JOC Article

Unexpected Differences in the α-Halogenation and Related Reactivity of Sulfones with Perhaloalkanes in KOH−*t*-BuOH

Cal Y. Meyers,*[,†,§] Roch Chan-Yu-King,[§,‡] Duy H. Hua,[§,¶] Vera M. Kolb,[§,⊥] Walter S. Matthews,[§,∥] Thomas E. Parady,[§,&] Toyokazu Horii,[§,#] Paul B. Sandrock,[†,§] Yuqing Hou,[†,§] and Songwen Xie[†,§]

Meyers Institute for Interdisciplinary Research in Organic and Medicinal Chemistry, and Department of Chemistry and Biochemistry-4409, Southern Illinois University, Carbondale, Illinois 62901

cal@chem.siu.edu

Received March 31, 2002

Most alkyl phenyl sulfones are readily α-chlorinated with CCl_4 and α-brominated with $CBrCl_3$ in KOH−*t*-BuOH via radical−anion radical pair (RARP) reactions. While isopropyl mesityl sulfone (**4**) is easily α-chlorinated with CCl_4, it was completely recovered when treated with the more reactive $CBrCl_3$. Subsequent investigations showed the latter result to be due to the poor acidity of **4** together with the rapid depletion of $CBrCl_3$ and KOH by their reaction with each other, and led to a variety of other important results. 4-Hydroxyphenyl isopropyl sulfone (**6**) is unreactive with either CCl_4 or $CBrCl_3$ in KOH−*t*-BuOH, its phenoxide anion strongly reducing the electronegativity of the sulfonyl group, thereby inhibiting α-anion formation. This effect is reversed by the electron-withdrawing influence of two α-phenyls, so that benzhydryl 4-hydroxyphenyl sulfone (**8**) is readily α-halogenated in KOH−*t*-BuOH with CCl_4 or $CBrCl_3$. On further contact with KOH−*t*-BuOH the α-halogenated sulfones from **8** are decomposed into benzophenone and phenol. While the α-halogenated derivatives of 4-methoxyphenyl benzhydryl sulfone (**9**) are stable to base, they are decomposed even under mildly acidic conditions into 4-methoxyphenyl 4-methoxybenzenethiolsulfonate (**9c**), phenol, and benzophenone. Mono-α-halogenation of benzyl phenyl sulfone (**10**) enhances the rate of the subsequent halogenation, so that α,α-dihalogenation is attained while much substrate is still present and the mono-α-halogenated product is not detected. The ease of reductive debromination of α-bromo sulfones with Cl_3C^- was correlated with the stability of the formed α-anions, explaining the success with α-bromobenzylic sulfones but failure with α-bromoalkyl sulfones. In the presence of air and the absence of competing halogenation, formation of the α-anions of alkyl aryl sulfones is quickly accompanied by oxidative cleavage by atmospheric O_2, leading to the formation of arenesulfonyl alcohols, arenesulfonyl halides, and haloarenes.

Introduction

Some years ago we published a series of reports noting the facile α-chlorination of sulfones and ketones in powdered KOH−*t*-BuOH with CCl_4 and α-bromination/chlorination with $CBrCl_3$, some subsequent reactions, and the reactions of alcohols with these reagents.[1] The potential utility of these reactions has received considerable attention.[2] Single-electron transfers proceeding from the α-sulfonyl carbanion or enolate anion via a radical−anion radical pair (RARP) transition state were suggested to account for these halogenations,[3] as illustrated in Scheme 1 for the chlorinations with CCl_4. The suggestion of a RARP transition state instead of an intermediate

* To whom correspondence should be addressed. E-mail: meyers@chem.siu.edu. FAX: 618-453-6408.
† Meyers Institute for Interdisciplinary Research in Organic and Medicinal Chemistry.
§ Department of Chemistry and Biochemistry.
‡ Present address: Science Division, University of Science and Arts of Oklahoma, Chickasha, OK 73018.
¶ Present address: Department of Chemistry, Kansas State University, Manhattan, KS 66506.
⊥ Present address: Department of Chemistry, University of Wisconsin−Parkside, Kenosha, WI 53141-2000.
∥ Present address: Intel Corp., Santa Clara, CA 90502.
& Present address: Roquette America, Keokuk, IA 52632.
# Present address: Radiation Center, Osaka Prefecture, Japan.

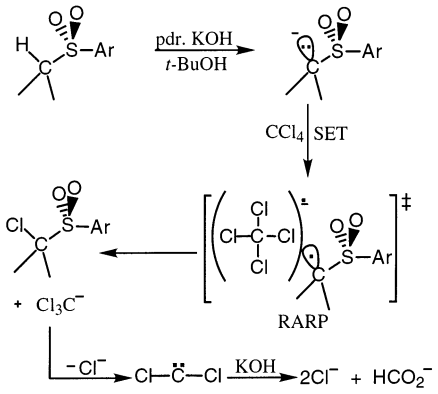
(1) (a) Meyers, C. Y.; Malte, A. M.; Matthews, W. S. *J. Am. Chem. Soc.* **1969**, *91*, 7510−7512. (b) Meyers, C. Y.; Malte, A. M.; Matthews, W. S. *Quart. Rept. Sulfur Chem.* **1970**, *5*, 229. (c) Meyers, C. Y.; Ho, L. L. *Tetrahedron Lett.* **1972**, 2319−2322. (d) Meyers, C. Y.; Sataty, I. *Tetrahedron Lett.* **1972**, 4323−4326. (e) Meyers, C. Y.; Ho, L. L.; McCollum, G. J.; Branca, J. C. *Tetrahedron Lett.* **1973**, 1843−1846. (f) Meyers, C. Y.; Matthews, W. S.; McCollum, G. J.; Branca, J. C. *Tetrahedron Lett.* **1974**, 1105−1108. (g) Meyers, C. Y. *Prepr. Am. Chem. Soc., Div. Pet. Chem.* **1974**, *19* (2), 199−203. (h) Meyers, C. Y.; Kolb, V. M. *J. Org. Chem.* **1978**, *43*, 1985−1990. Meyers, C. Y.; Kolb, V. M. *J. Org. Chem.* **1979**, *44*, 3739.

(2) (a) Meyers, C. Y.; Matthews, W. S.; Malte, A. M. U.S. Patent 3,830,862, August 20, 1974. (b) Meyers, C. Y.; Ho, L. L. U.S. Patent 3,876,689, April 8, 1975. (c) Meyers, C. Y.; Malte, A. M. U.S. Patent 3,896,164, July 22, 1975. (d) Meyers, C. Y.; Matthews, W. S.; Malte, A. M. U.S. Patent 3,949,001, April 6, 1976. (e) Meyers, C. Y.; Matthews, W. S. U.S. Patent 3,953,494, April 27, 1976. (f). Meyers, C. Y.; Ho, L. L. Japanese Patent 973405, Sept. 28, 1979. (g) Meyers, C. Y.; Read, R. B. U.S. Patent 5,022,983, June 11, 1991.

(3) (a) Meyers, C. Y.; Matthews, W. S.; Ho, L. L.; Kolb, V. M.; Parady, T. E. In *Catalysis in Organic Syntheses*; Smith, G. V., Ed.; Academic Press: New York, 1977; pp 197−278. (b) Meyers, C. Y. In *Topics in Organic Sulfur Chemistry*; Tisler, M., Ed.; University Press: Ljubljana, Yugoslavia, 1978; pp 207−60.

10.1021/jo025781w CCC: $25.00
Published on Web 12/13/2002

SCHEME 1

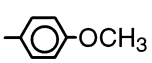
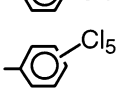
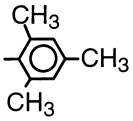
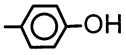
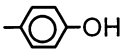
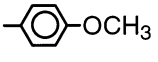


was based on the observation that α-chlorination was attained with retention of α-carbon configuration.[4] Illustrative examples of these halogenations are shown in Table 1. While isopropyl phenyl sulfone (**1**) as well as isopropyl mesityl ketone (**5**) were readily α-halogenated with CCl_4 or $CBrCl_3$, we were surprised, therefore, to find that isopropyl mesityl sulfone (**4**), although readily α-chlorinated with CCl_4, was *quantitatively recovered when treated with the more reactive CBrCl₃, even after prolonged reaction time*. As shown in Scheme 2, however, when treated with *n*-BuLi in THF followed by $CBrCl_3$, **4** was readily converted into α-bromoisopropyl mesityl sulfone (**4b**) along with some α-chloroisopropyl mesityl sulfone (**4a**); when the *n*-BuLi treatment was followed by the addition of Br_2, **4b** was formed in good yield, easily isolated chromatographically, and found to be a stable compound.[5,6] Thus, the following questions arose: How does **4** differ from related sulfones and even from the corresponding mesityl ketone? Why cannot **4** be halogenated by $CBrCl_3$ in KOH−*t*-BuOH when it is readily halogenated by CCl_4 in this medium? In studies seeking the answers, a variety of related reaction phenomena was uncovered.

Results and Discussion

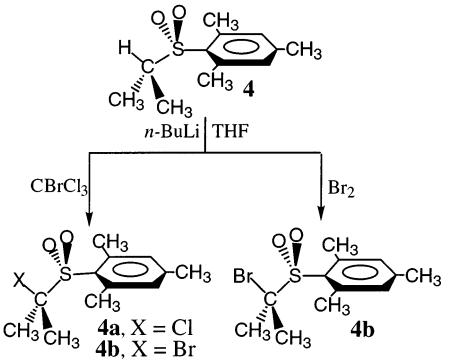
Solving the Isopropyl Mesityl Sulfone Enigma. The failure of **4b** to be detected as a product from the treatment of **4** with $CBrCl_3$ or CBr_4 in KOH−*t*-BuOH was originally associated with the possibility that it was indeed formed, but was reductively debrominated back to **4**-α-anion by reaction with the Cl_3C^- generated in these halogenations (see Scheme 1). Such a possibility seemed reasonable in light of the abundance of Br^- we found after many reaction attempts and from the reductive debromination of α-bromobenzhydryl phenyl sulfone (**7b**) and α,α-dibromobenzyl phenyl sulfone (**10b**)[7] with Cl_3C^-. However, this suggestion was ruled out: **4b** was quantitatively recovered when treated with Cl_3C^- ($CHCl_3$−KOH−*t*-BuOH) at 25 °C. These results are summarized in Scheme 3. The failure of **4** to react with $CBrCl_3$ was

TABLE 1. α-Halogenation of $R^1R^2CHSO_2Ar$ in KOH−*t*-BuOH with CCl_4 (a) and with $CBrCl_3$ (b)[a]

substrate $R^1R^2CHSO_2Ar$	R_1,R_2	Ar	product (% yield) $R^1R^2C(X)SO_2Ar$ with CCl_4 **a**, X = Cl	with $CBrCl_3$ **b**, X = Br
1	CH_3,CH_3		**1a** (100)	**1b** (80)
2	CH_3,CH_3		**2a** (91)	**2b** (55)
3	CH_3,CH_3		**3a** (76)	**3b** (80)
4	CH_3,CH_3		**4a** (100)	**4b** (0) recovered **4** 100%[b]
6	CH_3,CH_3		**6a** (0)	**6b** (0) recovered **6** 100%
7	Ph,Ph		**7a** (100)	**7b** (91)
8	Ph,Ph		**8a** (99)	**8b**[c]
9	Ph,Ph		**9a**[d]	**9b** (98)
10	H,Ph		**10a**[e] (95)	**10b**[f] (85) $PhCX_2SO_2Ar$

[a] The brominations of the sulfones with $CBrCl_3$ were sometimes accompanied by minor amounts of chlorination. [b] In contrast, the corresponding mesityl ketone (**5**) reacted with $CBrCl_3$ to form **5b** (100% yield), as well as with CCl_4 to form **5a** (100% yield). [c] Under the conditions of its formation, **8b** was rapidly fragmented into other products; see discussion. [d] Reaction with CCl_4 not carried out. [e] Also from **10**, C_2Cl_6, aq NaOH/P-T-C. [f] Also from **10**, $CBrCl_3$, aq NaOH/P-T-C.

SCHEME 2



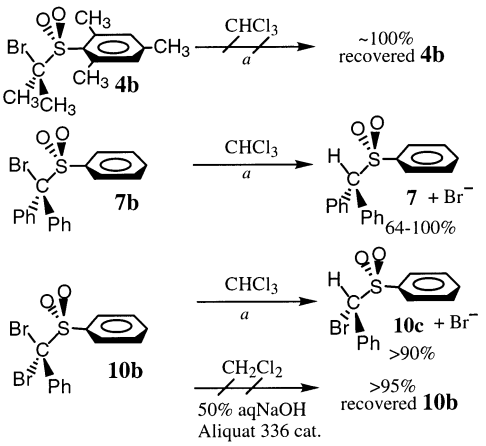
(4) (a) Meyers, C. Y.; Sam, T. W. International Conference on Conformational Analysis, University of New Hampshire, Durham, June 29−July 2, 1981; Abstracts. (b) Sam, T. W.; Hua, D. H.; Badanyan, Sh.; Kolb, V. M.; Rihter, B.; Meyers, C. Y. International Conference on Conformational Analysis, University of New Hampshire, Durham, June 29−July 2, 1981; Abstracts.

(5) Meyers, C. Y.; Hou, Y.; Sandrock, P.; Robinson, P. D.; Hua, D. H.; Chan-Yu-King, R. *Abstracts of Papers*, National Meeting of the American Chemical Society, Boston, MA, Aug 23−28, 1998; American Chemical Society: Washington, DC, 1998; ORGN 637.

(6) Chan-Yu-King, R.; Hou, Y.; Sandrock, P.; Meyers, C. Y.; Robinson, P. D. *Acta Crystallogr.* **2001**, Sect. E, *57*, 449−450.

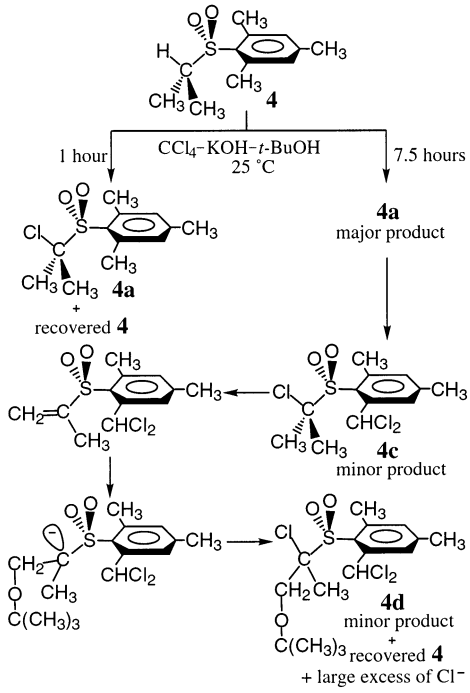
(7) Lauritzen, S. E.; Romming, C.; Skattebøl, L. *Acta Chem. Scand.* **1981**, *B35*, 263−268.

SCHEME 3



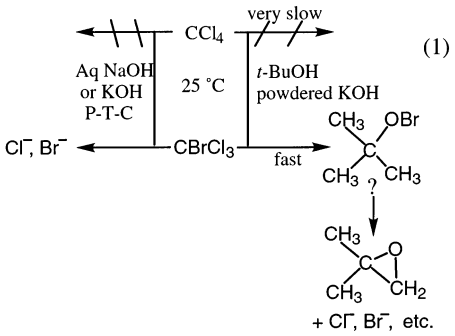
[a] 25 °C in KOH–*t*-BuOH or in 50% aq NaOH-Aliquat 336 catalyst.

SCHEME 4



in stark contrast to its ease of chlorination to provide **4a** with the less reactive CCl_4 at 25 °C. Furthermore, during several hours of contact with CCl_4 in KOH−*t*-BuOH, **4a** underwent dichlorination of one of its *o*-methyls, forming 2-chloro-2-propyl 4-(5-dichloromethyl-1,3-xylyl) sulfone (**4c**); subsequent dehydrochlorination followed by Michael addition and α-chlorination provided 1-*tert*-butoxy-2-chloro-2-propyl 4-(5-dichloromethyl-1,3-xylyl) sulfone (**4d**) (Scheme 4).

In light of the reactivity of **4a** with CCl_4 but unreactivity with $CBrCl_3$, it seemed paradoxical that KOH−*t*-BuOH was virtually *unreactive* with CCl_4 but very reactive with $CBrCl_3$. At 25 °C in this medium, the reaction of $CBrCl_3$ with KOH rapidly decomposed both, easily recognized by the generation of large amounts of Cl^- and Br^- as well as of isobutylene oxide.[1a,8,9] Similarly, reaction of $CBrCl_3$ with aqueous NaOH under phase-transfer catalysis also provided Cl^- and Br^- (eq 1).



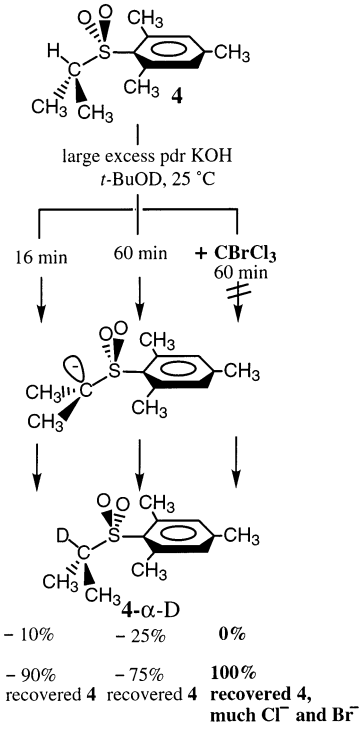
The rate of these halogenations is related to the acidity of the substrate and the reactivity of the generated carbanion with the perhaloalkane.[3] Regarding the first, we reasoned that if the formation of **4**-α-carbanion is slow, while $CBrCl_3$ and KOH, but *not* CCl_4 and KOH, are consumed rapidly by reaction with each other, this combination of factors might explain the contrasting activity between CCl_4 and $CBrCl_3$ with **4** in KOH−*t*-BuOH. Two D/H exchange experiments provided direct evidence of the poor acidity of **4**. When a solution of **4** in excess *t*-BuOD was stirred with KOH for 16 min, ca. 10% α-D/H exchange was observed; in an hour, only 28% D/H exchange was observed. But when a solution of $CBrCl_3$ in *t*-BuOD was added to a mixture of **4** and powdered KOH and the entity stirred for an hour, **4** was almost completely recovered, ***no*** α *D−H exchange was observed, the KOH was virtually consumed, and an abundance of* Br^- *and* Cl^- *was produced* (Scheme 5). The rapid depletion of $CBrCl_3$ and KOH by their reaction with each other was also borne out. When the KOH was added to a solution of **1**, $CBrCl_3$, and *t*-BuOH, 76% α-halogenation was observed in 1.25 h. However, when the same amounts of these reagents were used but a mixture of the $CBrCl_3$, KOH, and *t*-BuOH was stirred for an hour *before* **1** was added, then for an additional hour, only 5% α-halogenation occurred, although substantial amounts of Cl^- and Br^- were generated. Therefore, substantial amounts of KOH and $CBrCl_3$ were consumed by *their reaction with each other prior* to the addition of **1**, thereby precluding any significant amount of halogenation. These facts lead to the conclusion that the $CBrCl_3$ and KOH are consumed faster than **4** is deprotonated and can react with residual $CBrCl_3$. From its estimated pK_a, mesityl sulfone **4** is between 1 and 2 pK_a units *less* acidic than its counterpart phenyl sulfone **1**, and about 5 pK_a units *less* acidic than the mesityl ketone **5**, both of which undergo α-halogenation with $CBrCl_3$−KOH−*t*-BuOH.

The failure of isopropyl 4-hydroxyphenyl sulfone (**6**) to undergo α-halogenation in KOH−*t*-BuOH with *either* CCl_4 or $CBrCl_3$ is associated with its rapidly formed phenoxide anion, which greatly reduces the electronegativity of the sulfonyl group and, thereby, the α-CH acidity (Scheme 6),[3] precluding formation of **6**−α-anion. Since

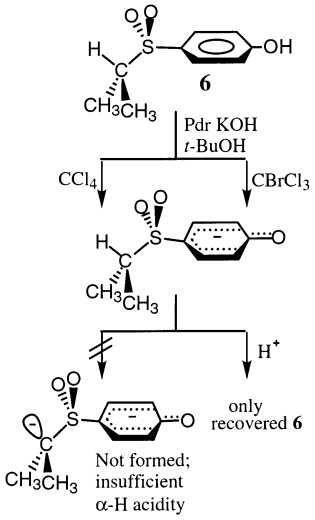
(8) (a) Meyers, C. Y.; Tykal, J. A. Midwest Regional Meeting of the American Chemical Society, Manhattan, KS, Oct 1968; American Chemical Society: Washington, DC, 1968; p 32. (b) Walling, C.; Kjellgren, J. *J. Org. Chem.* **1969,** *34*, 1487−1488.

(9) See, for example: (a) Walling, C.; Kjellgren, J. *J. Org. Chem.* **1969**, *34*, 1488−1489. (b) Pearson, D. E.; Buehler, C. A. *Chem. Rev.* **1974**, *74*, 45−86, especially pp 79−83 and references therein. (c) Mottley, C.; Mason, R. P. *Arch. Biochem. Biophys.* **1988**, *267*, 681−689.

SCHEME 5



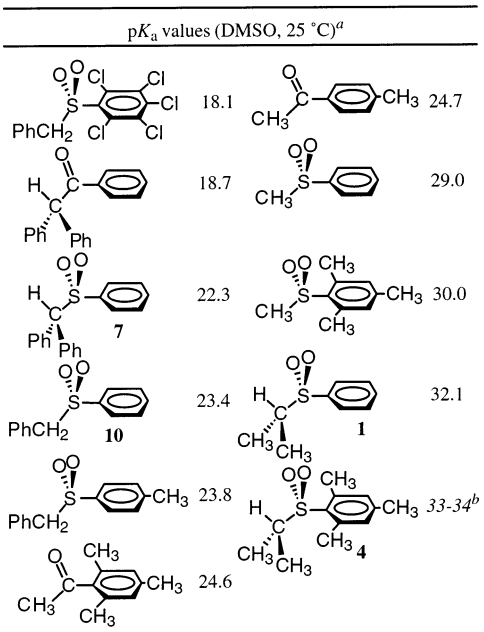
SCHEME 6



this is not the case with the corresponding 4-methoxy sulfone, **2**, it was halogenated with $CBrCl_3$ and also CCl_4, although much slower than was **1**.

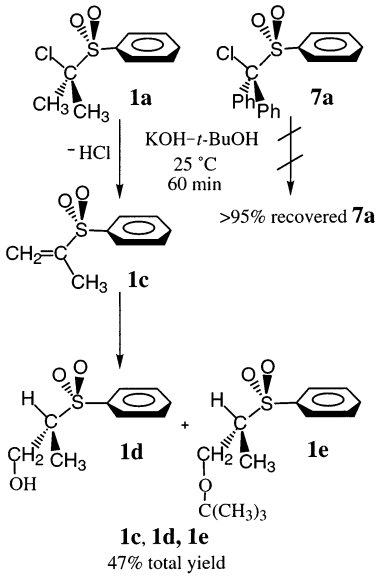
Benzhydryl Aryl Sulfones. The greater effectiveness of the benzhydryl group than the isopropyl group in promoting anion formation was exhibited by the halogenations of the benzhydryl aryl sulfones. Conversion of benzhydryl phenyl sulfone (**7**) to its α-chloro sulfone **7a** in theoretical yield required only a 30-min treatment with CCl_4−KOH−*t*-BuOH at 3 °C. Even more impressive, the α-bromo sulfone **7b** was obtained in over 90% yield upon treatment of **7** with $CBrCl_3$ at 0 ° C for only 10 min. For the same reason, α-halobenzhydryl sulfones are reductively dehalogenated far more readily than haloisopropyl sulfones, as already illustrated with **7b** vs **4b** in Scheme 3. Another significant difference between these two types of α-halo sulfones resides in their reactivity with excess

TABLE 2. Relative α-CH Acitities of Some Aromatic Sulfones and Ketones



a Reference 10. b Estimated.

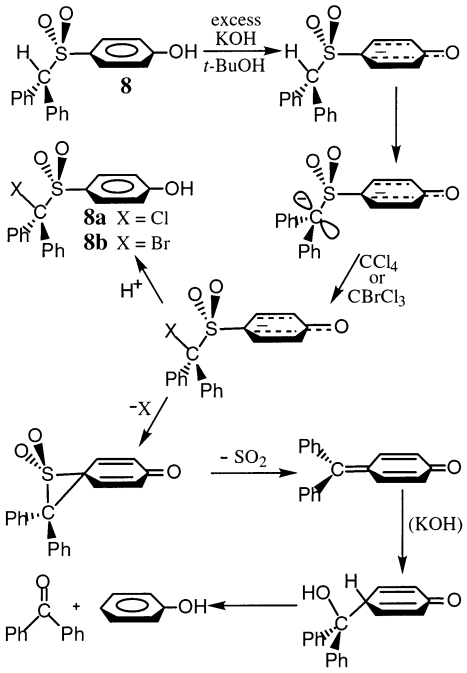
SCHEME 7



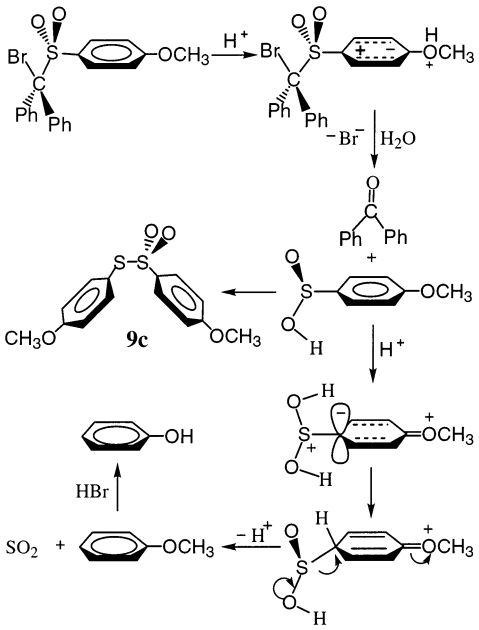
KOH alone. The effect on α-haloisopropyl sulfones was indirectly illustrated from the extended treatment of **4** with CCl_4 in KOH−*t*-BuOH (Scheme 4). Direct treatment of α-chloroisopropyl phenyl sulfone, **1a**, with excess KOH in *t*-BuOH at 25 °C for an hour resulted in its dehydrohalogenation into phenyl 2-propenyl sulfone (**1c**) and subsequent formation of the Michael addition products, 1-hydroxy-2-propyl phenyl sulfone (**1d**) and 1-*tert*-butoxy-2-propyl phenyl sulfone (**1e**), in an overall yield of about 47%. In contrast, over 95% of α-chlorobenzhydryl sulfone **7a** was recovered after similar treatment (Scheme 7).

The effect of the 4-hydroxyphenyl substituent in preventing α-halogenation of isopropyl sulfone **6** is overcome in the corresponding benzhydryl 4-hydroxyphenyl sulfone (**8**). Despite the rapid formation of its 4-phenoxide anion,

SCHEME 8



SCHEME 9



its effect is offset by the strong α-anion-stabilizing effect of the benzhydryl substituent, so that a theoretical yield of α-chlorobenzhydryl 4-hydroxyphenyl sulfone (**8a)** was isolated when **8** was treated with CCl_4−KOH−*t*-BuOH at 25 °C for a short time. When heated in this basic medium, **8a** underwent decomposition mainly into benzophenone and phenol. Its counterpart α-bromobenzhydryl 4-hydroxyphenyl sulfone (**8b**), decomposes much more rapidly. After treatment of **8** with $CBrCl_3$ in KOH−*t*-BuOH at 25 °C for only 2 h, benzophenone and phenol were the major products, along with only a very small amount of initially formed **8b** (Scheme 8).

As would be expected, benzhydryl 4-methoxyphenyl sulfone (**9**) undergoes α-halogenation substantially faster than **8**. Within 30 min at 25 °C, **9** was converted to α-bromobenzhydryl 4-methoxyphenyl sulfone (**9b**) in 98% yield by treatment with $CBrCl_3$−KOH−*t*-BuOH. The complete absence of decomposition products, in contrast to that observed in the preparation of **8b**, supports the suggested decomposition mechanism involving the phenoxide anion of **8a** and **8b** illustrated in Scheme 8. Decomposition of **9b** does occur under acidic conditions. Refluxed in aqueous acetic acid, **9b** was converted into benzophenone and 4-methoxyphenyl 4-methoxybenzenethiolsulfonate (**9c**) as major products, along with anisole.[11,12] Refluxing **9b** in acetic acid−48% HBr produced a 98% yield of benzophenone and 50% yield of phenol. However, refluxed in dioxane alone for 24 h, **9b** was ca. 100% recovered. A mechanism for the acid-catalyzed decomposition of **9b** is suggested in Scheme 9.

Benzyl Phenyl Sulfones. The two α-hydrogens of benzyl phenyl sulfone (**10**) make it unique among the other sulfones in these halogenation reactions. Mono-α-halogenation enhances the acidity of the residual α-H so that α,α-dihalogenation is attained while much **10** is still present and the monohalogenated product is not detected, viz. α,α-dichlorobenzyl phenyl sulfone (**10a**) was easily prepared in high yields from **10** treated with CCl_4 in KOH−*t*-BuOH or with C_2Cl_6−aq NaOH under phase-transfer catalysis. It was reported by Skattebøl et al.[7] that a 12-h treatment of **10** at 25 °C with a large excess of $CBrCl_3$ in 50% aq NaOH−CH_2Cl_2 under P-T-C conditions (TEBA) produced α,α-dibromobenzyl phenyl sulfone (**10b**) and the corresponding α-bromo-α-chloro sulfone. Since we previously found that **10b** was the *only* product when **10** was treated with $CBrCl_3$−KOH−*t*-BuOH for a very *short* time, we believed that reversibility of the brominations, and subsequent chlorination, was responsible for the formation of the α-chloro-α-bromo sulfone. Repeating the reaction under the Skattebøl conditions, we found that **10b** indeed was initially formed but was slowly converted into the α-bromo-α-chloro sulfone, which itself was transformed in ca. 20 h into the α,α-dichloro sulfone, **10a**. The reductive debrominations effected with the generated $Cl_3Cl:^-$ are fast and are followed by the much slower chlorinations, while subsequent reductive dechlorination is even slower and was not observed. Our observation (Scheme 3) that **10b** is readily reductively debrominated to α-bromobenzyl phenyl sulfone (**10c**) by treatment with $Cl_3C:^-$ reasonably accounts for the observed sequence, shown in Scheme 10. However, in KOH−*t*-BuOH, but in the *absence* of $CBrCl_3$ or CCl_4, **10a** reductively monochlorinated 1 equiv of **10**, forming 2 equiv of α-chlorobenzyl phenyl sulfone (**10d**), which was stable to further treatment (Scheme 11).

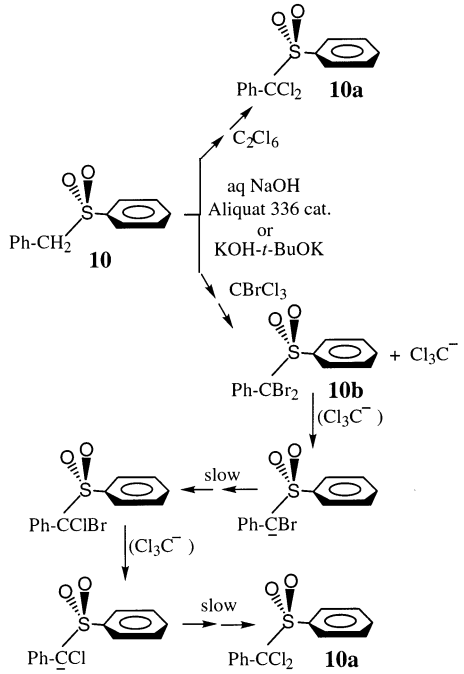
Effect of Atmospheric Oxygen on the Halogenation Reactions. Most of the halogenations with CCl_4,

(10) (a) Bordwell, F. G.; Branca, J. C.; Hughes, D. L.; Olmstead, W. N. *J. Org, Chem*. **1990**, *45*, 3305−3313. (b) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456−463. (c) Taft, R. W.; Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 463−469. (d) Bordwell, F. G.; Bares, J. E.; Bartmess, J. E.; McCollum, G. J.; Van Der Puy, M.; Vanier, N. R.; Matthews, W. S. *J. Org, Chem*. **1977**, *42*, 321−325. (e) Bordwell, F. G.; Matthews, W. S. *J. Am. Chem. Soc.* **1974**, *96*, 1216−1217. (f) Bordwell, F. G.; Jarvis, B. B. *J. Org. Chem*. **1968**, *33*, 1182−1185.

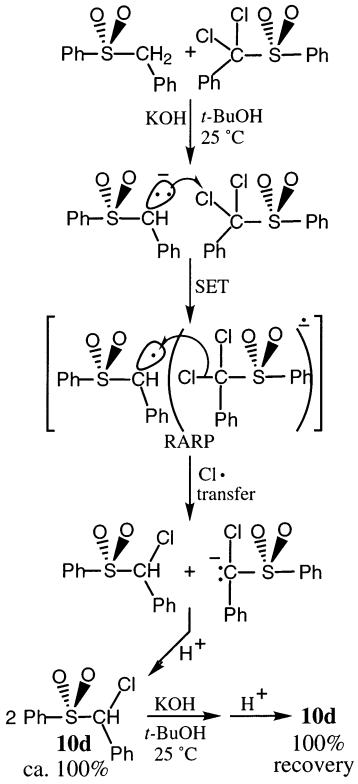
(11) Vinkler, E.; Klivenyl, F. *Acta Chim. Acad. Sci. Hung.* **1955**, *5*, 159−166.

(12) It is well-known that sulfinic acids undergo disproportionation, the corresponding thiolsulfonate being a major product. See: Oae, S. *Organic Chemistry of Sulfur*; Plenum Press: New York, 1977; pp 613−616 and references therein.

SCHEME 10

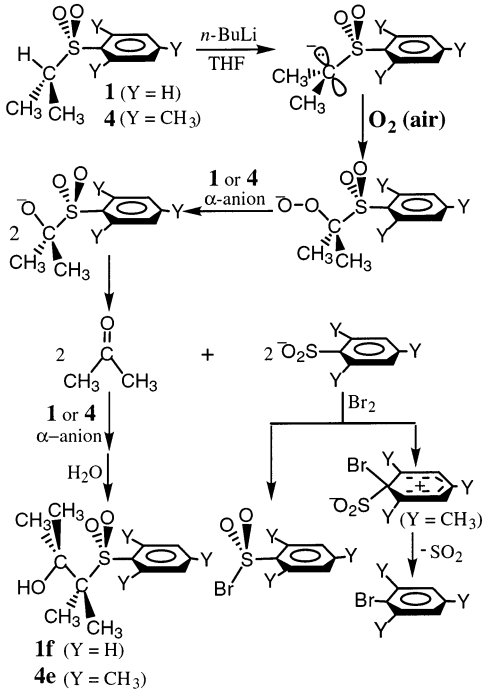


SCHEME 11



$CBrCl_3$, CBr_4, etc. in powdered KOH−*t*-BuOH described here were carried out under inert gas in sealed reaction flasks attached directly via Tygon tubing to the gas cylinder. No side reactions were observed. Some of the brominations in which the substrates were initially treated with *n*-BuLi and the Br_2 was added later were carried out under argon generally from an argon-filled rubber balloon. In the latter cases, other products were often formed, sometimes in significant yield, depending

SCHEME 12



on *when* the Br_2 was introduced. For example, when a solution of sulfone **1** and *n*-BuLi was stirred at −63 °C for an hour attached to such an argon-filled balloon *before* 1 equiv of Br_2 was added and the reaction was worked up after a few minutes, the *major* product was 2,3-dimethyl-3-benzenesulfonyl-2-butanol (**1f**) (49%), along with the expected α-bromo product **1b** (41%) and benzenesulfonyl bromide (10%). The same reaction carried out with twice the amount of Br_2 provided virtually identical results, suggesting that the unexpected major product, **1f**, was produced *before* the addition of Br_2.

This possibility was evaluated by eliminating the Br_2 and simply purging a flask containing **1** with argon from a rubber balloon that had been filled an hour earlier. THF was then added, followed by *n*-BuLi, and the mixture was stirred at −63 °C for an hour before being worked up. Compound **1f** was isolated in 95% yield, along with lithium benzenesulfinate and lithium benzenesulfonate. A number of related reactions were studied which provided corresponding results. Ultimately, the procedure was followed in which the initial argon purge was only for 1 min, the stopcock was then closed and the THF and *n*-BuLi were syringed into the closed flask and the mixture was stirred for an hour; **1** was 100% recovered. The products resulted from α-lithiated **1** being rapidly oxidized by the air diffusing through the rubber-balloon argon reservoir, precluding bromination by the subsequently added Br_2. The mechanistic reaction sequence suggested in Scheme 12 is similar to that reported for related air oxidations of α-nitro anions.[13,14] The same reactions of **1** were followed by the corresponding α-lithiated mesityl sulfone **4** maintained under argon from a rubber-balloon reservoir; **4b** and 2,3-dimethyl-3-mesitylenesulfonyl-2-butanol (**4e**) were obtained as major products, along with mesitylenesulfonyl bromide and a compound incompletely characterized as bromomesitylene as minor products.

Experimental Section

General Methods. Melting points are corrected, ^{1}H and ^{13}C NMR spectra were taken at 300 and 75 MHz, respectively, in $CDCl_3$, IR spectra were taken on Nujol mulls, and elemental analysis were performed by the Microanalysis Laboratory, University of Illinois − Urbana-Champaign, unless stated otherwise. All the reactions, except the oxidations, were generally carried out under argon or nitrogen. When KOH was used, it was powdered [from commercial pellets (85% KOH: 15% H_2O by weight; 9:5 mol ratio)[1,2]]. The unhalogenated sulfones were prepared by refluxing an aromatic thiol, the chloro or bromo compound, and K_2CO_3 in acetone to provide the sulfide, which was then oxidized with 30% H_2O_2−acetic acid. Unless stated otherwise, α-halogenation of the sulfones and ketones was carried out by treating them with a perhaloalkane in KOH−*t*-BuOH, the mixture was then diluted with water and extracted with ether, and the extracts were washed with water, dried, and evaporated in vacuo.

Isopropyl Phenyl Sulfone (1). As reported,[15] **1** was an oil. ^{1}H NMR δ 1.23 (d, J = 6.8 Hz, 6 H), 3.28 (hep, J = 6.8 Hz, 1 H), 7.48−8.10 (m, 5 H).

2-Chloro-2-propyl Phenyl Sulfone (1a). Reaction of 1 with CCl_4. A mixture of **1** (0.93 g, 5.05 mmol), CCl_4 (10 mL), *t*-BuOH (10 mL), and KOH (4.0 g, 61 mmol), refluxed for 30 min, provided white crystals (aq EtOH) of **1a** in quantitative yield, mp 89−90 °C. ^{1}H NMR (CCl_4): δ 1.84 (s, 6 H), 7.39−7.73 (m, 3 H), 7.85−8.10 (m, 2 H). Anal. Calcd for $C_9H_{11}ClO_2S$: C, 49.43; H, 5.07; Cl, 16.21; S, 14.66. Found: C, 48.95; H, 5.32, Cl, 16.38; S, 14.55.

Treatment of 1a with Excess KOH−*t*-BuOH. Formation of Phenyl 2-Propenyl Sulfone (1c), 1-Hydroxy-2-propyl Phenyl Sulfone (1d), and 1-*tert*-Butoxy-2-propyl Phenyl Sulfone (1e). A mixture of **1a** (0.354 g, 1.62 mmol) in *t*-BuOH (6 mL) and KOH (3.04 g, 54.3 mmol) was stirred at 25 °C for 1 h, water was added, the mixture was extracted with ether, and the dried extracts were evaporated leaving 0.346 g of colorless oil, which solidified on standing. ^{1}H NMR indicated recovered **1a** along with **1c**, **1d**, and **1e** in a ratio of 18:2:9:5, i.e., ca. 47% of **1a** was converted into various products: δ, **1c**, 1.96 (m, 3 H), 5.73 (q, J = 1.5 Hz, 1 H, =CH trans to SO_2), 6.29 (q, J = 1.2 Hz, 1 H, =CH cis to SO_2); **1d**, 1.26 (d, J = 6.9 Hz, 3 H), 2.88 (dd, J = 5.4, 7.8 Hz, 1 H), 3.30 (m, 1 H), 3.93 (dd, J = 5.4, 7.2 Hz, 1 H); **1e**, 1.07 (s, 9 H), 1.36 (d, J = 7.2 Hz, 3 H), 3.30 (m, 1 H), 3.44 (dd, J = 9.3, 7.2 Hz, 1 H), 3.76 (dd, J = 9.3, 4.8 Hz, 1 H). The aqueous layer was acidified with 2 N HNO_3, aq $AgNO_3$ was added, and the resulting white precipitate was isolated, washed with water and acetone, and dried; 0.108 g of AgCl, 0.75 mmol, i.e., 46.3% of the chlorine contained in the original substrate **1a**, confirmed its conversion into the corresponding equivalents of the products noted. The dehydrochlorination required a very large equivalent excess of KOH relative to the α-chloro sulfone.

2-Bromo-2-propyl Phenyl Sulfone (1b). (a) Reaction of 1 with CBr_4. A mixture of **1** (1.86 g, 10.1 mmol), CBr_4 (33 g, 100 mmol), *t*-BuOH (10 mL), and KOH (4.0 g, 61 mmol) stirred briefly in a cold water, then at 25 °C for ca. 1 h, provided **1b**, which crystallized on being triturated with pentane. Steam distillation removed residual CBr_4 and recrystallization (ligroin) provided white crystals (0.87 g, 33% yield) with mp 94−95 °C. ^{1}H NMR (CCl_4): δ 2.00 (s, 6 H), 7.48−7.75 (m, 3 H), 7.88−8.12 (m, 2 H). Anal. Calcd for $C_9H_{11}BrO_2S$: C, 41.08; H. 4.21; Br, 30.36; S, 12.18. Found: C, 41.31; H, 4.10; Br, 29.91; S, 11.93. The structure was unequivocally characterized by X-ray crystal analysis.[16]

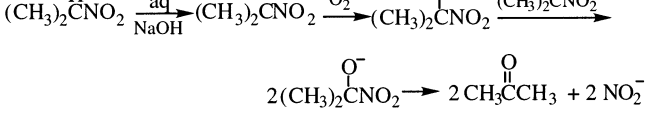
(b) Reaction of 1 with $CBrCl_3$. Formation of 1a and 1b. A mixture of **1** (0.92 g, 5.0 mmol), $CBrCl_3$ (10 mL, 101 mmol), *t*-BuOH (10 mL) and KOH (4.0 g, 61 mmol), treated as described in subsection (a) above, provided an oil that slowly solidified (mp 72−80 °C) shown by ^{1}H NMR to be composed of 24% recovered **1** and 76% of a mixture of **1b** and **1a** in a mole ratio of 80:20. Elemental analysis showed it contained 20.38% Br and 2.34% Cl, which is a mole ratio of 79.5:20.5 of **1b**:**1a**, essentially the same as that indicated by NMR. Varying the equivalent amounts of KOH substantially affected the relative amounts of **1a** and **1b** obtained as well as that of **1c**, often found as a secondary product readily detected from its characteristic ^{1}H NMR resonances (noted above). Similar reactions of **1** with CCl_2Br_2 or CBr_2F_2 instead of $CBrCl_3$ also provided varying yields of **1b**.

(c) Reaction of 1 with *n*-BuLi followed by Br_2, Attached to an Argon-filled Balloon. Formation of 1b, 2,3-Dimethyl-3-benzenesulfonyl-2-butanol (1f), and Benzenesulfonyl Bromide. A flask containing **1** (0.47 g, 2.6 mmol), connected to a vacuum line and an argon-filled balloon, was gently heated. Dried THF was added, and the solution was cooled to −63 °C and stirred while *n*-BuLi-hexane (1.65 mL, 1.55 M *n*-BuLi, 2.6 mmol) was added, then stirred for 1 h longer. A solution of Br_2 (0.13 mL, 2.6 mmol) in hexane (4.45 mL), maintained at −63 °C, was then added, and the mixture was stirred for 2 min, then worked up, leaving a dark oil (0.46 g), which, via column chromatography, afforded crystalline **1b** (41%, mp 90−92 °C), **1f** (49%), and benzenesulfonyl bromide (10%). Purification of **1f** by prep TLC (acetone:hexane 10:90) gave colorless crystals with mp 105.5−107 °C. ^{1}H NMR: δ 1.30 (s, 6 H), 1.50 (s, 6 H), 3.85 (br s, 1 H), 7.45−7.75 (m, 3 H), 7.75−8.00 (m, 2 H). Anal. Calcd for $C_{12}H_{18}O_3S$: C 59.48; H, 7.49; S, 13.23. Found: C, 59.33; H, 7.50; S, 12.95. The same reaction with 2 equiv of Br_2 instead of **1** gave essentially identical results.

Reaction of 1 with *n*-BuLi. The Effect of Air on the Formation of 2,3-Dimethyl-3-benzenesulfonyl-2-butanol (1f), Lithium Benzenesulfinate, and Lithium Benzenesulfonate. A procedure similar to the above was repeated, but without the addition of Br_2. A flask containing **1** (0.096 g, 0.5 mmol) was connected to the vacuum line and a rubber balloon that had been filled with argon 1 h earlier. THF (1.10 mL) was added, the solution was stirred at −63 °C, *n*-BuLi−hexane (0.36 mL, 1.55 M *n*-BuLi, 0.5 mmol) was added, and stirring was continued for 1 h, giving rise to a flocculent precipitate. Ether was added and the white precipitate was collected by filtration, washed with ether, and oven dried (0.052 g) and identified as a mixture of $PhSO_3Li$ (major) and $PhSO_2Li$. IR (Nujol): 1190 cm^{-1} (s, SO_3^-), 1040 cm^{-1} (s, SO_2^-). The combined filtrate and ether washings were dried and concentrated in vacuo leaving **1f**, 0.063 g (95% yield, based on the theoretical formation of 1 mol of **1f** from 2 mol of **1**; see Scheme 12), an oil, which slowly solidified. Its ^{1}H NMR spectrum was the same as that of **1f** shown above. No starting sulfone (**1**) was detected.

The above procedure was followed, except that the balloon was filled with argon 2 h prior to use and the mixture was stirred at −63 °C for only 15 min before being worked up; the yield of **1f** was only 52%, and 38% of **1** was recovered. Repeating this procedure but maintaining the mixture under argon from a balloon that had just been filled, only a 15% yield of **1f** was realized, and 84% of **1** was recovered. Finally, when the initial argon purge was for only 1 min, the stopcock then closed, the THF and *n*-BuLi-hexane added, and the solution stirred for 1 h, recovery of **1** was 100%.

(13) This reaction is analagous to the autoxidation of 2-nitropropane in alkaline solution reported by Russell (Russell, G. A. *J. Am. Chem. Soc.* **1954**, *76*, 1595−1600) and his suggested mechanism:



(14) Walling, C. *Free Radicals in Solution*; Wiley & Sons: New York, 1957; Chapter 9.

(15) Bohme, H.; Gran, H. J. *Ann. Chim.* **1952**, *577*, 68.

(16) Robinson, P. D.; Parady, T. E.; Hou, Y.; Meyers, C. Y. *Acta Crystallogr.* **2001**, Sect. E, *57*, o584−o586.

Source of the Benzenesulfonyl Bromide in the Reaction of 1 with *n*-BuLi followed by Br_2. Reaction of Lithium Benzenesulfinate with Br_2. The mixtures of lithium benzenesulfinate and lithium benzenesulfonate formed in the above reactions were isolated, combined, suspended in THF, and stirred for 1 h at −63 °C and a solution of Br_2 in hexane was added. The mixture was filtered and the filtrate dried and concentrated as a pale yellow oil. IR (Nujol): 1366 cm^{-1} (SO_2 asym), 1170 cm^{-1} (SO_2 sym). ^1H NMR: δ 7.42−7.80 (m, 3 H), 7.88−8.10 (m, 2 H). IR and ^1H NMR results are consistent with those of benzenesulfonyl bromide, whose preparation from a benzenesulfinate salt treated with Br_2 is well documented.[17] Lithium benzenesulfonate similarly treated with Br_2 failed to provide benzenesulfonyl bromide.

Isopropyl 4-Methoxyphenyl Sulfone (2). Colorless oil, bp 125−126 °C/0.08 mm. ^1H NMR: δ 1.28 (d, J = 7 Hz, 6 H), 3.17 (hep, J = 7 Hz, 1 H), 3.89 (s, 3 H), 7.05 (d, J = 9.5 Hz, 2 H), 7.85 (d, J = 9.5 Hz, 2 H). Anal. Calcd for $C_{10}H_{14}O_3S$: C, 56.05; H 6.59; S, 14.96. Found: C, 55.86; H, 6.87; S, 15.20.

2-Chloro-2-propyl 4-Methoxyphenyl Sulfone (2a). Reaction of 2 with CCl_4. A mixture of **2** (0.492 g, 2.30 mmol), *t*-BuOH (2 mL), CCl_4 (5 mL), and KOH (0.82 g, 12 mmol; 5.5 mol equiv relative to **2**) provided 0.503 g of a yellow oil, shown by ^1H NMR to be composed of 0.423 g of **2** (86% recovery) and 0.080 g of **2a** (14% yield). When 12 mol equiv of KOH was used, recovery of **2** was 20% and the yield of **2a** was 79%; with 18 equiv of KOH, the yield of **2a** was 91%; mp 88.5−89.5 °C (ethanol−petroleum ether). ^1H NMR: δ 1.84 (s, 6 H), 3.90 (s, 3 H), 7.07, (d, J = 9.5 Hz, 2 H), 7.92 (d, J = 9.5 Hz, 2 H). Anal. Calcd for $C_{10}H_{13}ClO_3S$: C, 48.29; H, 5.27; Cl, 14.25; S, 12.89. Found: C, 48.32; H, 5.28; Cl, 14.53; S, 12.96.

2-Bromo-2-propyl 4-methoxyphenyl Sulfone (2b). (a) Reaction of 2 with CBr_4. A mixture of **2** (2.14 g, 10 mmol), *t*-BuOH (20 mL), CBr_4 (33.2 g, 100 mmol), and KOH (12.0 g, 180 mmol), stirred for 1 h at 10 °C, provided an oil which, after the residual CBr_4 was removed by vacuum distillation, was shown by NMR to be composed of **2** (84% recovery) and **2b** (16% yield). Compound **2b** was isolated by column chromatography (silica gel; benzene−$CHCl_3$) as white crystals with mp 72−73 °C (ethanol−petroleum ether). ^1H NMR: δ 2.05 (s, 6 H), 3.90 (s, 3 H), 7.07 (d, J = 9.5 Hz, 2 H), 7.92 (d, J = 9.5 Hz, 2 H). Anal. Calcd for $C_{10}H_{13}BrO_3S$: C, 40.97; H, 4.47; Br, 27.25; S, 10.94. Found: C, 41.04; H, 4.50; Br, 27.03; S, 10.76.

(b) Reaction of 2 with $CBrCl_3$. Formation of 2a and 2b. A mixture of **2** (1.07 g, 5 mmol), $CBrCl_3$ (5 mL), *t*-BuOH (5 mL), and KOH (4.0 g, 60 mmol) stirred for 30 min at 25 °C afforded 1.26 g of yellow oil shown by NMR to be composed of recovered **2** (27%), **2b** (43% yield), **2a** (14% yield), and 4-methoxyphenyl 2-propenyl sulfone (16%). The ^1H NMR resonances of the latter's propenyl group, δ 1.95 (m, 3 H, α-CH_3), 5.68 (m 1 H, =CH trans to SO_2), 6.23 (m, 1 H, =CH cis to SO_2), were almost identical with those which identified the corresponding phenyl compound **1c**.

Relative Rates of Reaction of 1 vs 2 with $CBrCl_3$. In separate vessels, 5 mmol of **1** and 5 mmol of **2** were treated with $CBrCl_3$ (5 mL), *t*-BuOH (5 mL), and KOH (30 mmol). Each mixture was stirred for 10 min at 0 °C. Recovery of **1** was 78%, the yield of **1b** was18%, and that of **1a** was 4%, while 93% of **2** was recovered, the yield of **2b** was 5.5%, and that of **2a** was 1.5%.

Isopropyl Pentachlorophenyl Sulfone (3). Isopropyl pentachlorophenyl sulfide was prepared from pentachlorobenzenethiol [mp 242−243 °C (lit.[18] mp 241.5−242 °C)] and 2-bromopropane [mp 66−67 °C (ethanol)]. ^1H NMR: δ 1.26 (d, J = 6.5 Hz, 6 H), 3.58 (hep, J = 6.5 Hz, 1 H). Anal. Calcd for $C_9H_7Cl_5S$: C, 33.31; H, 2.17; Cl, 54.63; S, 9.88. Found: C, 33.24; H, 2.09; Cl, 54.49; S, 9.76. The sulfide was quantitatively converted into **3** as white crystals with mp 135.5−136 °C (ethanol). ^1H NMR: δ 1.50 (d, J = 6.5 Hz, 6 H), 3.88 (hep, J = 6.5 Hz, 1 H). Anal. Calcd for $C_9H_7Cl_5O_2S$: C, 30.30; H, 1.98; Cl, 49.73; S, 8.99. Found: C, 30.40; H, 2.05; Cl, 49.61; S, 8.86. Sulfone **3** was almost quantitatively recovered when treated with KOH−*t*-BuOH at 25 °C for 1 h.

2-Chloro-2-propyl Pentachlorophenyl Sulfone (3a). A mixture of **3** (1.78 g, 5 mmol), CCl_4 (6 mL), *t*-BuOH (10 mL), and KOH (4.0 g, 70 mmol), stirred for 1 h at 25 °C, provided 1.54 g of yellow crystals, shown by ^1H NMR to be composed of **3a** (76% yield) and recovered **3** (3.2%). Trituration with ethanol washed away **3**, leaving **3a** with mp 195−196 °C (ethanol). ^1H NMR: δ 2.11 (s). Anal. Calcd for $C_9H_6Cl_6O_2S$: C, 27.65; H, 1.55; Cl, 54.41; S, 8.20. Found: C, 27.68; H, 1.55; Cl, 54.26; S, 8.09.

2-Bromo-2-propyl Pentachlorophenyl Sulfone (3b). The addition of KOH (0.80 g, 14 mmol) to a stirred mixture of **3** (0.71 g, 2 mmol), $CBrCl_3$ (5 mL), and *t*-BuOH (5 mL) led to a vigorous exotherm. The mixture was immediately cooled in an ice bath and stirred at 25 °C for 20 min, to provide 0.80 g of yellow crystals shown by ^1H NMR to be composed of **3b** (80% yield), **3a** (4.2% yield), and recovered **3** (10%). Recrystallization (benzene) afforded hair-like white needles of **3b** with mp 211−213 °C, not suitable for X-ray analysis. ^1H NMR: δ 2.24 (s). Anal. Calcd for $C_9H_6BrCl_5O_2S$: C, 24.83; H, 1.39; Br, 18.35; Cl, 40.72; S, 7.36. Found: C, 24.84; H, 1.43; Br, 18.43; Cl, 40.90; S, 7.36.

2-Chloro-2-propyl Mesityl Sulfone (4a). Reaction of Isopropyl Mesityl Sulfone (4) with CCl_4. (a) For 1 h. Sulfone **4** was prepared as reported[19] with mp 74.5−76 °C (lit.[19] mp 80 °C). ^1H NMR: δ 1.33, (d, J = 7 Hz, 6 H), 2.27 (s, 3 H), 2.68 (s, 6 H), 3.28 (hep, J = 7 Hz, 1 H), 6.98 (s, 2 H). A mixture of **4** (0.226 g, 1 mmol), CCl_4 (1 mL, 10.4 mmol), *t*-BuOH (1 mL), and KOH (1.2 g, 18 mmol) stirred at 25 °C for 1 h provided a viscous yellow oil shown by NMR to be composed of 0.096 g (37% yield) of **4a** and 0.142 g (63%) of recovered **4**. White crystalline **4a** was obtained via column chromatography (silica gel; benzene−chloroform) with mp 87−89 °C (petroleum ether). ^1H NMR: δ 1.90 (s, 6 H), 2.30 (s, 3 H), 2.74 (s, 6 H), 6.98 (s, 2 H). Anal. Calcd for $C_{12}H_{17}ClO_2S$: C, 55.27; H 6.57; Cl, 13.59; S, 12.29. Found: C, 55.40; H, 6.65; Cl, 13.63; S, 12.06. The crystals were unequivocally characterized by X-ray analysis.[20]

The aqueous residue from the workup was acidified with 2 N HNO_3, a 5% $AgNO_3$ solution was added, and the mixture was washed with ether. The AgCl precipitate was collected and dried: 0.524 g, 3.65 mmol, which represents about four times the amount of Cl^- expected from this reaction in which 63% of **4** was recovered and only 37% of **4a** was obtained. The ether washings were washed with brine, dried, and concentrated to a yellow oil, 0.52 g, whose respective IR and ^1H spectra were identical with those of formic acid, which we have previously found to form from the reaction of KOH with the Cl_2C: formed in similar α-chlorinations with CCl_4.[1,2]

(b) For 7.5 h. Formation of 4a, 2-Chloro-2-propyl 4-(5-Dichloromethyl-1,3-xylyl) Sulfone (4c), and Possibly 1-*tert*-Butoxy-2-chloro-2-propyl 4-(5-Dichloromethyl-1,3-xylyl) Sulfone (4d). A mixture of **4** (1.13 g, 5 mmol), CCl_4 (5 mL, 51.8 mmol), *t*-BuOH (5 mL), and KOH (5.85 g, 90 mmol) stirred at 25 °C for 4 h provided a viscous oil, which was treated again with the same amounts of CCl_4, *t*-BuOH, and KOH for an additional 3.5 h, to give a yellow oil, 1.18 g. Column chromatography (silica gel) led to the isolation of **4a** (1.56 mmol, 31.2% yield) as white crystals with mp 89.5−90.5 °C (petroleum ether) (see above); **4c** (0.22 mol, 4.4% yield) as white crystals with mp 123−124 °C ((petroleum ether) [^1H NMR: δ 1.93 (s, 6 H), 2.44 (s, 3 H), 2.77 (s, 3 H), 7.18 (s, 1 H), 7.96 (s, 1 H), 8.15 (s, 1 H). Anal. Calcd for $C_{12}H_{15}Cl_3SO_2$: C, 43.72; H, 4.59; Cl, 32.26; S, 9.73. Found: C, 43.99; H, 4.57;

(17) Suter, C. M. *The Organic Chemistry of Sulfur*, reprinted ed.; Intra-Science Research Foundation: Santa Monica, CA, 1969; p 513 and references therein.

(18) Lucas, C. R.; Peach, M. E. *Can. J. Chem.* **1970**, *48*, 1869−1875.

(19) Shostakovskii, S. M.; Bobrov, A. V. *Zh. Org. Khim.* **1969**, *5*, 908−913.; *J. Org. Chem. USSR (Engl. Transl.)* **1969**, *5*, 896−900.

(20) Meyers, C. Y.; Hua, D. H.; Hou, Y.; Robinson, P. D. *Acta Crystallogr.* **2001**, Sect. E, *57*, o587−o589.

Cl, 32.48; S, 9.94]; a compound suggested by ^{1}H NMR to be **4d** (1.56 mmol, 2.4% yield) [^{1}H NMR: δ 1.16 (s, 9 H), 1.90 (s, 3 H), 2.44 (s, 3 H), 2.77 (s, 3 H), 7.18 (s, 1 H), 7.96 (s, 1 H), 8.15 (s, 1 H)]; and **4** (2.89 mmol, 57.8% recovery) with mp 73.5−74.5 °C.

Treatment of CCl_4 with KOH−*t*-BuOH. A mixture of KOH (1.20 g, 18.0 mmol), CCl_4 (1 mL, 10.3 mmol), and *t*-BuOH (1 mL) was stirred for 1 h at 25 °C, acidified with 1 N HNO_3, and washed with ether, a 5% solution of $AgNO_3$ was added, and the precipitated AgCl was isolated and dried: 0.0450 g, 0.30 mmol, amounting to only 0.75% decomposition of CCl_4 from its direct reaction with excess KOH.

Failure of α-Bromination of Isopropyl Mesityl Sulfone (4). (a) With CBr_4−KOH−*t*-BuOH. The identical procedure described for the bromination of **1** to **1b** with CBr_4 was followed. A mixture of **4** (0.452 g, 2 mmol), CBr_4 (6.64 g, 20 mmol), *t*-BuOH (10 mL), and KOH (0.800 g, 10.7 mmol) was stirred for 1 h at 25 °C. Crystalline **4**, 0.430 g (95%), was recovered. There was no indication of the formation of α-bromoisopropyl mesityl sulfone (**4b**).

(b) With $CBrCl_3$−KOH−*t*-BuOH.[5] The same procedure described for the conversion of **1** to **1a** and **1b** with $CBrCl_3$ was followed. A mixture of **4** (0.226 g, 1 mmol), $CBrCl_3$ (1 mL), *t*-BuOH (1 mL), and KOH (0.400 g, 6.1 mmol) was stirred for 1 h at 25 °C. Again, crystalline **4** (0.210 g (93%) was recovered; neither **4b** nor **4a** was detected. The aqueous residue from the workup was acidified with 2 N HNO_3 and treated with 5% aq $AgNO_3$, which provided 0.48 mmol of AgBr and 1.4 mmol of AgCl. In light of the fact that virtually all of **4** was recovered, the amount of halide ion observed here is exceptionally high. Extending this treatment for 24 h likewise afforded only near-quantitative recovery of **4**.

2-Bromo-2-propyl Mesityl Sulfone (4b). Bromination of 4 with *n*-BuLi Followed by Bromine. (a) Reaction Maintained under Argon by a Tube Directly Attached to the Argon Cylinder. In a sealed flask, a solution of **4** (0.476 g, 2.1 mmol), THF (5 mL), and *n*-BuLi-hexane (1.2 mL, 2.6 mmol of *n*-BuLi), maintained between −70 and −60 °C and under argon via a Tygon tube *directly attached to the argon cylinder*, was stirred for 1 h. A bromine−hexanes solution (2.8 mL, 1.126 M, 3.15 mmol of Br_2) was added, and the mixture was stirred for 30 min at −65 °C, diluted with ether, and worked up, giving a yellow oil shown by ^{1}H NMR to be mainly **4b**. Chromatographic purification (silica gel, 20:1 hexanes−ethyl acetate) provided 0.438 g (69% yield) of **4b** as a yellow solid: recrystallization (hexanes) provided colorless square plates with mp 87−88 °C. ^{1}H NMR: δ 2.07 (s, 6H), 2.33 (s, 3H), 2.78 (s, 6H), 7.11 (s, 2H). ^{13}C NMR: δ 21.01, 24.46, 28.60, 77.88, 127.14, 132.76, 142.99, 144.07. Anal. Calcd for $C_{12}H_{17}BrO_2S$: C, 47.22; H, 5.61; S, 10.50; Br, 26.18. Found: C, 47.04; H, 5.59; S, 10.58; Br, 26.25. The structure of **4b** was unequivocally characterized by X-ray crystal analysis.[5,6]

(b) Reaction Maintained under Argon from an Argon-Filled Balloon. Formation of 4b, 2,3-Dimethyl-3-mesitylenesulfonyl-2-butanol (4e), Mesitylenesulfonyl Bromide, and Bromomesitylene. A flask containing **4** (0.37 g. 1.6 mmol) and connected to a rubber balloon previously filled with argon was purged with argon from the balloon for several minutes before THF (3.25 mL) followed by *n*-BuLi−hexane (1.55 M, 1.1 mL, 1.7 mmol) were added. The mixture was stirred for 1 h at −63 °C while *being maintained under argon from the balloon*, Br_2 (0.17 mL, 3.3 mmol) in hexane (3.25 mL) was then added, and stirring was continued for 1.5 h at −55 °C. Ether and water were then added and the mixture worked up as usual, leaving 0.42 g of yellow oil, which was column chromatographed (silica gel).

Fraction 1 (eluent: benzene−petroleum ether 20:80): bromomesitylene (0.031 g, 6% yield) (^{1}H NMR δ 2.20 (s, 3 H), 2.33 (s, 6 H), 6.87 (s, 2 H), and minor extraneous singlets at δ 1.85 and 1.21.

Fraction 2 (eluent: benzene−petroleum ether 40:60): mesitylenesulfonyl bromide (0.020 g, 5% yield) with mp (crude) 76−86 °C (lit.[21] mp 85−86 °C). ^{1}H NMR: δ 2.35 (s, 3 H), 2.75 (s, 6 H), 6.98 (s, 2 H).

Fraction 3 (eluent, as above): **4b**, 0.22 g (48% yield). The mp and NMR spectra were virtually identical with those for **4** noted in subsection (a) above.

Fraction 4 (eluent: benzene−CH_2Cl_2 10:90; then EtOAc−CH_2Cl_2 10:90): 2,3-dimethyl-3-mesitylenesulfonyl-2-butanol (**4e**, 0.12 g). Purification via thick layer chromatography (silica gel plate, eluent: acetone−hexane 10:40) (0.083 g, 37% yield) gave white crystals (pentane) with mp 105.5−107 °C. ^{1}H NMR: δ 1.34 (s, 6 H), 1.48 (s, 6 H), 2.30 (s, 3 H), 2.71 (s, 6 H), 4.23 (s, 1 H), 6.99 (s, 2 H). Anal. Calcd for $C_{15}H_{24}O_3S$: C, 63.35; H, 8.51; S, 11.27. Found: C, 63.25; H, 8.68; S, 11.00.

Formation of 4a and 4b from Reaction of 4 with *n*-BuLi Followed by $CBrCl_3$. To solution of **4** (0.225 g, 1 mmol) in THF (5 mL) maintained at −70 to −60 °C was added *n*-BuLi in hexane (2.2 M, 0.6 mL, 1.3 mmol) and the mixture was stirred for 15 min. The cold bath was removed, $CBrCl_3$ (0.16 mL, 1.6 mmol) was injected, and the mixture was stirred at 25 °C for 2 h, then worked up: 0.21 g of yellow oil shown by ^{1}H NMR to be composed of **4b**, **4a**, and **4** in a molar ratio of 1.54:1.09:1.0, i.e., 42% bromination, 30% chlorination, and 28% recovery of **4**.

Treatment of 1 with $CBrCl_3$−KOH−*t*-BuOH which was Previously Stirred for 1 h. A mixture of KOH, *t*-BuOH (1 mL), and $CBrCl_3$ (1.40 g, 7.1 mmol) was stirred at 25 °C under argon for 1 h. Sulfone **1** (0.203 g, 1.09 mmol) was *then* added and the mixture was stirred for another 1 h. A light yellow oil (0.203 g) was obtained, shown by ^{1}H NMR to be composed of **1**, **1b**, and **1a** in a mole ratio of 87:4:1, i.e., only 5.4% of **1** underwent halogenation.

Failure of Reductive Debromination of 4b with $CHCl_3$−KOH−*t*-BuOH. KOH (1.14 g) was added to a stirred solution of **4b** (0.129 g 0.42 mmol) in *t*-BuOH (1 mL) and $CHCl_3$ (1 mL), and the mixture was cooled in an ice bath, then stirred at 25 °C and monitored by TLC after 30, 45, and 90 min and 2.5 h, all of which showed the presence mainly of **4b**. The mixture, then worked up and column chromatographed (silica gel; hexanes−ethyl acetate 5:1), provided only **4b**, 0.120 g (93% recovery).

Reaction of $CBrCl_3$ with KOH−*t*-BuOH and with *t*-Bu−O−Li−*t*-BuOH. A mixture of KOH (4.0 g, 60 mmol), $CBrCl_3$ (10 mL, 101.5 mmol), and *t*-BuOH (10 mL) was stirred vigorously at 25 °C for 1 h. A very small sample of the suspended material was withdrawn and dissolved in water; litmus paper indicated neutral pH. The main mixture was acidified with 1 N HNO_3 and washed with ether, and a 5% aq solution of $AgNO_3$ was added to the aq solution. The precipitated silver halide, washed with water and dried, weighed 1.92 g (3.1 mmol of AgBr and 9.3 mmol of AgCl, assuming a molar ratio of 1 AgBr:3 AgCl). That is, much of the KOH was used up rapidly in reacting with the $CBrCl_3$ leading to the formation of KBr, KCl, HC(O)OK, etc.[1,2]

In a similar procedure, a solution of *t*-BuOH (3 mL) into which *n*-BuLi in hexane (3.5 mL, 2.2 M, 7.8 mmol) was injected was flushed with argon and cooled in a ice−water bath, and $CBrCl_3$ (1 mL, 10.15 mmol) was added. The mixture was stirred at 25 °C for 1 h, then acidified with HNO_3, and excess aq $AgNO_3$ was added. The precipitated silver halides were washed and dried: 0.183 g, virtually the same as found in the reaction with KOH, on a per-mole basis.

Treatment of 4 with KOH−*t*-BuOD. A suspension of **4** (0.45 g, 2 mmol) and KOH (0.8 g, 12 mmol) in *t*-BuOD (2 mL) was cooled in an ice−water bath for 2 min then stirred at 25 °C. Small samples were taken at successive intervals and put into small vials containing ether; dilute aq HCl was then added. Since not all of **4** was dissolved after 36 min, another 2 mL of *t*-BuOD was then injected into the stirred mixture, followed by the addition of ether and, 24 min later, aq HCl,

(21) Huthmacher, K.; Effenberger, F. *Chem. Ber.* **1976**, *109*, 2315−2326.

i.e., 1 h total reaction time. The respective ether layers from the removed samples were separated, dried, and evaporated leaving colorless crystals composed of **4** and **4**-α-D. The amount of α-deuteration was determined by ^{1}H NMR: 2 min, 2.4%; 6 min, 7.7%; 11 min, 11%; 16 min, 25%; 26 min, 29.2%; and 36 min, 29%.

Treatment of 4 with $CBrCl_3$−KOH−*t*-BuOD. The above procedure was followed, except that $CBrCl_3$ (0.8 g, 14.2 mmol) was present, dissolved in the *t*-BuOD (2 mL). This solution was added to a mixture of **4** (0.45 g, 2 mmol) and KOH (0.8 g. 12.1 mmol), and the mixture was cooled in an ice bath for 2 min then stirred at 25 °C. At intervals of 5, 10, 16, 26, and 36 min, small samples were removed and diluted with ether and dilute HCl. After 1 h, the main reaction mixture was similarly treated. The respective ether layers were separated, dried, and evaporated in vacuo leaving a crystalline mass, shown by ^{1}H NMR to be only *undeuterated* **4**, i.e., no **4b** was found and no deuterium was incorporated into **4** in any of the samples, including that from the mixture stirred for 1 h. Total recovery of *undeuterated* **4** was over 90%.

2-Chloro-2-propyl Mesityl Ketone (5a). Reaction of Isopropyl Mesityl Ketone (5). (a) With CCl_4. Isopropyl mesityl ketone (**5**)[22] (0.95 g, 5.0 mmol) was added to a stirred mixture of CCl_4 (7.5 mL), KOH (2 g), and *t*-BuOH (3 mL), producing an exotherm. The mixture was cooled to 25 °C, stirred for 5 h, and worked up: 1.12 g (quantitative yield) of **5a**, distilled as a colorless oil, bp 113−115 °C/3 mm. ^{1}H NMR (CCl_4): δ 1.75 (s, 6 H), 2.16 and 2.23 (2 s, 9 H), 6.68 (s, 2 H). Anal. Calcd for $C_{13}H_{17}ClO$: C, 69.50; H, 7.62; Cl, 15.78. Found: C, 70.22; H, 7.70; Cl, 16.10.

(b) With SO_2Cl_2. A solution of **5** (0.85 g, 4.5 mmol) and SO_2Cl_2 (1.68 g, 12.5 mmol) in absolute ether (10 mL) was refluxed for 5 h, then maintained at 25 °C for 13 h and concentrated to an oil, identified by ^{1}H NMR to be composed mainly of **5a** (ca. 90% yield).

2-Bromo-2-propyl Mesityl Ketone (5b). Reaction of Isopropyl Mesityl Ketone (5) with $CBrCl_3$. Ketone **5** (0.30 g, 1.58 mmol) was added to a stirred mixture of KOH (1.20 g), *t*-BuOH (5 mL), and $CBrCl_3$ (5 mL). When the exotherm subsided, stirring was continued at 25 °C for 1 h, providing 0.42 g of an oil that did not solidify on standing (lit.[23] mp 27 °C), identified by NMR as essentially pure **5b** (quantitative yield). ^{1}H NMR (CCl_4): δ 1.86 (s. 6 H), 2.16 (s, 6 H), 2.22 (s, 3 H), 6.63 (s, 2 H). No α-chlorination occurred; some of the sulfones, similarly treated, underwent minor α-chlorination.

α-Bromo sulfone **5b** was also prepared by the reaction of mesitylene with α-bromoisobutyryl bromide (general method of Fisher et al.[23]) as a colorless oil with bp 83−90 °C/0.8 mm (79% yield). ^{1}H NMR ($CDCl_3$): δ 1.97 (s, 6 H), 2.26 (s, 6 H), 2.28 (s, 3 H), 6.86 (s, 2 H). ^{13}C NMR: δ 20.59, 20.89, 31.75, 63.65, 128.29, 132.48, 137.49, 138.16, 208.93. These NMR spectra of **5b** were obtained in $CDCl_3$; that above was taken in CCl_4.

4-Hydroxyphenyl Isopropyl Sulfone (6). A mixture of 4-hydroxybenzenethiol (10.71 g, 85 mmol), 2-bromopropane (17.22 g, 140 mmol), and K_2CO_3 (12.42 g, 90 mmol) in acetone (100 mL) was stirred for 12 h. The mixture was filtered, the filtrate was concentrated leaving an oil, ether was added, and the solution was washed with 2 N NaOH; the washings were acidified with 6 N HCl and extracted with ether and the extracts were concentrated to an oil (13.42 g, 93% yield) of 4-hydroxyphenyl isopropyl sulfide, purified by distillation, with bp 154 °C/12 mm. ^{1}H NMR: δ 1.23 (d, J = 6.5 Hz, 6 H), 3.23 (hep, J = 6.5 Hz, 1 H), 6.25 (br s, 1 H), 6.88 (d, J = 8.5 Hz, 2 H), 7.45 (d, J = 8.5 Hz, 2 H). Anal. Calcd for $C_9H_{12}OS$: C, 64.25; H, 7.19; S, 19.05. Found: C, 64.69; H, 7.22; S, 19.46. A solution of the sulfide (6.77 g, 40 mmol) and 30% H_2O_2 (25 mL, 300 mmol) in 50 mL of acetic acid was heated on a steam bath for 2 h, diluted with water, neutralized with aq $NaHCO_3$, and extracted with ether. Concentration of the dried extracts left 7.44 g (92% yield) of **6**, which was distilled (bp 202−210 °C/0.75 mm) as a colorless oil. ^{1}H NMR: δ 1.29 (d, J = 7 Hz, 6 H), 3.24 (hep, J = 7 Hz, 1 H), 7.04 (d, J = 9 Hz, 2 H), 7.50 (br s, 1 H), 7.72 (d, J = 9 Hz, 2 H). Anal. Calcd for $C_9H_{12}O_3S$: C, 53.98; H, 6.04; S, 16.01. Found: C, 53.96; H, 6.32; S, 16.10.

Failure of α-Halogenation of 6 with Either CCl_4 or $CBrCl_3$. A mixture of KOH (4.0 g, 70 mmol), **6** (1.0 g, 5 mmol), *t*-BuOH (10 mL), and CCl_4 (10 mL) was stirred at 25 °C for 18 h, acidified with 1 N HNO_3 (100 mL), and worked up, providing only **6** (0.95 g, 95% recovery). Repeating this procedure but under reflux (82 °C) for 1 h, only **6** (0.96 g, 96%) was again recovered, and when reflux was continued for 18 h, 93% of **6** was recovered and no products were detected.

Bromination was attempted with a mixture of KOH (1.60 g, 28 mmol), **6** (0.40 g, 2 mmol), *t*-BuOH (7 mL), and $CBrCl_3$ (7 mL), treated as above at 25 °C for 48 h. Workup provided only **6** (0.38 g, 94% recovery). When the mixture was stirred under reflux for 3 h, again only **6** (0.37 g, 96% recovery) was found. There was no indication that **6** underwent halogenation or any other transformation by treatment with CCl_4 or $CBrCl_3$ in KOH−*t*-BuOH.

α-Chlorobenzhydryl Phenyl Sulfone (7a). Benzhydryl phenyl sulfone (**7**) was prepared via the sulfide as reported;[24] white needles, mp 186−187 °C (ethanol; lit. mp 187−188 °C). A mixture of **7** (1.00 g, 3.4 mmol), CCl_4 (10 mL), *t*-BuOH (10 mL), and KOH (4.0 g) was stirred at 3 °C for 30 min, quantitatively yielding crystalline **7a** (1.15 g, 3.4 mmol) as colorless needles (ethanol) with mp 141−141.5 °C. ^{1}H NMR: δ 7.10−7.80 (m). ^{13}C NMR: δ 91.61, 127.85, 127.95, 129.37, 129.91, 131.31, 133.95, 134.70, 136.48. Carrying out the reaction at 25 °C for 4 h provided identical results.

A mixture of **7a** (0.636 g, 1.86 mmol), KOH (3.05 g, 54.5 mmol), and *t*-BuOH (6 mL) stirred at 25 °C for 1 h afforded 0.606 g (95.3% recovery) of **7a** and a trace of **7** (^{1}H NMR: δ 5.29). The aqueous layer from the workup was acidified with 2 N HNO_3 and 5% $AgNO_3$ was added. Only 0.006 g of AgCl was formed, representing 2.2% of the chlorine contained in the original substrate **7a**, which is consistent with the minute conversion of **7a** to **7** by the KOH treatment.

α-Bromobenzhydryl Phenyl Sulfone (7b). KOH (1.0 g, 15 mmol) was added to a stirred solution of **7** (0.77 g, 2.50 mmol) in $CBrCl_3$ (2.5 mL, 25 mmol) and *t*-BuOH (2.5 mL), producing a large exotherm. The thick mixture was stirred in an ice bath for 10 min, then at 25 °C for another 10 min, ether and water were added, and the solids (mp 185−188 °C dec) were removed. The ether layer was evaporated leaving a solid, which was combined with the removed solid material: 0.88 g, shown by NMR to be **7b** (91% yield) as white crystals (from ether) with mp 186.5−187.5 °C dec. ^{1}H NMR: δ 7.03−7.82 (m). Anal. Calcd for $C_{19}H_{15}BrO_2S$: C, 58.92; H, 3.90; Br, 20.63; S, 8.28. Found: C, 59.04; H, 3.91; Br, 20.66; S, 8.19. The α-chloro sulfone **7a** was not coformed in this reaction.

Benzhydryl 4-Hydroxyphenyl Sulfone (8). A mixture of 4-hydroxybenzenethiol (6.3 g, 50 mmol), benzhydryl chloride (10.13 g, 50 mmol), and K_2CO_3 (7.0 g, 50 mmol) in acetone (100 mL) was stirred under reflux for 17 h. The solid inorganic salts were removed by filtration and the filtrate was concentrated leaving a blue viscous oil. The isolated inorganic salts were dissolved in water, the solution was extracted with ether and the extracts were combined with the blue oil, washed with 5% NaOH, and concentrated to provide a viscous blue oil (3.67 g), suggested by ^{1}H NMR to be composed of recovered benzhydryl chloride, diphenylmethane, and 1,4-cyclohexadiene-3-one-6-thione. The NaOH washings were acidified with 6 N HCl and extracted with ether and the dried extracts concentrated, leaving benzhydryl 4-hydroxyphenyl sulfide (11.0 g, 75% yield) as white crystals ($CHCl_3$−pentane) with mp 126.5−127.5 °C. ^{1}H NMR: δ 2.82 (s, 1 H), 5.54 (s, 1 H), 6.69 (d, J =

(22) Klages, A.; Stamm, C. *Chem. Ber.* **1904**, *37*, 924.
(23) Fisher, C. H.; Oakwood, T. S.; Fuson, R. C. *J. Am. Chem. Soc.* **1930**, *52*, 5036−5040.
(24) Bordwell, F. G.; Pitt, B. M. *J. Am. Chem. Soc.* **1955**, *77*, 572.

9 Hz, 2 H), 7.1−7.6 (m, 12 H). Anal. Calcd for $C_{19}H_{16}OS$: C, 78.05; H, 5.52; S, 10.96. Found: C, 77.73; H, 5.46; S, 11.10.

The sulfide was converted to crystalline sulfone **8** (5.64 g, ca. 90% yield) with mp 211−212 °C dec (ethanol−pentane). ^{1}H NMR: δ 3.21 (s, 1 H), 5.68 (s, 1 H), 6.84 (d, J = 9 Hz, 2 H), 7.16−7.83 (m, 12 H). Anal. Calcd for $C_{19}H_{16}O_3S$: C, 70.35; H, 4.97; S, 9.88. Found: C, 70.16; H, 5.08; S, 9.97. Unlike **8**, the corresponding 4-methoxyphenyl sulfone (**9**) (below) melts sharply *without* decomposition.

α-Chlorobenzhydryl 4-Hydroxyphenyl Sulfone (8a). Reaction of 8 with CCl_4. To a solution of **8** (1.62 g, 5 mmol) in CCl_4 (30 mL) and *t*-BuOH (30 mL) at 5 °C was added KOH (8.0 g, 140 mmol), the mixture was stirred at 25 °C for 3 h and 1 N HNO_3 (100 mL) was then added. Workup provided **8a** (1.77 g, 99% yield) as white crystals (benzene) with mp 149−149.5 °C dec. ^{1}H NMR: δ 3.10 (s, b, 1 H), 6.79 (d, J = 9 Hz, 2 H), 7.1−7.9 (m, 12 H). Anal. Calcd for $C_{19}H_{15}ClO_3S$: C, 63.60; H, 4.21; Cl, 9.88; S, 8.93. Found: C, 63.79; H, 4.24; Cl, 9.88; S, 9.00.

Hydrolytic Fragmentation of 8a with KOH−*t*-BuOH. Formation of Benzophenone and Phenol. A mixture of **8a** (0.359 g, 1.00 mmol), KOH (1.20 g, 18.2 mmol), and *t*-BuOH (6 mL) was stirred under reflux for 1 h, cooled, acidified with 1 N HNO_3 (100 mL), and extracted with ether. The extracts were concentrated and the residue column chromatograhed (silica gel; $CHCl_3$−petroleum ether), providing benzophenone (0.180 g, 99% yield), phenol (0.028 g, 30% yield), and unidentified material (0.10 g). Addition of a 5% solution of $AgNO_3$ to the aqueous residue from the ether extractions precipitated AgCl, 0.137 g, representing 95% fragmentation of **8a**.

Reaction of 8 with $CBrCl_3$ in KOH−*t*-BuOH. In Situ Formation−Hydrolytic Fragmentation of α-Bromobenzhydryl 4-Hydroxyphenyl Sulfone (8b) into Benzophenone as the Major Product. A mixture of **8** (1.35 g, 4.17 mmol), KOH (6.70 g, 102 mmol), $CBrCl_3$ (25 mL), and *t*-BuOH (25 mL) was stirred at 10 °C for 5 min, then at 25 °C for 2 h, diluted with 1 N HNO_3 (120 mL), and extracted with ether. The combined extracts were washed with aq NaOH and concentrated, leaving 0.791 g of dark yellow crystals shown by ^{1}H NMR to be composed of benzophenone (2.97 mmol, 71% yield) and fuchsone (0.125 mmol, 3% yield). The aq NaOH washings were combined, acidified with 1 N HNO_3, and extracted with ether. Concentration of the extracts left dark-colored crystals which were column chromatographed (silica gel; $CHCl_3$−petroleum ether) to provide 0.42 g of a mixture consisting (by TLC) of five compounds, including phenol, possibly 4-hydroxybenzenesulfinic acid, and a small amount of **8b**.

Benzhydryl 4-Methoxyphenyl Sulfone (9). A mixture of 4-methoxybenzenethiol (5.70 g, 40 mmol), benzhydryl chloride (8.25 g, 40 mmol), and K_2CO_3 (8.0 g, 60 mmol) in acetone (50 mL) refluxed for 12 h provided benzhydryl 4-methoxyphenyl sulfide (11.3 g, 91% yield) with mp 87.5−88.5 °C ($CHCl_3$). ^{1}H NMR: δ 3.69 (s, 3 H), 5.34 (s, 1 H), 6.68 (d, J = 9 Hz, 2 H), 7.05−7.55 (m, 12 H). Anal. Calcd for $C_{20}H_{18}OS$: C, 78.39; H, 5.92; S, 10.46. Found: C, 78.50; H, 6.09; S, 10.41. The sulfide (8.20 g, 27 mmol), heated with 30% H_2O_2 (30 mL 260 mmol) in acetic acid on a steam for 2 h, was converted into benzhydryl 4-methoxyphenyl sulfone (**9**) as white crystals (8.36 g, 92% yield) with mp 163.5−164.5 °C ($CHCl_3$−petroleum ether). ^{1}H NMR: δ 3.76 (s, 3 H), 5.30 (s, 1 H), 6.82 (d, J = 9 Hz, 2 H), 7.05−783 (m, 12 H). Anal. Calcd for $C_{20}H_{18}O_3S$: C, 70.98; H, 5.36; S, 9.47. Found: C, 71.16; H, 5.56; S, 9.33.

α-Bromobenzhydryl 4-Methoxyphenyl Sulfone (9b). Reaction of 9 with $CBrCl_3$. A mixture of **9** (1.69 g, 5 mmol), KOH (4.00 g, 61 mmol), *t*-BuOH (30 mL), and $CBrCl_3$ (30 mL) stirred at 25 °C for 30 min provided crystals of **9b** (2.04 g, 98% yield)with mp 169.5−170.5 °C ($CHCl_3$). ^{1}H NMR [$CDCl_3$−$(CD_3)_2C{=}O$]: δ 3.78 (s, 3 H), 6.72 (d, J = 9 Hz, 2 H), 7.10−748 (m, 8 H), 7.50−783 (m, 4 H). Anal. Calcd for $C_{20}H_{17}BrO_3S$: C, 57.56; H, 4.11; Br, 19.15; S, 7.68. Found: C, 57.41; H, 4.12; Br, 19.11; S, 7.60. There was no indication of decomposition of **9b** during its preparation or purification.

Acid-Catalyzed Hydrolytic Fragmentation of 9b. Formation of Benzophenone, 4-Methoxyphenyl 4-Methoxybenzenethiolsulfonate (9c), and Phenol as Major Products. A solution of **9b** (0.417 g, 1.0 mmol) in acetic acid and water (3 mL) was stirred under reflux for 24 h, diluted with water (50 mL), and extracted with ether. Evaporation of the dried extracts left a mass of yellow crystals (0.285 g) that was column chromatographed (silica gel; benzene−petroleum ether) to provide benzophenone (0.162 g, 0.89 mmol, 89% yield), anisole (0.0108 g, 0.10 mmol, 10% yield), unidentified material (0.057 g), and a white crystalline compound suggested by its ^{1}H NMR spectrum and mp 83−84 °C (methanol) to be **9c** (0.062 g, 0.20 mmol (40% yield; lit.[11] mp 86−88 °C)). ^{1}H NMR: δ 3.81 (s, 3 H), 3.85 (s, 3 H), 6.79 (d, J = 9 Hz, 2 H), 6.82 (d, J = 9 Hz), 7.34 (d, J = 9 Hz, 2 H), 7.53 (d, J = 9 Hz, 2 H).

Identical treatment of a solutuon of **9b** (1.50 g, 3.6 mmol) in acetic acid (17 mL), but to which 48% HBr (22 mL) was added, provided a yellow oil (0.994 g) composed of benzophenone (0.640 g, 98% yield), phenol (0.169 g, 50% yield), and unidentified material (0.183 g).

A solution of **9b** (0.417 g, 1 mmol) in dioxane (20 mL) containing 1 mL of water was refluxed for 24 h and extracted with ether. The aqueous residue was acidified with 1 N HNO_3 (10 mL) and a 5% solution of $AgNO_3$ added, affording precipitated AgBr (0.0175 g, 0.093 mmol), i.e., 9% Br^- was generated from the **9b**. The ether extracts were worked up leaving 0.410 g of a semisolid mass that was composed of benzophenone (0.0091 g, 5% yield) and **9b** [0.375 g (90% recovery)]. When **9b** was treated exactly as above but in dry dioxane, no benzophenone was formed and recovery of **9b** was 97%.

α,α-Dichlorobenzyl Phenyl Sulfone (10a). Reaction of Benzyl Phenyl Sulfone (10). (a) With C_2Cl_6 in Aqueous NaOH Under Phase-Transfer Catalysis. Sulfone **10** was prepared as reported,[7] mp 147−148 °C. A mixture of **10** (0.10 g, 0.4 mmol), C_2Cl_6 (0.31 g, 1.3 mmol), Aliquat 336 (0.01 g, 0.025 mmol), 2 mL of CH_2Cl_2, and 50% aq NaOH (0.65 mL, 12 mmol) was stirred for 12 h. Water and CH_2Cl_2 were then added and the organic layer was separated, dried, and concentrated as white crystals of **10a** (0.12 g, 93% yield) with mp 151−152 °C (lit.[25] mp 151−152 °C). ^{1}H NMR: δ 7.23−7.63 (m, 6 H), 7.75 (dd, J = 8 and 2 Hz, 4 H). ^{13}C NMR: δ 99.61 (CCl_2), 127.75, 128.24, 129.47, 130.91, 131.57, 131.97.132.38, 134.79.

(b) With CCl_4−KOH−*t*-BuOH. A stirred solution of **10** with excess CCl_4 in KOH−*t*-BuOH at 25 °C likewise provided **10a** (95% yield).[1a,3a]

Reaction of 10 with 1 Equiv of 10a in KOH−*t*-BuOH. Quantitative Formation of 2 Equiv of α-Chlorobenzyl Phenyl Sulfone (10d). A mixture of **10a** (0.10 g, 0.3 mmol), **10** (0.077 g, 0.3 mmol), and KOH (3.0 g) in *t*-BuOH (10 mL) was stirred at 25 °C for 17 h, then diluted with water and extracted with ether. The combined extracts were dried and evaporated leaving a pale yellow solid (0.16 g, 80% yield), shown by NMR to be exclusively **10d** with mp 180−181 °C (lit.[26] mp 185−186 °C), with no indication of any recovered **10** or **10a**. The overall yield of **10d** was estimated to be well over 90%, its poor solubility in ether accounting for some loss. ^{1}H NMR (very dilute $CDCl_3$): δ 5.65 (s, 1 H), 7.28−7.68 (m, 8 H), 7.75 (dd, J = 8 Hz, 2 Hz, 2 H). A mixture of **10d**−KOH−*t*-BuOH was stirred at 25 °C for 17 h, diluted with water, and extracted with ether; **10d** was ∼100% recovered.

α,α-Dibromobenzyl Phenyl Sulfone (10b). Reaction of 10 with $CBrCl_3$ in Aqueous NaOH Under Phase-Transfer Catalysis. (a) For 1 h At 25 °C. A mixture of **10** (1.50 g, 6.5 mmol), $CBrCl_3$ (20 mL, 200 mmol), CH_2Cl_2 (10 mL), 50% aq NaOH (10 mL, 190 mmol), and Aliquat 336 (0.172 g, 0.42 mmol) was stirred at 25 °C for 1 h, and CH_2Cl_2 (10 mL) was

(25) Shirota, Y.; Nagai, T.; Tokura, N. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 405.

(26) Tuleen, D. L.; Marcum, C. *J. Org. Chem.* **1967**, *32*, 204−206.

added. The organic layer was separated and evaporated in vacuo leaving yellow crystals shown by ^{1}H NMR to be composed of **10b** (2.36 g, 85% yield) and **10** (0.20 g, 13% recovery). Column chromatography (silica gel; methylene chloride/low-boiling petroleum ether) afforded the separation of **10b** as white needles with mp 125.5−126 °C. ^{1}H NMR ($CDCl_3$): δ 7.10−7.65 (m, 8 H), 7.75 (dd, J = 8 and 2 Hz, 2 H). ^{13}C NMR: δ 79.17 (CBr_2), 127.87, 128.22, 130.85, 131.34, 132.39, 133.78, 134.80. Anal. Calcd for $C_{13}H_{10}Br_2O_2S$: C, 40.03; H, 2.58; Br, 40.97; S, 8.22. Found: C 40.14; H, 2.31; Br, 40.72; S, 8.19.

(b) For Increasing Periods of Time. Formation of 10b, α-Bromo-α-Chlorobenzyl Phenyl Sulfone, and 10a. A mixture similar that in subsection a above was stirred at 25 °C, and aliquots (6 mL) were removed at the end of 1, 2, 4, 7, and 12 h and worked up as above. Analysis via ^{13}C NMR indicated that **10b** was initially formed exclusively, and was slowly converted into the α-chloro-α-bromo sulfone during the 12-h period. When the reaction was repeated but stirring was continued for 24 h, the composition of the mass of white crystals that formed was identified by ^{13}C NMR as **10b** (20%; δ 79.25, CBr_2), the α-Cl-α-Br sulfone (55%; δ 90.07, CBrCl), and **10a** (20%; δ 99.69, CCl_2).

Reductive Debromination of α,α-Dibromobenzyl Phenyl Sulfone (10b) to α-Bromobenzyl Phenyl Sulfone (10c) with $CHCl_3$. (a) In Aqueous NaOH/CH_2Cl_2 under Phase-Transfer Catalysis. A mixture of **10b** (0.350 g, 0.90 mmol), Aliquat 336 (0.022 g, 0.054 mmol), 2.0 mL of CH_2Cl_2, and 1.4 mL of a 50% aq solution of NaOH (27 mmol) was stirred at 25 °C for 10 min; $CHCl_3$ (0.72 mL, 8.9 mmol) was then added and stirring was continued for 1 min. Water and CH_2Cl_2 were added and the organic layer was separated and worked up as usual, providing **10c** (0.253 g, 91% yield) as white crystals ($CHCl_3$) with mp 190−192 °C (lit.[10f] mp 193−194 °C). ^{1}H NMR (very dil $CDCl_3$): δ 5.71 (s, 1 H), 7.61−7.25 (m, 8 H), 7.75 (dd, J = 8 Hz, 2 Hz, 2H).

(b) In KOH−*t*-BuOH. A mixture of **10b** and KOH in *t*-BuOH was stirred at 25 °C for a few minutes, $CHCl_3$ was then added, and the mixture was stirred for an additional 1−2 min. Water was added, the mixture was acidified with dil HNO_3 and extracted with ether, and the extracts were dried and evaporated, leaving **10c** in over 90% yield: mp as above.

Failure of Reductive Debromination of α,α-Dibromobenzyl Phenyl Sulfone (10b) with CH_2Cl_2 in Aqueous NaOH Under Phase-Transfer Catalysis. A mixture of **10b** (0.131 g, 0.30 mmol), Aliquat 336 (0.008 g, 0.02 mmol) in CH_2Cl_2 (3.30 mL, 52 mmol), and 0.51 mL of a 50% aq solution of NaOH (9.6 mmol) was stirred at 25 °C for 12 h, then diluted with CH_2Cl_2 and water. The usual workup provided a mass of crystals that was washed with cold pentane to remove residual Aliquat 336 and give white crystals (0.124 g, 95% recovery) of **10b**, confirmed by mp, ^{1}H NMR, IR, and R_f ,which were identical, respectively, to those of the starting material.

Acknowledgment. Special gratitude is expressed to Professor Frederick G. Bordwell for his consultation and input in this investigation. V.M.K. expresses her thanks for a Fulbright Fellowship, and D.H.H. and W.S.M. thank Southern Illinois University for graduate fellowships, during the course of these studies. P.B.S. and S.X. express gratitude for the Graduate Research Assistantships provided them by the Meyers Institute for Interdisciplinary Research in Organic and Medicinal Chemistry at Southern Illinois University. C.Y.M. expresses appreciation for the special research funding associated with his Distinguished Professorship.

JO025781W