homolytic substitution at sulfur: (a) Patai, S., Rapoport, Z., Stirling, C. J. M., Eds. *The Chemistry of Sulfones and Sulfoxides*; Wiley: New York, 1988; p 1210. (b) Simpkins, N. S. *Sulphones in Organic Synthesis*; Pergamon: Oxford, 1993. (c) Bertrand, M. P. *Org. Prep. Proc. Int.* **1994**, *26*, 257. (d) Chatgilialoglu, C.; Bertrand, M. P.; Ferreri, C. In *S-Centered Radicals*; Alfassi, Z. B., Ed.; Wiley: Chichester, 1999; p 311.

(9) (a) Van Dort, P. C.; Fuchs, P. L. *J. Org. Chem.* **1997**, *62*, 7137. (b) Van Dort, P. C.; Fuchs, P. L. *J. Org. Chem.* **1997**, *62*, 7142.

SCHEME 3. Mechanism for the Release of Alkyl Radicals from Sulfones 17 According to Van Dort and Fuchs



SCHEME 4. Preparation of Anilinosulfones 27 and 28



SCHEME 5. Preparation of Anilinosulfone 33

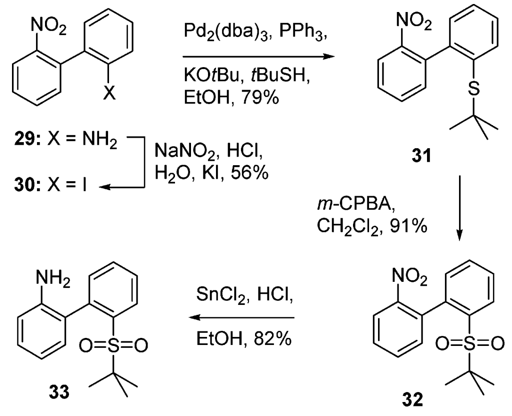
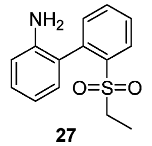
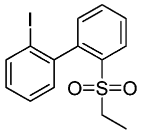
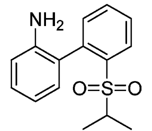
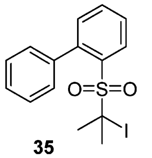
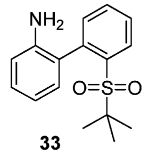
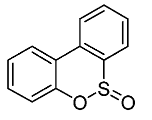
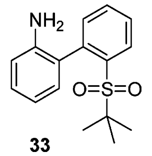
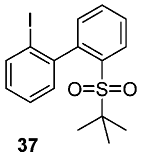


TABLE 1. Sandmeyer Reactions

Substrate	Conditions[a]	Product	% Yield
 **27**	A	 **34**	49
 **28**	A	 **35**	49
 **33**	A	 **36**	84
 **33**	B	 **37**	89

[a] Key: (A) $NaNO_2$, HCl, H_2O, KI; (B) $NaNO_2$, HCl, CH_2Cl_2, KI.

Preparation of Substrates

A biphenyl system related to the one originally employed in the sulfide series by Kampmeier (**1**) was selected for this investigation on the grounds that any cyclization would be enhanced by the presence of only two rotating single bonds, as was clearly recognized by Kampmeier.[2,10] Primary and secondary 2-alkylsulfonyl-2′-aminobiphenyls (**27** and **28**) were prepared by crossed Ullmann protocols from the known iodosulfide **21**[11] and from **22**, at the level of the sulfide oxidation state as outlined in Scheme 4. Subsequent oxidation of the sulfide with *m*-CPBA afforded the corresponding sulfones and treatment with zinc and calcium chloride in ethanol[11] effected reduction of the nitro groups in the presence of the sulfones.

Attempted preparation of the corresponding biphenyl *tert*-butyl sulfone via a similar crossed Ullmann reaction was unsuccessful, and an alternative method was sought. Iodination of 2-nitro-2′-aminobiphenyl **29**[12] followed by a Pd-catalyzed aryl iodide/thiol cross-coupling[13] proved more profitable, permitting installation of the *tert*-butyl sulfide moiety to the biphenyl system. Oxidation with *m*-CPBA then afforded the nitrosulfone **32** which, on treatment with stannous chloride, finally yielded the desired anilinosulfone **33** (Scheme 5).

With a series of anilines in hand, formation of the desired iodobiphenyl systems was attempted via the Sandmeyer reaction, with the results set out in Table 1.

Iodination of the primary alkyl aminosulfone **27** proceeded without incident to give the aryl iodide **34** in a yield of 49%. However, the secondary alkyl aminosulfone **28** gave none of the expected aryl iodide, instead affording the 2-iodo-2-propyl sulfone **35** as the only isolated

---

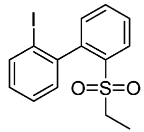
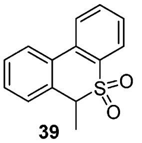
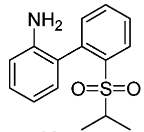
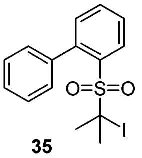
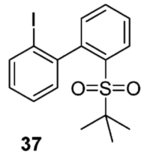
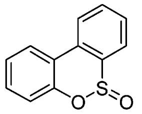
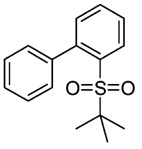
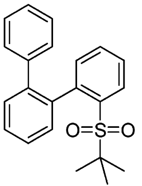
[10] Interestingly, in his very first paper on this subject[2a] Kampmeier reports in a footnote that the sulfone corresponding to **1** (R = Me) was prepared but no comment was made on any chemistry of this sulfone.

[11] Hori, M.; Shimizu, H.; Matsuo, K.; Kataoka, T. *Chem. Pharm. Bull.* **1984**, *32*, 4360.

[12] Heck, R. F.; Terpko, M. O. *J. Org. Chem.* **1980**, *45*, 4992.

[13] (a) Migita, T.; Shimizu, T.; Asami, Y.; Shiobara, J.-i. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1385. (b) Kondo, T.; Mitsudo, T. *Chem. Rev.* **2000**, *100*, 3205.

TABLE 2. Radical Reactions

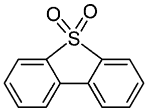
Substrate	Conditions[a]	Product	% Yield
 **34**	A	 **39**	55
 **28**	B	 **35**	49
 **37**	A	 **36**	13
		 **40**	10
		 **41**	3

[a] Key: (A) Bu_3SnH, AIBN, C_6H_6, Δ; (B) $NaNO_2$, HCl, KI.

product. Formation of this compound can be rationalized as proceeding via a radical mechanism, discussion of which is deferred to the following section. Under the classical Sandmeyer conditions, in dilute hydrochloric acid, the *tert*-butyl sulfone **33** provided none of the desired iodide, but gave the cyclic sultine **36**[14] as the only isolated product. Formation of the desired iodide **37** was eventually achieved in high yield through the use of a biphasic CH_2Cl_2/hydrochloric acid system for the Sandmeyer reaction. We speculate that this change in product may be due to two different mechanisms operating in the two solvent systems. In the monophasic aqueous system it may be that an intramolecular nucleophilic attack by the sulfonyl oxygen competes with the classical Sandmeyer process,[15] but that this component is suppressed in the organic phase of the biphasic conditions. The fact that we only observed this process with the tertiary system **33** suggests that it is either facilitated by the highly substituted nature of the system, as is common for cyclizations in general, or by a concerted loss of the *tert*-butyl cation.

Radical Reactions

The two iodosulfones **34** and **37** were treated with tributyltin hydride, with AIBN initiation, in benzene at reflux in the usual manner with the results presented in Table 2. In the absence of an aryl iodide in the secondary alkyl sulfone case, the results obtained from the Sandmeyer reaction of the amine **28** were taken as indicative of the behavior of the corresponding aryl radical and are thus reproduced in Table 2. All radical reactions were relatively complex, and only major products were identified. Nevertheless, with the aid of an authentic sample[16] and examination the crude reaction mixtures, it is possible to state that simple homolytic attack at sulfonyl sulfur with expulsion of an alkyl radical and formation of dibenzothiophene *S*,*S*-dioxide **38** did not take place for any of the substrates.



38

The primary and secondary systems exhibited similar fundamental behavior, namely hydrogen abstraction from the α-position of the sulfone through a seven-membered cyclic transition state. In the primary case, conducted in the presence of tributyltin hydride in hot, dilute benzene solution, the alkyl radical formed on intramolecular hydrogen abstraction underwent oxidative cyclization onto the second aromatic ring leading eventually to the known[17] cyclic sulfone **39**. The oxidation of intermediate cyclohexadienyl radicals under these conditions is typical and is currently thought to be achieved by means of the azo initiator.[18,19] In the secondary case, with aryl radical generation from the amine **28** via electron transfer to the corresponding diazonium ion and the Sandmeyer reaction,[3c,20] the secondary alkyl radical formed on intramolecular hydrogen atom transfer was trapped with iodine to give **35** as the major product. It may be that in the case of the secondary radical derived from **28**, cyclization to a product corresponding to **39** is retarded by the bulk of the attacking radical or, simply, that the high concentration of iodide under the Sandmeyer conditions ensures trapping of the alkyl radical before this cyclization can take place. Whatever the reason for the divergent nature for the final products, it is clear that both **35** and **39** arise from the same primary process of intramolecular hydrogen atom abstraction through a seven-membered transition state. Furthermore, this

---

(14) Squires, T. G.; Venier, C. G.; Hodgson, B. A.; Chang, L. W.; Davis, F. A.; Panunto, T. W. *J. Org. Chem.* **1981**, *46*, 2373.

(15) A recent discussion of the mechanisms of substitution of arene diazonium ions: Ussing, B. R.; Singleton, D. A. *J. Am. Chem. Soc.* **2005**, *127*, 2888.

(16) Noyori, R.; Zheng, X.; Aoki, M.; Hyodo, M.; Sato, K. *Tetrahedron* **2001**, *57*, 2469.

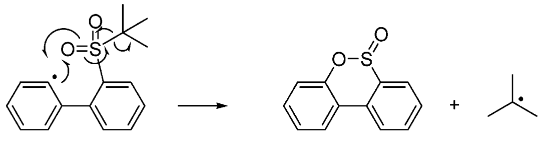
(17) Pagani, G.; Bradamante, S. *J. Chem. Soc., Perkin Trans. 1* **1973**, 163.

(18) (a) Beckwith, A. L. J.; Bowry, V. W.; Bowman, W. R.; Mann, E.; Parr, J.; Storey, J. M. D. *Angew. Chem., Int. Ed. Engl.* **2004**, *43*, 95. (b) Engel, P. S.; Wu, W.-X. *J. Am. Chem. Soc.* **1989**, *111*, 1830. (c) Curran, D. P.; Yu, H.; Liu, H. *Tetrahedron* **1994**, *50*, 7343. (d) Curran, D. P.; Liu, H. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1377.

(19) For related reactions involving intramolecular hydrogen abstraction by an aryl radical followed by cyclization onto the aromatic ring, see: Storey, J. M. D. *Tetrahedron Lett.* **2000**, *41*, 8173.

(20) (a) Beckwith, A. L. J.; Meijs, G. F. *J. Org. Chem.* **1987**, *52*, 1922. (b) Murphy, J. A. In *Radicals in Organic Synthesis*; Renaud, P., Sibi, M. P., Eds.; Wiley-VCH: Weinheim, 2001; Vol. 1, p 298. (c) Bashir, N.; Patro, B.; Murphy, J. A. *Adv. Free Radical Chem.* **1999**, *2*, 123.

SCHEME 6. Formation of Sultine 36



42 36

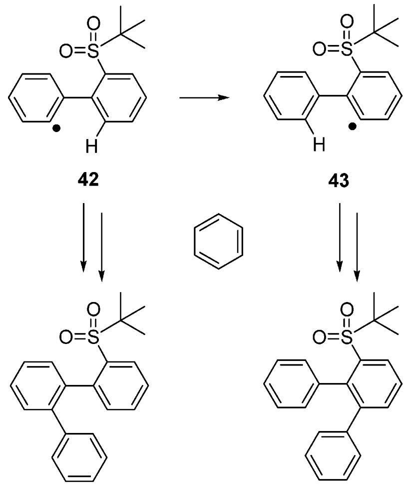
process is significantly favored over homolytic attack at sulfur and hydrogen atom abstraction of a more remote hydrogen through an eight-membered transition state as postulated by Van Dort and Fuchs for the formation of radical **12** (Scheme 2).[9]

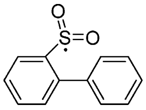
With the tertiary iodide **37**, hydrogen atom abstraction through a seven-membered transition state to yield a sulfone-stabilized alkyl radical is not possible, and the reaction mixture was considerably more complex, perhaps reflecting the absence of any one facile pathway for the initial aryl radical. The main product identified was the sultine **36** which, in this case, must arise by radical attack at the sulfonyl oxygen with expulsion of a *tert*-butyl radical (Scheme 6). This process is the open-shell equivalent of the cationic mechanism proposed above for the formation of **36** under the monophasic Sandmeyer conditions.

The formation of the simple deiodination product **40** is not unexpected in a tin hydride mediated radical reaction, but the isolation of appreciable amounts of phenylated products **41** deserves comment. Phenyl radicals add to benzene with a rate constant of 4.5×10^{5} M^{-1} s^{-1} at 25 °C,[21] which is small when compared to the rate of trapping by tributyltin hydride which approaches the diffusion controlled limit.[22] However, in neat benzene (11.2 M) as solvent, an effective first-order rate constant of 5×10^{6} s^{-1} is reached which is comparable with many alkyl radical cyclizations, if not yet aryl and vinyl radical cyclizations.[23] Thus, in reality, for reactions generating aryl radicals with no effective reaction pathways and in the presence of only low concentrations of stannane it should not be surprising to see phenylated products arising from reaction with the solvent benzene. As discussed above for the formation of **39**, rearomatization of the intermediate cyclohexadienyl radical presumably involves the AIBN used as initiator.[18,24] Compound **41** was the only isolated product from a mixture containing at least two apparently related substances. Owing to difficulties with separation, we are not able to determine whether the mixture is one of atropisomers or regioisomers arising from 1,5-hydrogen atom migration at the level of radical **42** (Scheme 7)[25] or both.[26]

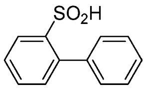
We cannot categorically rule out hydrogen atom abstraction through an eight-membered transition state as a further pathway for the decomposition of radical **42**, similar to the one postulated by Van Dort and Fuchs, for radical **11** in Scheme 2,[9] leading to the biphenyl sulfonyl radical **45** after loss of isobutylene. However, while a minor fraction containing several des-*tert*-butyl products was obtained,[27] the obvious product of chain transfer with the stannane, 2-biphenylsulfinic acid **46**,[28] was not among them.

SCHEME 7. Possible 1,5-Hydrogen Migrations in Radical 42





45



46

Discussion

Our results clearly show that homolytic substitution at sulfur in sulfones is not a facile process, in line with the original comments of Kampmeier.[2] When intramolecular hydrogen atom abstraction adjacent to the sulfone is possible this is the predominant process. When such hydrogen atom abstractions adjacent to the sulfone are blocked, as in the case of the tertiary system **37**, other processes dominate, including attack at sulfonyl oxygen and addition to the solvent. These results obviously are in contrast with the results of Van Dort and Fuchs,[9] especially for the systems presented in Schemes 1 and

---

(21) Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 3609.

(22) Garden, S. J.; Avila, D. V.; Beckwith, A. L. J.; Bowry, V. W.; Ingold, K. U.; Lusztyk, J. *J. Org. Chem.* **1996**, *61*, 805.

(23) (a) Ingold, K. U.; Griller, D. *Acc. Chem. Res.* **1980**, *13*, 317. (b) Newcomb, M. *Tetrahedron* **1993**, *49*, 1151. (c) Newcomb, M. In *Radicals in Organic Synthesis*; Renaud, P., Sibi, M. P., Eds.; Wiley-VCH: Weinheim, 2001; Vol. 1, p 317.

(24) In other circumstances the aryl-substituted cyclohexadienyl radicals, such as the ones implied in the formation of either **39** or **41**, may be trapped in stannane-mediated systems with catalytic diphenyl diselenide, resulting in a synthetically useful process. (a) Crich, D.; Hwang, J.-T. *J. Org. Chem.* **1998**, *63*, 2765. (b) Crich, D.; Sannigrahi, M. *Tetrahedron* **2002**, *58*, 3319. (c) Crich, D.; Rumthao, S. *Tetrahedron* **2004**, *60*, 1513. (d) Crich, D.; Grant, D. *J. Org. Chem.* **2005**, *70*, 2384.

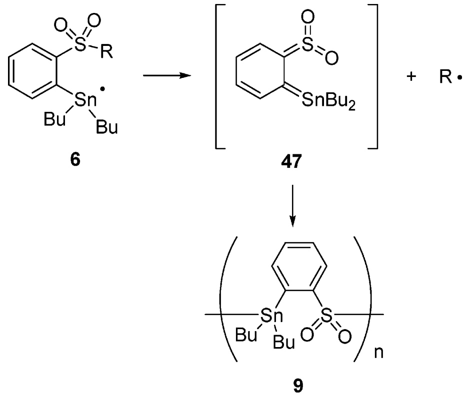
(25) (a) Karady, S.; Abramson, N. L.; Dolling, U.-H.; Douglas, A. W.; McManemin, G. J.; Marcune, B. *J. Am. Chem. Soc.* **1995**, *117*, 5425. (b) Cummins, J. M.; Dolling, U.-H.; Douglas, A. W.; Karady, S.; Leonard, W. R.; Marcune, B. F. *Tetrahedron Lett.* **1999**, *40*, 6153. (c) Chandler, S. A.; Hanson, P.; Taylor, A. B.; Walton, P. H.; Timms, A. W. *J. Chem. Soc., Perkin Trans. 2* **2001**, 214. (d) Karady, S.; Cummins, J. M.; Dannenberg, J. J.; del Rio, E.; Dormer, P. G.; Marcune, B. F.; Reamer, R. A.; Sordo, T. L. *Org. Lett.* **2003**, *5*, 1175. (e) Gribble, G. W.; Fraser, H. L.; Badenock, J. C. *Chem. Commun.* **2001**, 805. (f) Qian, X.; Cui, J.; Zhang, R. *Chem. Commun.* **2001**, 2656.

(26) Compound **41** is tentatively assigned as shown rather than as regioisomer **44** on the basis of the number of chemically distinct resonances in the ^{13}C NMR spectrum.

(27) The main components of this mixture contained both an electron-rich and an electron-poor aromatic ring, suggesting that they are derived from opening of the sultine ring in **36**.

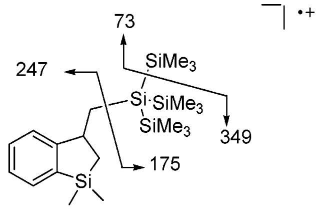
(28) An authentic sample of **46** was prepared: Davies, W.; Middleton, F. C. J. S.; Porter, Q. N. *J. Chem. Soc.* **1955**, 1565.

SCHEME 8. Alternative Mechanism for the Fragmentation of Radical 6



3, which as written imply homolytic attack at sulfur by much less reactive radicals than the aryl radicals employed in our study. It may be that the alkyl and stabilized alkyl radicals employed by Van Dort and Fuchs, in contrast to our aryl radicals, enable them to avoid the side reactions we encountered thereby providing time for the S_H2 process. This is unlikely, however, as the S_H2 process itself would also be expected to be slower with alkyl rather than aryl radicals. Rather, we believe that alternative explanations exist for the results of Van Dort and Fuchs that do not involve direct homolytic substitution at sulfone sulfur. Thus, the chemistry reported in Scheme 1 may be explained as outlined in Scheme 8 with formation of an unstable intermediate **47** rather than the benzo-fused four-membered ring **8** proposed originally.

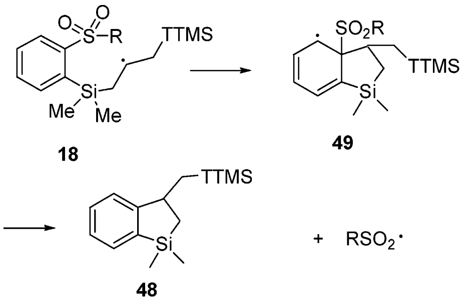
The chemistry presented in Scheme 2 does not involve homolytic attack at sulfur and the hydrogen atom abstractions β to the sulfone are reasonable in the absence of α-hydrogens. The alkyl nature of radical **11** explains the apparent absence of products arising from radical addition to the solvent. On careful examination of the data, we are led to the conclusion that the apparent dichotomy between Schemes 2 and 3 discussed in the Introduction is best explained by misidentification of product **20**. Thus, Van Dort and Fuchs identified this product on the basis of its ^{1}H and ^{13}C NMR spectral data as well as by the low-resolution mass spectrum.[9b] While the NMR spectral data[29] appears to be consistent with structure **20**, the mass spectrum is not. Thus, the molecular formula of structure **20** is $C_{20}H_{42}O_2Si_5S$, leading to a nominal molecular weight of 486 amu. The reported EI mass spectrum[9b] has *m/z* 349, 175, and 73 requiring a loss of a fragment(s) of 137 amu to give the ion at *m/z* 349. The loss of a 137 amu fragment can only be explained by cleavage of a $SiMe_3$ group (73 amu) and the elements of SO_2 (64 amu), and while either of these is conceivable individually, the combination or sequencing of the two is improbable in the context of structure **20**. Rather, we believe that the data is better accommodated by the alternative structure **48** with the mass spectral fragmentation indicated (Figure 1).



48: $C_{20}H_{42}Si_5$, MW 422 amu

FIGURE 1. Structure **48** and the anticipated mass spectral fragmentation pattern.

SCHEME 9. Mechanism for the Formation of 48



The formation of this structure is very readily explained by a homolytic substitution reaction involving attack of the initial adduct **18** on the aromatic ring to give a cyclohexadienyl radical **49**, which then expels a sulfonyl radical to give **48**. Substantial precedent exists for related homolytic aromatic substitution reactions, including ones in which a sulfonyl radical is displaced by an alkyl radical.[30] Finally, facile loss of sulfur dioxide from the sulfonyl radical[31] would afford the alkyl radical (Scheme 9).

Conclusion

The answer to the title question is a cautious no. Early indications from Kampmeier[2] together with the work described here strongly suggest that homolytic attack at sulfonyl sulfur, if it exists at all, is such a slow process that competing reactions, be they inter- or intramolecular, always take precedence. Earlier work by Van Dort and Fuchs,[9] suggesting that homolytic displacement from sulfonyl sulfur takes place, is open to alternative interpretations which both remove the original dichotomies and bring it in line with the work described here and that of Kampmeier. The possibility that S_H2 at sulfonyl sulfur may occur in systems designed to prevent all competing reactions cannot be excluded, as was found

---

(29) ^{1}H NMR (CDCl$_3$):[9b] 0.21 (s, 27H), 0.27 (s, 3H), 0.36 (s, 3H), 0.71 (dd, J = 4.8, 14.5, 1H), 0.93 (dd, J = 12.3, 14.3, 1H), 1.28 (dd, J = 8.1, 14.5, 1H), 1.53 (dd, J = 2.1, 14.3, 1H), 3.30 (dddd, J = 2.1, 4.8, 8.1, 12.3, 1H), 7.21 (br, t, J = 7.3, 1H), 7.28 (br, d, J = 7.3, 1H), 7.35 (br, t, J = 7.3, 1H), 7.50 (br, d, J = 7.3, 1H). ^{13}C NMR (CDCl$_3$): −1.6, −0.2, 1.5 (9 carbons), 20.2, 21.5, 43.6, 124.8, 125.8, 129.7, 131.8, 138.8, 159.6.

(30) (a) Studer, A.; Bossart, M. In *Radicals in Organic Synthesis*; Renaud, P., Sibi, M., Eds.; Wiley-VCH: Weinheim, 2001; Vol. 2, p 62. (b) Loven, R.; Speckamp, W. N. *Tetrahedron Lett.* **1972**, *13*, 1567. (c) Köhler, H. J.; Speckamp, W. N. *J. Chem. Soc., Chem. Commun.* **1980**, 142. (d) Motherwell, W. B.; Pennell, A. M. K. *J. Chem. Soc., Chem. Commun.* **1991**, 877. (e) da Mata, M. L. E. N.; Motherwell, W. B.; Ujjainwalla, F. *Tetrahedron Lett.* **1997**, *38*, 137. (f) da Mata, M. L. E. N.; Motherwell, W. B.; Ujjainwalla, F. *Tetrahedron Lett.* **1997**, *38*, 141. (g) Studer, A.; Bossart, M. *J. Chem. Soc., Chem. Commun.* **1998**, *19*, 2127. (h) Caddick, S.; Shering, C. L.; Wadman, S. N. *Tetrahedron* **2000**, *56*, 465. (i) Aldabbagh, F.; Bowman, W. R. *Tetrahedron* **1999**, *55*, 4109.

(31) (a) Rosenstein, I. J. In *Radicals in Organic synthesis*; Renaud, P., Sibi, M., Eds.; Wiley-VCH: Weinheim, 2001; Vol. 1, p 50. (b) Le Guyader, F.; Quicelet-Sire, B.; Seguin, S.; Zard, S. Z. *J. Am. Chem. Soc.* **1997**, *119*, 7410. (c) Sire, B.; Seguin, S.; Zard, S. Z. *Angew. Chem., Int. Ed.* **1998**, *37*, 2864. (d) Bertrand, F.; Quiclet-Sire, B.; Zard, S. Z. *Angew. Chem., Int. Ed.* **1999**, *38*, 1943. (e) Quiclet-Sire, B.; Zard, S. Z. *J. Am. Chem. Soc.* **1996**, *118*, 1209.

to be the case for S_H2 at sp^3 carbon.[32] However, it is unlikely that any such highly engineered systems will have broad synthetic utility.

Acknowledgment. We thank the NSF (CHE 9986200) for partial support of this work. We are grateful to Professor P. L. Fuchs, Purdue University, for a helpful discussion and exchange of information.

Supporting Information Available: Full experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

JO050990C

---

[32] Johnson, M. D. *Acc. Chem. Res.* **1983**, *16*, 343.