The Reaction of Sodium Methoxide with α-Bromobenzyl Sulfone and with 2,3-Diphenylthiirene 1,1-Dioxide

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Kinetic and product determination studies have shown that $(PhCHBr)_2SO_2$ (**1**) reacts with methoxide ion in methanol to give 2-bromo-2,3-diphenylthiirane 1,1-dioxide (**3**, not isolated), which is rapidly converted into 2,3-diphenylthiirene 1,1-dioxide (**4**). The latter cannot be isolated under these conditions, since it too reacts very rapidly with base. However, a steady-state concentration of **4** was detected spectroscopically. In the absence of base the decomposition of **4** (synthetic) to diphenylacetylene (**8**) was over four powers of 10 slower than that of its saturated analog (to *trans*-stilbene) despite the greater strain in **4**. Photolysis of **4** resulted in a relatively rapid conversion into **8**. With methoxide ion **4** underwent competitive first-order reactions to give methyl *cis*-1,2-diphenylethenesulfonate (**6**) and **8**. Reaction of **1** with hydroxide ion in aqueous dioxane gave small amounts of *cis*- and *trans*-1-bromo-1,2-diphenylethylene (derived from **3**) in addition to **6** (as the salt) and **8**. Similar results were obtained with potassium *t*-butoxide in *t*-butyl alcohol.

On treatment with sodium hydroxide in aqueous dioxane α,α- and α,α′-dihalo sulfones are known to form ethenesulfonates,[2] alkenes,[3] alkynes,[3,4] and vinyl halides.[4] Paquette and coworkers[4] have recently presented convincing evidence for the formation of halothiirane 1,1-dioxide and thiirene 1,1-dioxide intermediates in these reactions and have elucidated most of the paths by which they react.

The product and kinetic studies described in the present paper provide additional information concerning the detailed steps and mechanisms occurring in these reactions.

Evidence for a Thiirene 1,1-Dioxide Intermediate.—Reaction of α-bromobenzyl sulfone (**1**) with sodium methoxide in methanol at 0° was observed to give a rapid and essentially quantitative release of bromide ion $t_{1/2}$ = 25 sec with 1 *M* base. If the reaction mixture was processed after a short time, the major product was methyl *cis*-1,2-diphenylethenesulfonate (**6**). The latter reacted slowly with methoxide ion to form sodium *cis*-1,2-diphenylethenesulfonate (**7**). Besides the sulfonates (**6** and **7**), 16% of diphenylacetylene (**8**) was formed. When the reaction was carried out in refluxing methanol (65°), the amount of diphenylacetylene was increased to 28%. Experiments carried out with 2,3-diphenylthiirene 1,1-dioxide (**4**) at 0 and at 65° under comparable conditions gave the same ratios of diphenylacetylene to total sulfonates (**6** plus **7**) as were obtained from **1** (Table I).[5]

The observation that the ratio of **6** plus **7** to **8** varied in an identical manner with changing temperature for and for **4** (from 4.7:1 at 0° to 2.3:1 at 65°) constitutes strong evidence for the formation of **4** as an intermediate in the reaction of **1** with methoxide ion. These results suggest that **1** reacts quantitatively with methoxide ion in the manner shown to form **4**, which, in turn, is converted in competitive reactions to **6** and **8**. The over-all scheme is comparable with that suggested earlier,[3,4] except that the decomposition **4** → **8** is represented as a methoxide ion promoted reaction instead of a thermal decomposition (*vide infra*).

TABLE I

PRODUCT ANALYSES FOR THE REACTION OF α-BROMOBENZYL SULFONE (**1**) AND 2,3-DIPHENYLTHIIRENE 1,1-DIOXIDE (**4**) WITH SODIUM METHOXIDE IN METHANOL

Compound	Temp, °C	$[MeO^-]$, *M*	PhC≡CPh,[a] %	PhCH=CPhSO$_3$H,[b] %
1	0	0.46	16	75
1	0	2.0	17	75
4	0	0.46	16	75
4	0	2.0	16	75
4	15	0.46	19	72
4	25	0.46	21	70
4	65	0.46	28	65
4	65	2.0	28	65
1	65	0.46	28	65
1	65	2.0	28	65

[a] By vapor phase chromatographic (vpc) analysis. [b] Isolated as the *p*-toluidinium salt.

The formation of **3** from **1** has strong precedent from the work of Paquette,[4] and in the behavior of $PhCH_2SO_2CHBrPh$ (**9**), the monobromo analog of **1**.[6] Reversible formation of carbanion **2** is expected from the evidence accumulated concerning the mechanism of the reaction with **9**.[6]

Episulfones, such as **3**, are known to be subject to base-initiated decomposition to form alkenes,[7] but none of the expected product (PhCBr=CHPh) from this mode of action was observed with sodium methoxide in methanol.[8] Instead, dehydrobromination to **4** occurred exclusively.

The rate of reaction of saturated episulfone, such as that formed from **9**, with methoxide ion is known to be rapid compared to its rate of formation from the parent halo sulfone.[6,7] In view of the demonstrated thermal stability of **4**,[9] and the possibility that it possesses aromatic character,[9] there was some reason to believe that **4** might be more stable toward base than its saturated analog (the episulfone from **9**) and might even be iso-

(1) National Institutes of Health Predoctoral Fellow, 1964–1966.

(2) L. Ramberg and B. Bäcklund, *Ark. Kemi Mineral. Geol.*, **13A**, No. 27 (1940).

(3) F. Scholnick, Ph.D. Dissertation, University of Pennsylvania, Philadelphi, Pa., 1955; *Dissertation Abstr.*, **15**, 708 (1955).

(4) (a) L. A. Paquette, *J. Amer. Chem. Soc.*, **86**, 4089 (1964); (b) L. A. Paquette and L. S. Wittenbrook, *ibid.*, **89**, 4483 (1967); (c) L. A. Paquette, L. S. Wittenbrook, and V. V. Kane, *ibid.*, **89**, 4487 (1967).

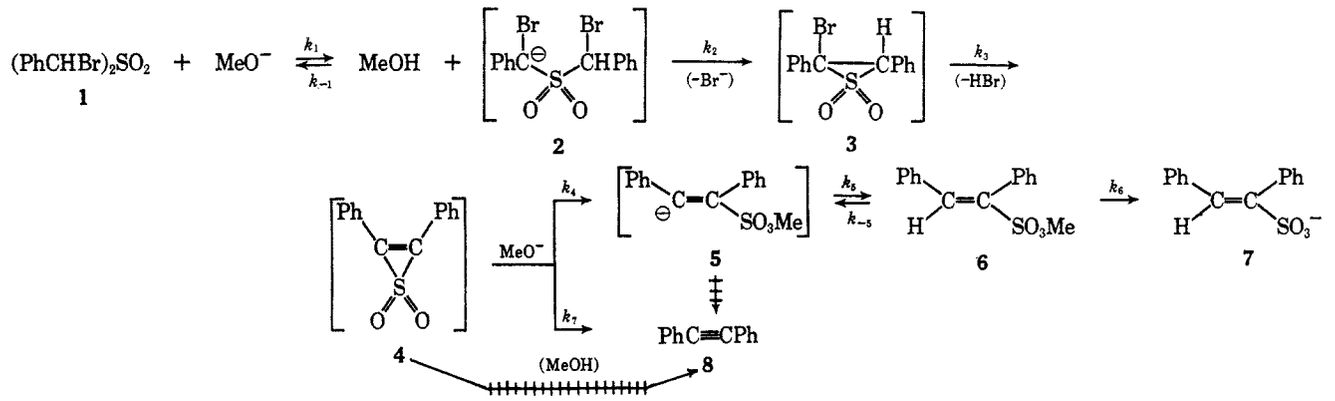
(5) The constancy of the product ratio (**6**/**7**) with changing base concentration has been observed previously with α,α-dichlorodibenzyl sulfone.[4b]

(6) F. G. Bordwell and J. M. Williams, Jr., *J. Amer. Chem. Soc.*, **90**, 435 (1968).

(7) F. G. Bordwell, J. M. Williams, Jr., E. B. Hoyt, Jr., and B. B. Jarvis, *ibid.*, **89**, 429 (1967).

(8) However, the reaction of **1** with sodium hydroxide in aqueous dioxane was found to give small amounts (~1% each) of *cis*- and *trans*-α-bromostilbenes (*vide infra*). *cis*- and *trans*-α-chlorostilbenes have previously been observed in the reaction of $PhCH_2SO_2CCl_2Ph$.[4]

(9) L. A. Carpino and L. V. McAdams, III, *J. Amer. Chem. Soc.*, **87**, 5804 (1965).



lable. It was therefore of particular interest to see whether or not the decomposition of **4** was rate controlling in the sequence **1** → **6** plus **8**. This was accomplished by comparing the rates of reaction of **1** and **4** (synthetic) with sodium methoxide in methanol. The rate of release of bromide ion from **1** was determined titrimetrically, and the rate of formation of **6** from **1** was determined spectrophotometrically. The rate of disappearance of **4** was determined spectrophotometrically. The rate data are summarized in Table II.

TABLE II

KINETIC DATA FOR THE REACTIONS OF α-BROMOBENZYL SULFONE (1) AND 2,3-DIPHENYLTHIIRENE 1,1-DIOXIDE (4) WITH SODIUM METHOXIDE IN METHANOL

Compd	Temp, °C	[MeO⁻],[a] *M*	*k*, M^{-1} sec^{-1}[b]	E_a,[c] kcal/mol	ΔS^* (25°), eu
1	0.0	1.63×10^{-2}	2.4×10^{-2}		
	25.0	1.558×10^{-2}	1.1	25	+24
	0.2	1.63×10^{-2}	(2.4×10^{-2})[d]		
4	0.0	1.84×10^{-3}	23		
	10.0	1.84×10^{-3}	71		
	25.0	1.84×10^{-3}	1.8×10^{2}	10	−16
	0.0	1.76×10^{-2}	24		
4	3.4	1.85×10^{-2}	33.8[e]		

[a] Substrate concentrations were of the order of 10^{-5} *M*. [b] Rates for **1** were determined spectrophotometrically from the (pseudo first order) rates of appearance of **6** plus **8**, both of which absorb strongly in the region monitored (279 mμ). Rates for **4** were determined spectrophotometrically from the disappearance of **4**; the rates given were extrapolated. [c] Determined from an Arrhenius plot at three temperatures. [d] Titrimetric rate. [e] Rate in 40% dioxane–water (v/v); in the absence of base the rate of decomposition is very slow (1.8×10^{-4} at 60.8° in 10% aqueous dioxane).

Examination of Table II reveals that at 25° the rate constant for the reaction of **4** with methoxide ion is over 100 times that for the reaction of **1** with methoxide ion. Therefore, the rate of formation of **6** (and **8**) from **1** is governed by a step (or steps) prior to the formation of **4**. The fact that the methoxide ion promoted dehydrobromination of **3** is much faster than the methoxide ion promoted decomposition of **3** to give PhCBr=CHPh (see above) shows that reaction **3** → **4** must be very fast.[10] This suggests that the rate of formation of **3** is rate controlling, and this view is supported by the observation that the rate of bromide ion release from **1** is equal, within experimental error, to the rate of formation of **6** from **1** (Table II).

The rapidity of the reaction of **4** with methoxide ion makes its isolation from the reaction of **1** impractical under the conditions of the Ramberg–Bäcklund reaction.[11] Nevertheless, it was possible to observe spectroscopically the formation and decay of a small steady-state concentration of an intermediate which is presumed to be **4**. Inasmuch, as the starting materials and final products (**1**, **6**, **8**, etc.) do not absorb strongly at the wavelength (320 mμ) where the appearance of the intermediate was observed (λ_{max} of **4** is 322 mμ[9]), we believe that this experiment confirms the generation of **4** as an intermediate. In ethanol at 3.5°, where the rate constant for the decomposition of **4** is only about 30 times that of the production of **6** + **8** from **1**, the concentration of **4** reached a maximum of about 4% the original concentration of **1** after about 9 sec and then slowly subsided.

Effect of Variation of the Base and Solvent.—The results obtained with **1** and **4** and hydroxide ion in 40% dioxane–water (Table III) were similar to those obtained in methanol, except that small amounts of *cis* and *trans*-α-bromostilbenes were detectable by vpc analysis.

TABLE III

PRODUCTS FROM THE REACTION OF α-BROMOBENZYL SULFONE (1) AND OF 2,3-DIPHENYLTHIIRENE 1,1-DIOXIDE (4)

Compd	Base[a]	Temp, °C	PhC≡CPh,[b] %	PhCH=CBrPh, % *trans*	PhCH=CBrPh, % *cis*	PhCH=CPhSO₃H,[c] %
1	OH⁻	0	13	1	1	80
4	OH⁻	0	15	...	...	80
1	OH⁻	85	17	1	5	70
4	OH⁻	85	20	...	...	75
1	*t*-BuO⁻	25	26	1	3	65
4	*t*-BuO⁻	25	26	...	...	70
1	*t*-BuO⁻	83	28	0	3	65
4	*t*-BuO⁻	83	25	...	...	70

[a] Sodium hydroxide (0.4 *M*) in 60% aqueous dioxane; potassium *t*-butoxide (0.46 *M*) in *t*-butyl alcohol. [b] By vapor phase chromatographic (vpc) analysis. [c] Isolated as the *p*-toluidinium salt.

Again the close agreement in the nature of the products indicates that **1** is reacting primarily by way of **4** as an intermediate. However, the appearance of small amounts of *cis*- and *trans*-α-bromostilbenes shows that attack of hydroxide on **3** is competitive to some degree with dehydrobromination. There is a considerably smaller increase in the quantity of diphenyl-

(10) The rate constant for the methoxide ion promoted decomposition of an episulfone identical with **3**, except that the bromine atom is replaced by the hydrogen atom, is 5.5 M^{-1} sec^{-1} in methanol at 25°.[7] The rate of dehydrobromination is, therefore, of the order of at least 10^3 M^{-1} sec^{-1} at 25°.

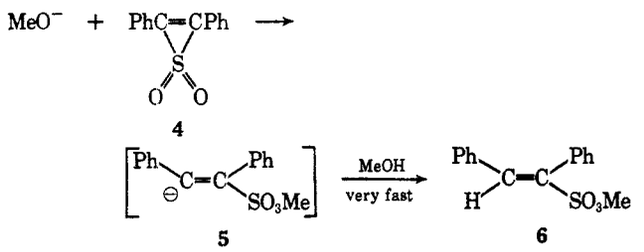
(11) Preparation of **4** from **1** can be accomplished readily, however, with triethylamine in methylene chloride.[9]

acetylene (**8**) at higher temperature than for the reaction in methanol (Table I).

When the reaction of **4** was carried out with potassium *t*-butoxide in *t*-butyl alcohol at 25°, 25% of **8**, and 66% of **7** (isolated as the *p*-toluidine salt) were formed. There was little or no increase in the amount of **8** when the reaction was carried out at the reflux point (83°).[12] Comparable results were obtained with **1** except that a small amount of *cis*-α-bromostilbene was also detected. The absence of *trans*-α-bromostilbene is understandable since the *trans*, but not the *cis*, isomer was found to undergo dehydrobromination under these conditions. The lesser amount of *trans* than *cis* isomer obtained at 85° in aqueous dioxane (Table III) is also no doubt due to loss through dehydrobromination.

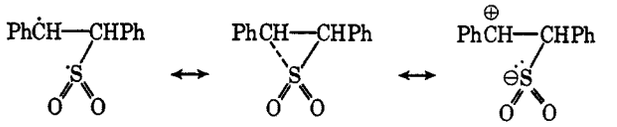
Discussion

The principal product from the attack of methoxide ion on **4** (or **1**) is methyl *cis*-1,2-diphenylethenesulfonate (**6**). The structure assignment is based on analogy with the comparable reaction of benzyl dichloromethyl sulfone to give *trans*-phenylethenesulfonate,[4c] and of 2,3-diphenylcyclopropenone to give methyl *cis*-1,2-diphenylethenecarboxylate.[13] This is the stereochemistry anticipated from a mechanistic standpoint, since the reaction appears to be best visualized as attack of methoxide ion on sulfur leading, either directly, or by way of a pentacovalent sulfur adduct, to carbanion **5**.[4c] The latter should abstract a proton from methanol at an extremely rapid rate (of the order of 10^{10} sec^{-1}). In view of the demonstrated ability of *cis*-1,2-diphenylethenyllithium to maintain its configuration for over 30 min in benzene–pentane at 2°, or 3:1 ether–benzene at −54°,[14] one would expect protonation of carbanion **5** to be much faster than isomerization.



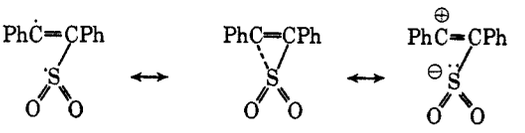
The presence of the C=C bond in 2,3-diphenylthiirene 1,1-dioxide (**4**) must introduce a high degree of strain relative to its saturated analogs, *cis*- and *trans*-2,3-diphenylthiirane 1,1-dioxides (**10** and **11**, respectively). One would expect on this basis that **4** would undergo decomposition much more rapidly than **10** or **11**. Instead, in the absence of base, **4** decomposes very slowly.[9] In 10% dioxane–water at 60.8° its rate of decomposition to diphenylacetylene was 1.8×10^{-4} sec^{-1}, which is *ca.* 10^4 slower than that of **10** under comparable conditions. The rate for **11** (or 1-phenylthiirane 1,1-dioxide) is more than four powers of 10 faster than that of **4**.[7]

There are at least two factors that can account for the relatively low reactivity of 4. It is likely, by analogy to 2,3-diphenylcyclopropenone,[13] that **4** possesses aromatic character.[9] The resultant lowering of the ground-state energy, relative to the transition-state energy, could lead to an appeciably slower rate of decomposition on this account. A second factor that may be contributory is lesser conjugative stabilization of the transition state for the decomposition of **4** compared to **10** (or **11**). The decomposition of **10** (or **11**) exhibits a surprising sensitivity to the ionizing power of the solvent, which indicates a high degree of dipolar character in the transition state.[7] The representation **10a** has been suggested for the transition state; this is believed to be transformed to a singlet diradical intermediate.[7]



10a (or **11a**, transition state)

Qualitative data in aqueous dioxane mixtures of varying water content indicate that the decomposition of **4** is also accelerated by increasing the ionizing power of the solvent. Therefore, the transition state for the decomposition of **4** must also possess considerable dipolar character. Comparison of the suggested transition state (**4a**) with that of **10a** shows that delocalization of the electron (or positive charge) to the phenyl group may be less effective in **4a** because it occurs at the expense of conjugation between the phenyl group and the C=C bond. The slower rate of decomposition of **4** to diphenylacetylene perhaps can be rationalized in these terms. It is, of course, also possible that the decomposition of **4** proceeds by a completely different mechanism.



4a (transition state)

A concerted decomposition for **4** is not expected on the basis of the Hoffmann–Woodward rules.[4b,15] The increase in the rate of decomposition with increasing ionizing power of the solvent also supports a stepwise mechanism. When a solution of **4** in methanol was illuminated with ultraviolet light, a 93% conversion to diphenylacetylene and sulfur dioxide was realized at 0° within 10 hr. A concerted decomposition is expected under these conditions according to the Hoffmann–Woodward rules.[15]

The decomposition of **4** is accelerated by base to a much greater degree than that of its saturated analog **11**.[16] For **11** the k_{MeO^-}/k_{MeOH} ratio is 230 at 25°. The rate for **4** in methanol has not been measured but, judging from the rate in aqueous dioxane, methoxide ion must accelerate the rate by at least 10^4. For **11** (or 2-phenylthiirane 1,1-dioxide) methoxide ion accelerates the reaction without changing its course. For **4**, however, formation of methyl *cis*-1,2-diphenylethenesulfonate (**6**) becomes the principal product in the

(12) These results contrast with that with $PhCH_2SO_2CCl_2Ph$ which gave 65–70% of $PhCH{=}C(Ph)SO_3^-$ with HO^- but none with *t*-BuO^-.[4c]

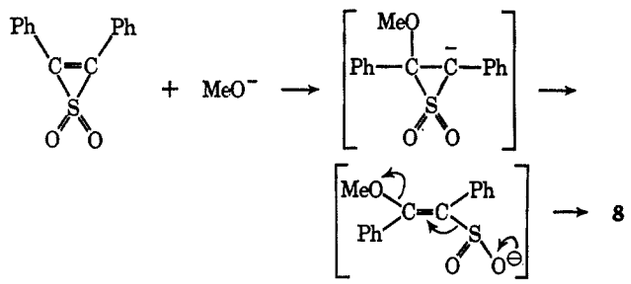
(13) R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *J. Amer. Chem. Soc.*, **87**, 1320 (1965); S. C. Crooks, unpublished results.

(14) A. N. Nesmeyanov and A. E. Borisov, *Tetrahedron*, **1**, 158 (1957).

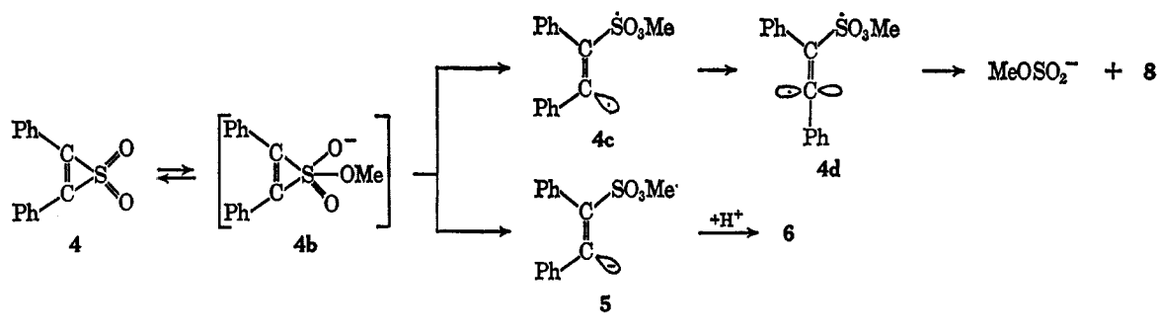
(15) R. W. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046 (1965).

(16) *cis*-2,3-Diphenylthiirane 1,1-dioxide (**10**) is rapidly epimerized to the *trans* isomer (**11**); its rate with methoxide is, therefore, unknown.

presence of methoxide ion; diphenylacetylene (8) is formed in amounts varying from 16–28% depending on the temperature. The relatively low activation energies for these reactions (~9 and ~11$_5$ kcal/mol respectively)[17] are noteworthy. For 11 the activation energy for the methoxide reaction is 21 kcal/mol, which is actually 2 kcal *higher* than that for the methanol reaction.[7] The approximately 10-kcal/mol lower activation energy for the methoxide-promoted decomposition of 4 to diphenylacetylene than for the decomposition of 11 to *trans*-stilbene is suggestive of a change in mechanism. It would seem most likely that this change is associated with the presence of the C=C bond in 4, which not only greatly increases the strain, but also provides another reaction site. One possibility is that diphenylacetylene (8) is formed by attack at the C=C bond.[18]



It is evident that the reactions by which 6 and 8 are formed have different transition states since they have different activation energies. The postulate that formation of 8 occurs by attack at the C=C bond and formation of 6 occurs by attack at sulfur meets this requirement. A mechanism in which 6 and 8 are formed from a common intermediate (4b) produced by attack of methoxide ion on sulfur is in some respect more attractive.



According to this representation intermediate 4b can either undergo heterolytic cleavage to give carbanion 5 or homolytic cleavage to give the singlet diradical 4c. Rehybridization of the vinyl radical would give 4d wherein the odd electron can be delocalized to the phenyl group. Loss of methyl sulfite ion from 4c or 4d would give diphenylacetylene (8). This mechanism would fit the requirement that the processes which give 6 and 8 must each be first order in methoxide ion [at 0 or 65° the ratio of 6 to 8 did not change significantly when the methoxide ion concentration was increased by a factor of more than 4 (see Table I)].

(17) Calculated from the rates (Table II) and product distribution (Table I) at 0 and 65°.

(18) 2,3-Diphenylcyclopropenone is known to undergo attack by some reagents, such as hydroxylamine, at the C=C bond, see ref 12.

Experimental Section[19]

General Methods.—Vpc analyses were performed on an F & M Model 300. The conditions were as follows: 2-ft copper tubing (0.25-in. o.d.) with 8% SE-30 gum rubber on Chromosorb P; column temperature 185°. The flow rate was constant within a run but varied from run to run. Because of this variance, the retention times are not given, but it can be said that diphenylacetylene was first off the column followed by *cis*-α-bromostilbene and then the *trans* isomer.

The samples were prepared by diluting the resulting reaction mixtures from the organic extracts to 1.0 ml. From these stock solutions a 5-μl sample was injected into the vpc apparatus. The peak areas for these samples were compared to those for standard samples of diphenylacetylene and *trans*-α-bromostilbene.[20]

Preparation of Methyl *cis*-1,2-Diphenylethenesulfonate (6).[21]—To a solution containing 1.0 g (4.1 mmol) of the thiirene dioxide 4[9] dissolved in 100 ml of methanol at 0° was added a solution prepared by dissolving 300 mg of sodium metal in 25 ml of methanol. The resulting solution was held at 0° for 15 min and then quenched with water and worked up by an ether extraction. The resulting solid was recrystallized from chloroform–hexane to give 1.0 g (89%) of white needles, mp 121–122°.

Anal. Calcd for $C_{15}H_{14}O_3S$: C, 65.67; H, 5.14. Found: C, 65.58; H, 5.28.

Treatment of the methyl sulfonate 6 with 0.4 *M* sodium methoxide in methanol at reflux for 1 hr gave the corresponding sulfonic acid, characterized as its *p*-toluidine salt, mp 198–200.[4a]

Reaction of α-Bromobenzyl Sulfone (1) with Bases. A. Sodium Methoxide in Methanol. 1.—To a solution of 1.1 g of sodium methoxide dissolved in 50 ml of methanol was added 832 mg (2.06 mmol) of 1 (a mixture of *dl* and *meso* isomers, mp 128–135°) dissolved in 50 ml of methanol. This mixture was stirred at 0° for 20 hr, and was then heated at reflux for 2 hr. This solution was poured into 200 ml of water and extracted well with ether. The combined ether portions were washed with water and the aqueous fractions were combined and saved. The ether was washed with saturated salt solution and dried with anhydrous magnesium sulfate. The ether was removed *in vacuo*, and the resulting oil was diluted to 1.0 ml with ether. Vpc analysis showed the presence of 61 mg (16%) of diphenylacetylene (8) and no bromostilbenes.

The aqueous fraction was concentrated to 25 ml made slightly acidic with concentrated hydrochloric acid, and 300 mg of *p*-toluidine dissolved in 5 ml of 5% hydrochloric acid was added. The resulting precipitate of *p*-toluidinium *cis*-1,2-diphenylethenesulfonic acid (7) was collected and washed with cold water: 605 mg (80%); mp 196–200°.

2.—To a stirring solution of 1.1 g of sodium methoxide dissolved in 50 ml of methanol at reflux under an atmosphere of nitrogen was added, dropwise, over a period of *ca.* 20 min, 832 mg (2.06 mmol) of 1 dissolved in 50 ml of methanol. This mixture was held at reflux for 1 hr and was then worked up as in the previous example: vpc analysis, 28% 8; no bromostilbenes. The aqueous layer gave 490 mg (65%) of 7.

B. Sodium Hydroxide in 40% Dioxane. 1.—To a solution containing 1.5 g of sodium hydroxide dissolved in 60 ml of water and 20 ml of dioxane was added 832 mg (2.06 mmol) of 1 dissolved in 20 ml of dioxane. This mixture was held at 0° for 2 hr and was then worked up as usual: vpc analysis—13% 8;

(19) Analyses were performed by Micro-Tech Laboratories, Skokie, Ill.

(20) G. Drefahl and C. Zimmer, *Chem. Ber.*, **93**, 505 (1960).

(21) We wish to thank Dr. E. B. Hoyt, Jr., for working out the synthesis of this compound.

1% each of *cis*- and *trans*-α-bromostilbenes. The aqueous layer gave 600 mg (79%) of **7**.

2.—To a solution containing 1.5 g of sodium hydroxide dissolved in 60 ml of water and 25 ml of dioxane held at 87° under a nitrogen atmosphere was added slowly 832 mg (2.06 mmol) of **1** dissolved in 15 ml of dioxane. The mixture was held at 87° for 2.5 hr and then worked up as usual: vpc analysis—17% of **8**; 5% *cis*-bromostilbene; 1% *trans*-α-bromostilbene. The aqueous phase yielded 570 mg (75%) of **7**.

C. Potassium *t*-Butoxide in *t*-Butyl Alcohol. 1.—To a solution containing 832 mg (2.06 mmol) of **1** dissolved in 170 ml of *t*-butyl alcohol was added 3.2 g of potassium *t*-butoxide. This mixture stirred for 2 days at *ca.* 25 and was worked up by concentrating the solution *in vacuo* to *ca.* 30 ml and pouring it into water followed by extraction with ether: vpc analysis—26% **8**; 3% *cis*-α-bromostilbene; 1% *trans*-α-bromostilbene. The aqueous phase gave 500 mg (66%) of **7**.

2.—To a solution of 832 mg (2.06 mmol) of **1** in 100 ml of *t*-butyl alcohol at reflux under an atmosphere of nitrogen was added over a period of *ca.* 5 min 70 ml of *t*-butyl alcohol containing 3.2 g of potassium *t*-butoxide. This mixture was held at reflux for 30 min and then concentrated *in vacuo* to *ca.* 30 ml followed by the usual work-up: vpc analysis—28% **8**; 3% *cis*-α-bromostilbene.[22] The aqueous phase yielded 500 mg (66%) of **7**.

Reaction of 2,3-Diphenylthiirene 1,1-Dioxide (4) with Bases.—The reactions of **4** with sodium methoxide in methanol, sodium hydroxide in 40% dioxane, and potassium *t*-butoxide in *t*-butyl alcohol were carried out in the same manner as for **1** with these various bases. Owing to the high rate of reaction of **4** with these base systems, the reaction times were generally decreased by about a factor of 5.

Increasing the base concentration from 0.2 to 2.0 *M* in the sodium methoxide–methanol base system at either 0 or 65° had no apparent effect on the ratio of reaction products. The results are listed in Tables I and III.

Photolysis of 2,3-Diphenylthiirene 1,1-Dioxide (4).—A solution containing 900 mg (3.7 mmol) of **4** in 200 ml of methanol was cooled to 0° with stirring under a nitrogen atmosphere while illuminating the quartz flask with ultraviolet light (Hanovia). The odor of sulfur dioxide could be detected after about 1 hr; after 10 hr the reaction mixture was poured into water and extracted well with ether. After drying over anhydrous magnesium sulfate, the ether was removed *in vacuo*. An infrared spectrum of the resulting solid showed that solid to be nearly all diphenylacetylene (**8**). Analysis by vpc showed the product to be 95% **8** and 5% unidentified material. The total conversion was 93%.

(22) Treatment of a 50:50 mixture of *cis*- and *trans*-α-bromostilbene under these conditions gave a 50:50 mixture of **8** and recovered *cis*-α-bromostilbene.

Observation of a Steady-State Concentration of 4.—To 3.0 ml of *ca.* 5×10^{-4} *M* sodium methoxide in methanol cooled to 10.0° in a Cary 15 spectrometer compartment was added 25 μl of a stock solution (2.3 mg of **1** in 1.0 ml of methanol). A rapid increase in absorption at 320.5 mμ, presumably due to the formation of **4**, was observed. Within 15 sec absorption was at its maximum value after which it slowly decreased until it reached a value of nearly zero after *ca.* 8 hr.

A comparable experiment was carried out with sodium ethoxide at 3.5°. Under these conditions the rate constant for the formation of **6** + **8** was 2.3 M^{-1} sec^{-1}, and the rate constant for the disappearance of **4** was 7.7×10^{1} M^{-1} sec^{-1}. The peak at 320.5 mμ reached its maximum absorption (4% of the initial concentration of **1**) within 9 sec, and then slowly subsided.[23,24]

Thermal Decomposition of 4 in 75% Aqueous Dioxane.—A solution of 200 mg (0.83 mmol) of **4** in 12.5 ml of dioxane and 37.5 ml of water was held at reflux for 4 days. The solution was poured into water and extracted well with ether. The aqueous portion was stripped *in vacuo* to dryness to give 10 mg of a white solid which was presumably inorganic material since it was noncombustible. The ether fractions were combined, dried over anhydrous magnesium sulfate, and removed *in vacuo* to give 140 mg (95%) of diphenylacetylene (**8**) as shown by vpc analysis.

Kinetic Procedure.—The rate of reaction of **4** with various bases or thermally was followed by observing the decrease in absorbance at 320.5 mμ on either a Cary 14, Cary 15, or Beckman DU spectrophotometer. Details of the general procedure and handling of the data have been described previously.[7]

The titrimetric rate measurements of **1** were performed in the same manner as was described previously with similar compounds.[6]

Registry No.—**1**, 16003-67-1; **4**, 5162-99-2; **6**, 16003-69-3; **7** *p*-toluidine salt, 16003-70-6; sodium methoxide, 124-41-4.

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(23) As pointed out by a referee, the maximum build-up of **4** can be estimated by assuming that, in the sequence **1** $\xrightarrow{k_1}$ **4** $\xrightarrow{k_2}$ **6** + **8**, k_1 and k_2 are pseudo-first-order constants. Then $[4] = \beta_{max} = \kappa^{\kappa/(1-\kappa)}$, where $\kappa = k_2/k_1$.[24] In ethanol at 3.5°, $k = 77/2.3 = 33$, and $\beta_{max} = 33^{33/(1-33)} = 0.03$, which agrees satisfactorily with the value of 4% determined experimentally.

(24) See A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1961, p 168.

The Reaction of Bases with Benzyl Dibromomethyl Sulfone and with Benzhydryl Dihalomethyl Sulfone

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Reaction of $PhCH_2SO_2CHBr_2$ with methoxide ion at 0° gave methyl *trans*-β-phenylethenesulfonate as the principal product. At higher temperatures and higher base concentrations appreciable quantities of phenylacetylene and some styrene were obtained. Under similar conditions $Ph_2CHSO_2CHBr_2$ gave $Ph_2C{=}CHBr$ (**11**) and $Ph_2C{=}CHSO_3H$ (**12**). The ratio of **11** to **12** was increased substantially by an increase in reaction temperature. Possible reaction pathways are discussed.

In the preceding paper in this series[2] an analysis of the nature of products formed from the reaction of the α,α′-dibromo sulfone $PhCHBrSO_2CHBrPh$ (**1**) with base, together with a kinetic study, established a mechanistic path involving bromothiirane 1,1-dioxide and thiirene 1,1-dioxide intermediates. The study has now been extended to the α,α-dibromo sulfone $PhCH_2SO_2CHBr_2$ (**2**) which has the same mechanistic pathways open to its as does **1**, and to $Ph_2CHSO_2CHBr_2$ (**9**) which does not.

The mechanistic pathways anticipated for **2** by analogy with the reactions of **1** with methoxide ion and from the work of Paquette,[3] *et al.*, are shown in eq 1 and 2.

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(2) F. G. Bordwell, J. M. Williams, Jr., and B. B. Jarvis, *J. Org. Chem.*, **33**, 2026 (1968).

(3) (a) L. A. Paquette and L. S. Wittenbrook, *J. Amer. Chem. Soc.*, **89**, 4483 (1967); (b) L. A. Paquette, L. S. Wittenbrook, and V. V. Kane, *ibid.*, **89**, 4487 (1967).