BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(2), 503—504 (1974)

The Reaction of Styryl Sulfoxides or Sulfones with Boranes[1]

Norioki Miyamoto, Daisuke Fukuoka, Kiitiro Utimoto, and Hitosi Nozaki
Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606

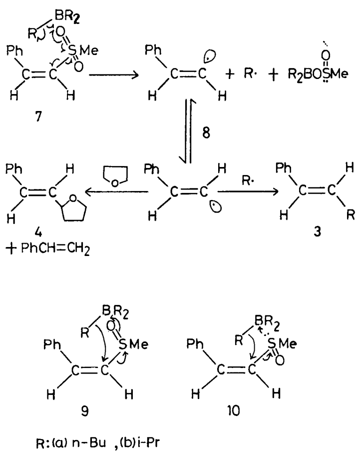
(Received July 24, 1973)

Synopsis. The title reaction produces β-alkylated styrene **3** in preparative yields. The formation of *trans* **3** from the *cis* sulfoxide **2** or the sulfone **7** is explained by considering the vinylic radical **8** as the intermediate.

Studies of the reaction of the trialkylboranes with the α,β-unsaturated carbonyl compounds[2] have opened a valuable route to the β-alkylated ketones. We now wish to describe the reaction of the boranes with the styryl sulfoxides or sulfones,[3] which are formally the S-analogs of the α,β-enones.

The reaction of methyl styryl sulfoxide (**2**) with a trialkylborane (**1**) in THF was performed under reflux in a nitrogen atmosphere; it gave mainly the β-alkylated styrene (**3**),[4] along with *trans*-β-(2-tetrahydrofuryl)styrene (**4**), styrene itself, methyl styryl sulfide (**5**),[5–7] and methyl 2-tetrahydrofuryl sulfide (**6**).[8] Practically the same results were obtained in toluene, except for the formation of *trans*-1,3-diphenylpropene[9] instead of **4**. Each product was characterized by glc analyses prior to the oxidative work-up of the reaction mixture to decompose the remaining **1**. The results are summarized in Table 1.

Whereas no trace of *cis* **3**[4] was produced from the *trans* sulfoxide **2**,[5] a similar reaction of the *cis* isomer of **2** with **1** gave rise to a mixture of *trans* and *cis* **3**.[4] In sharp contrast to the vinylic sulfoxides, both of the corresponding *trans*[5] and *cis*[6] sulfones (**7**) afforded the *trans* **3** exclusively; the *cis* isomer of **3** was not observed in the reaction mixture.[11] The vinylic sulfoxides and sulfones were found to be stable in the absence of **1**.[12] Apparently, the formation of styrene and the solvent-incorporation product (**4** or *trans*-1,3-diphenylpropene) should be ascribed to the formation of the vinylic radical (**8**)[13] resulting from the homolytic cleavage of the C–S bond induced by the attack of **1**. The exclusive formation[14] of the *trans* isomers of **3** and **4** from the *cis* sulfones (**7**)[6] may be ascribed to the rapid equilibration[13] between the sterically-hindered *cis* form and the more reactive *trans* form of the vinylic radical (**8**). Similarly, the formation of the *trans* isomers of **3** and **4** from the *cis* sulfoxide (**2**) can be explained by assuming the vinylic radical (**8**)[13] as the intermediate. Meanwhile, the preferential formation of the *cis* **3** from the *cis* sulfoxide (**2**) is presumably due to the ionic pathway (**9** or **10**), which is reminiscent of the S_N1 mechanism. Thus, the two competing routes would account for the formation of the mixture of *trans* and *cis* **3** from the *cis* sulfoxide (**2**) (Scheme 1).



Scheme 1

The substitution reaction has been successfully extended to the methyl phenethynyl sulfone.[15] The products isolated were found to be the 1-phenylalkyne-1 (*a*,[16] 70%; *b*,[17] 73%),[10] phenyl(2-tetrahydrofuryl)-acetylene (8.4% and 10% respectively),[10] and phenylacetylene (6.3% and 3.2% respectively).[10] The corresponding sulfoxides[15] gave practically the same results, though the reaction proceeded rather sluggishly.

Table 1. Reaction of styryl sulfoxides or sulfones with boranes

Sulfoxide or sulfone	Borane R:	Yield[a] (%)						
		3[b]		**4**	styrene	**5**		**6**[e]
		trans	*cis*			*trans*[c]	*cis*[d]	
trans **2**[c]	*n*-Bu	57	—	11	8.0	3.2	—	*trace*
	i-Pr	68	—	3.0	9.2	2.1	—	*trace*
cis **2**	*n*-Bu	11	58	6.3	5.2	—	1.5	*trace*
	i-Pr	26	46	9.2	5.0	—	1.5	*trace*
trans **7**[c]	*n*-Bu	70	—	10	5.0	—	—	—
	i-Pr	75	—	5.0	8.1	—	—	—
cis **7**[d]	*n*-Bu	76	—	3.2	4.5	—	—	—
	i-Pr	78	—	3.6	4.3	—	—	—

a) See Foot-note 10. b) See Ref. 4. c) See Ref. 5. d) See Ref. 6. e) See Ref. 8.

Experimental

The IR spectra were obtained on a Shimadzu IR-27-G spectrometer in neat liquid films unless otherwise stated. The NMR spectra were obtained on a JEOL-60-H spectrometer in $CDCl_3$. The chemical shifts are given in ppm from the TMS internal standard; the abbreviations of s, d, t, q, and m are used with their common meanings.

Preparation of cis *Methyl Styryl Sulfoxide (**2**).* The oxidation was carried out according to the method of Russell and Ochrymowycz.15) An aqueous solution (50 ml) of $NaIO_4$ (4.5 g, 21 mmol) was added to an acetonitrile (50 ml) solution containing *cis* methyl styryl sulfide6) (**5**, 3.0 g, 20 mmol) at −10 °C. The mixture was stirred at room temperature for 12 hr, filtered to remove $NaIO_3$, and extracted with chloroform. The removal of the solvent *in vacuo* and subsequent column chromatography afforded the *cis* sulfoxide (**2**) (3.1 g, 93%10)) as a viscous oil; bp 130—134 °C/0.3 mmHg IR 1030 cm^{-1}, NMR δ 2.56 (s, 3H, Me), 6.50 (d, 1H, vinylic), and 7.00 ppm (d, 1H, vinylic). Found: C, 65.1; H, 6.1%. Calcd for $C_9H_{10}OS$: C, 65.4; H, 6.2%.

*Reaction of Methyl Styryl Sulfoxide (**2**), the Corresponding Sulfone (**7**), or Methyl Phenethynyl Sulfone with the Boranes (**1**).* The borane (**1**, 3.1 mmol) was added to a THF (20 ml) solution of the sulfoxide or the sulfone (3.0 mmol) under nitrogen. The mixture was stirred under reflux. The progress of the reaction was followed by the tlc analyses of the aliquots. After 48 hr, the reaction mixture was oxidized with alkaline H_2O_2 and extracted twice with ether. The extracts were dried (Na_2SO_4), and concentrated *in vacuo*, and the residue was distilled (or alternatively chromatographed on silica gel). The products were purified by means of preparative glc (HVSG 20%, 2 m, 200°). *trans-β*-(2-Tetrahydrofuryl)styrene (**4**): bp 120—123 °C/4 mmHg, IR 1050 and 963 cm^{-1}; NMR δ 4.33 (m, 1H, methine) and 6.11—6.62 ppm (m, 2H, vinylic). Found: C, 83.1; H, 8.0%. Calcd for $C_{12}H_{14}O$: C, 82.7; H, 8.1%. Phenyl(2-tetrahydrofuryl)acetylene: bp 118—120 °C/5 mmHg. IR 1050 cm^{-1}, NMR δ 4.92 ppm (m, 1H, methine). Found: C, 83.4; H, 6.9%. Calcd for $C_{12}H_{12}O$: C, 83.7; H, 7.0%.

References and Footnotes

1) Part of this work was presented in a preliminary form. See N. Miyamoto, K. Utimoto, and H. Nozaki, *Tetrahedron Lett.*, **1972**, 2895.

2) H. C. Brown and G. W. Kabalka, *J. Amer. Chem. Soc.*, **92**, 710 (1970); *ibid.*, **92**, 714 (1970).

3) (a) The vinylic sulfoxides or sulfones with an aliphatic carbon-chain instead of a phenyl group gave rise to a complicated mixture of products, whose structures have not yet been determined. (b) The styryl sulfide (**5**) failed to react with **1**.

4) K. Yasufuku, S. Hirose, S. Nozakura, and S. Murahashi, This Bulletin, **40**, 2149 (1967).

5) G. A. Russell, E. Sabourin, and G. J. Mikol, *J. Org. Chem.*, **31**, 2854 (1966).

6) W. E. Truce and J. A. Simms, *J. Amer. Chem. Soc.*, **78**, 2756 (1956).

7) The reduction of the sulfoxide with **1** has been recorded with respect to dimethyl sulfoxide. See A. Arase, Y. Masuda, M. Itoh, M. Itoh, and A. Suzuki, *Nippon Kagaku Kaishi*, **1972**, 395.

8) H. C. Brown and M. M. Midland, *J. Amer. Chem. Soc.*, **93**, 3291 (1971).

9) M. Tout and M. Guyard, *Bull. Soc. Chim. Fr.*, **1947**, 1086.

10) The yields were based on the compounds containing the sulfur atom.

11) The isomerization of the sulfoxide **2** or the sulfone **7** initially employed was not observed upon the NMR analyses during the reaction.

12) The heating of **2** or **7** dissolved in THF for 48 hr afforded only a trace of **4** (<0.1%) besides the recovered **2** or **7**.

13) O. Simamura, "Topics in Stereochemistry," Vol. 4, ed. by E. L. Eliel and N. L. Allinger, Wiley-Interscience, New York (1969), p. 1.

14) The addition-elimination mechanism for the formation of the *β*-alkylstyrene **3** seems to be improbable, if it involves the 1,2-addition of **1** to the double bond of **7** and the following vicinal elimination of R_2B–SO_2Me. This is because that the more electron-rich sulfide **5** than the sulfone **7** failed to react with **1**. See footnote **3b**.

15) G. A. Russell and L. A. Ochrymowycz, *J. Org. Chem.*, **35**, 2107 (1970).

16) H. K. Black, D. H. S. Horn, and B. C. L. Weedon, *J. Chem. Soc.*, **1954**, 1704.

17) H. H. Schlubach and K. Reppenning, *Ann. Chem.*, **614**, 37 (1958).