

THE RAPID REACTION OF BENZHYDRYL SULFONES WITH  $\text{CCl}_4$ -KOH.  
A NEW ROUTE TO 1,1-DIARYLALKENES<sup>1,2</sup>

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We have previously described reactions of sulfones with  $\text{CCl}_4$ -KOH-t-BuOH in which  $\alpha$ -chloro sulfones (and dichlorocarbene) are initially formed and are usually rapidly transformed in situ into different types of products.<sup>2</sup> Thus, dibenzyl sulfone is monochlorinated and converted into trans-stilbene;<sup>2a-c</sup> di-sec-alkyl sulfones are monochlorinated but are converted mainly into 1,1-dichlorocyclopropanes (: $\text{CCl}_2$ -alkene adducts);<sup>2a,c</sup> di-n-alkyl sulfones are gem-dichlorinated and transformed into cis-1,2-dialkylethenesulfonic acids;<sup>2d-f</sup> and benzyl n-alkyl sulfones are mono- and dichlorinated so that  $\beta$ -alkylstyrenes and cis-1-alkyl-2-phenylethenesulfonic acids are formed.<sup>4</sup>

The remarkable differences in rates, mechanisms, and products of these reactions with various classes of sulfones<sup>5</sup> prompted the investigation of benzhydryl systems. This report describes the rapid, quantitative conversion of benzhydryl sulfones (1)<sup>6</sup> into 1,1-diarylalkenes (4) on treatment with  $\text{CCl}_4$ -KOH-t-BuOH (Table I).<sup>7</sup> In a typical reaction, 4 g of powdered KOH was added to a stirred solution (0-25°) of 1 g of 1 in 10 ml of  $\text{CCl}_4$  and 10 ml of t-BuOH. Within minutes the mixture thickened noticeably; it was diluted with water, extracted with ether, and the extracts were evaporated to provide 4. Under these conditions benzhydryl phenyl sulfone (5) was immediately converted into  $\alpha$ -chlorobenzhydryl phenyl sulfone (6) which was quantitatively isolated. The pathways responsible for these conversions are suggested in Scheme 1.

Scheme 1

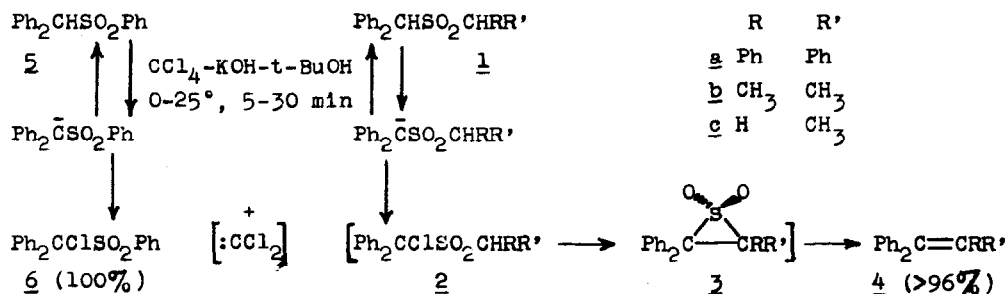
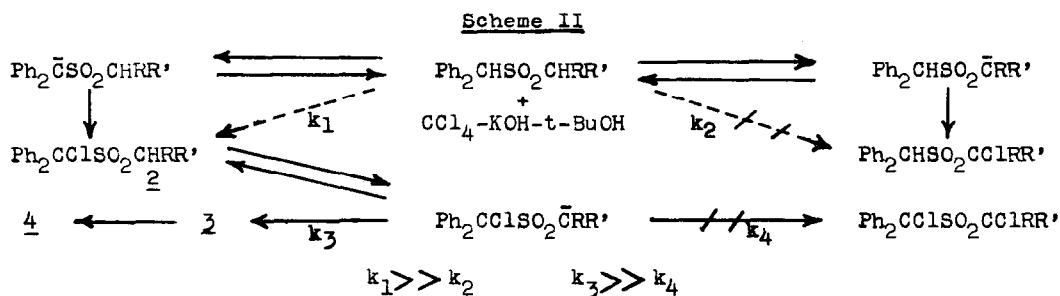


Table I

REACTIONS OF BENZHYDRYL SULFONES WITH $\text{CCl}_4$ -KOH-t-BuOH <sup>a</sup>	
Sulfone (mp, °C) Nmr, $\delta$ $\text{CDCl}_3$	Product <sup>b</sup> (mp, °C) Nmr, $\delta$ $\text{CDCl}_3$
<u>1a</u> $\text{Ph}_2\text{CHSO}_2\text{CHPh}_2$ (192-193) <sup>c</sup> 7.59-7.14 (m, 20 H, Ph) 5.13 (s, 2 H, CH)	<u>4a</u> $\text{Ph}_2\text{C}=\text{CPh}_2$ (221-223) <sup>d</sup> 7.10 (s, Ph) <sup>e</sup>
<u>1b</u> $\text{Ph}_2\text{CHSO}_2\text{CH}(\text{CH}_3)_2$ (191-192) <sup>f</sup> 7.86-7.28 (m, 10 H, Ph) 5.44 (s, 1 H, $\text{CHPh}$ ) 3.04 (hep, 1 H, $\text{CHCH}_3$ ) 1.32 (d, 6 H, $\text{CH}_3$ )	<u>4b</u> $\text{Ph}_2\text{C}=\text{C}(\text{CH}_3)_2$ (oil) <sup>g</sup> 7.11 (s, 10 H, Ph) 1.74 (s, 6 H, $\text{CH}_3$ )
<u>1c</u> $\text{Ph}_2\text{CHSO}_2\text{CH}_2\text{CH}_3$ (134-136) <sup>h</sup> 7.80-7.27 (m, 10 H, Ph) 5.33 (s, 2 H, CH) 2.83 (q, 2 H, $\text{CH}_2$ ) 1.28 (t, 3 H, $\text{CH}_3$ )	<u>4c</u> $\text{Ph}_2\text{C}=\text{CHCH}_3$ (49-51) <sup>i</sup> 7.46-7.02 (m, 10 H, Ph) 6.14 (q, 1 H, CH) 1.70 (d, 3 H, $\text{CH}_3$ )
<u>5</u> $\text{Ph}_2\text{CHSO}_2\text{Ph}$ (186-187) <sup>j</sup> 7.76-7.20 (m, 15 H, Ph) 5.32 (s, 1 H, CH)	<u>6</u> $\text{Ph}_2\text{CClSO}_2\text{Ph}$ (142-143) <sup>k</sup> 7.83-7.23 (m, Ph)

<sup>a</sup> At 0-25°, 5-30 min. <sup>b</sup> All products were isolated in yields >96%.  
<sup>c</sup> Quantitatively decomposes on melting; lit mp 185-186°, H. Dannenberg and A. Rahman, *Chem. Ber.*, **89**, 1625 (1956). <sup>d</sup> Mixed mp with an authentic sample (Aldrich, mp 223-224°) was not depressed. <sup>e</sup> In  $\text{C}_6\text{D}_6$ , broad-base singlet (in 5%  $\text{CDCl}_3$  an authentic sample exhibited a sharp singlet; gratitude is extended to Dr. H. Yamada, Kyushu University, for the latter determination). <sup>f</sup> Lit mp 190-192°, S. Archer, C. M. Suter, and B. J. Tullar, British Patent 668,562 (March 19, 1952). <sup>g</sup> Lit (oil) bp 98°/0.5 mm, E. W. Garbisch, *J. Org. Chem.*, **26**, 4165 (1961). <sup>h</sup> Lit mp 135-136, ref. f. <sup>i</sup> Lit mp 48-48.5°, ref. g; 51-51.5°, G. Wittig and H. D. Frommelt, *Chem. Ber.*, **97**, 3548 (1964). <sup>j</sup> Lit mp 187-188°, F. G. Bordwell and B. M. Pitt, *J. Amer. Chem. Soc.*, **77**, 572 (1955). <sup>k</sup> Not previously reported; elem. anal. satisfactory.

The quantitative conversion of sulfones 1 into the respective alkenes 4 indicates that initial  $\alpha$ -chlorination was followed exclusively by 1,3 elimination; *i.e.*, no dichlorination occurred. In related reactions of sulfones with  $\text{CCl}_4$ -KOH-*t*-BuOH we have observed that initial  $\alpha$ -chlorination is rate determining,  $\alpha$ -phenyl substitution enhances the rate ( $\text{PhCH}_2\text{SO}_2^- \gg \text{RCH}_2\text{SO}_2^-$ ), and the  $\alpha$ -chloro-sulfone intermediates undergo 1,3 elimination and *gem*- $\alpha$ -dichlorination much faster than  $\alpha,\alpha'$ -dichlorination.<sup>1,2,4,5</sup> The chlorination of 5 and the conversions of sulfones 1 into alkenes 4 all proceeded at similar rates, considerably faster than the corresponding reactions of alkyl sulfones. Together, these data justify the conclusion that even sulfones 1b and 1c were initially converted into their respective  $\alpha$ -chlorobenzhydryl sulfones (2), thereby precluding dichlorination (Scheme II).



Although the four benzhydryl sulfones exhibited reactivities of the same order of magnitude, dibenzhydryl sulfone (1a) appeared to react the slowest. When treated at 0-5° for 30 min, sulfones 1b, 1c, and 5 were completely converted, while 1a was largely recovered (although it reacted promptly at 25°).<sup>8</sup> Sulfone 1a might have been expected to react the fastest in view of its slightly greater equilibrium acidity;<sup>9</sup> *i.e.*, of the respective benzhydryl anions, which are required in the rate-determining  $\alpha$ -chlorination, that of 1a would be present in the greatest concentration.<sup>10</sup> However, while increased reactivity of simple sulfones may follow increases in their relative acidities<sup>9,11</sup> (*e.g.*, benzyl vs alkyl sulfones, *vide supra*), factors other than acidity may also influence reactivity. Molecular models demonstrate that 1a is conformationally more constrained than 1b, 1c, and 5, a fact which may account for its reduced reactivity despite its greater acidity. In this regard, the unexpected shielding of the benzhydryl proton of 1a ( $\delta$  5.13) relative to that of 1b, 1c, and 5 ( $\delta$  5.44, 5.33, and 5.32; *cf.* Table I) may also be associated with conformational constraint.

It is noteworthy that the 1,1-diphenylalkenes (4) showed no evidence of reacting with the mol equiv of  $:\text{CCl}_2$  initially generated. In this respect alkenes 4 resemble *trans*-stilbene (similarly formed from dibenzyl sulfone) and

contrast with the tetraalkylalkenes (from di-sec-alkyl sulfones) which were isolated mainly (60-70%) as their adducts.<sup>1,2a,c,5</sup> Electronic and steric effects of the phenyl substituents may account for the contrast.<sup>12</sup> However, the difference in relative rates of decomposition of polyphenyl- va tetraalkyl-substituted thiirane 1,1-dioxides (viz., 3 → 4)<sup>13</sup> may also be responsible, since the  $\text{:CCl}_2$  is generated in a prior step and is competitively consumed in a rapid reaction with  $\text{KOH-t-BuOH}$ .<sup>1,4,14</sup>

#### NOTES AND REFERENCES

1. Taken in part from the PhD Dissertation of W. S. Matthews, Southern Illinois University, 1972.
2. Previous papers in this series: (a) C. Y. Meyers, A. M. Malte, and W. S. Matthews, *J. Amer. Chem. Soc.*, 91, 7510 (1969); (b) C. Y. Meyers and A. M. Malte, *ibid.*, 91, 2123 (1969); (c) C. Y. Meyers, A. M. Malte, and W. S. Matthews, *Quart. Rept. Sulfur Chem.*, 5, 229 (1970); (d) C. Y. Meyers and L. L. Ho, *Tetrahedron Lett.*, 4319 (1972); (e) C. Y. Meyers and I. Sataty, *ibid.*, 4323 (1972); (f) C. Y. Meyers, L. L. Ho, G. J. McCollum, and J. Branca, *ibid.*, 1843 (1973); (g) C. Y. Meyers, L. L. Ho, A. Ohno, M. Kagami, *ibid.*, 4751 (1973).
3. Undergraduate honors-research participants, 1971-72.
4. L.L.Ho, PhD Dissertation, Southern Illinois University, 1974.
5. C. Y. Meyers, US-Japan Symposium on Organosulfur Chemistry, 1971, Abstracts, pp 28-35; C. Y. Meyers, Amer. Chem. Soc. Symposium on New Sulfur Chem. Los Angeles, April 1974 National Meeting, Petroleum Division Preprints.
6. Prepared from the sulfides (benzhydryl chloride + thiol, neat or in acetone or ethanol containing anhydrous  $\text{K}_2\text{CO}_3$ ) by oxidation with  $\text{H}_2\text{O}_2$ -HOAc.
7. Benzhydryl benzyl sulfone provided unexpected results (cf. ref. 2g).
8. In each case dissolution was complete before the KOH was added.
9. pKa values (DMSO as reference):  $\text{Ph}_2\text{CHSO}_2\text{CHPh}_2$  (1a), 19.82 (stat. corr., 20.12);  $\text{Ph}_2\text{CHSO}_2\text{Ph}$  (5), 20.23;  $\text{Ph}_2\text{CHSO}_2\text{CH}_2\text{CH}_3$  (1c), 21.75;  $\text{PhCH}_2\text{SO}_2\text{Ph}$ , 21.42;  $\text{CH}_3\text{CH}_2\text{SO}_2\text{Ph}$ , 29.15. Determined by F. G. Bordwell and W. S. Matthews, whose series of results are now being published. We are grateful to Prof. Bordwell for permission to use these data.
10. The mechanism of chlorination with  $\text{CCl}_4$ -KOH-t-BuOH, now under study, may involve the carbanion directly or the free radical formed from it.
11. F. G. Bordwell, R. H. Imes, and E. C. Steiner, *J. Amer. Chem. Soc.*, 89, 3905 (1967); F. G. Bordwell, D. Phillips, and J. M. Williams, *ibid.*, 90, 426 (1968); F. G. Bordwell and J. M. Williams, *ibid.*, 90, 435 (1968).
12. P. S. Skell and M. S. Cholod, *ibid.*, 91, 7131 (1969); P. S. Skell and A. Y. Garner, *ibid.*, 78, 5430 (1956); R. A. Moss and A. Mamantov, *Tetrahedron Lett.*, 3425 (1968).
13. F. G. Bordwell in "Organosulfur Chemistry. Reviews of Current Research," M. Janssen, Ed., Interscience Publishers, New York, 1967, Chapter 16.
14. J. A. Tykal, PhD Dissertation, Southern Illinois University, 1972.