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%.

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.

Acknowledgment.—We are grateful to the National Science Foundation (NSF GP-4208) for support of this work.

---

[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.

[23] As pointed out by a referee, the maximum build-up of **4** can be estimated by assuming that, in the sequence $\mathbf{1} \xrightarrow{k_1} \mathbf{4} \xrightarrow{k_2} \mathbf{6} + \mathbf{8}$, k_1 and k_2 are pseudo-first-order constants. Then $[\mathbf{4}] = \beta_{\max} = \kappa^{\kappa/(1 - \kappa)}$, 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

F. G. Bordwell, Earle B. Hoyt, Jr., Bruce B. Jarvis, and Joel M. Williams, Jr.[1]

Department of Chemistry, Northwestern University, Evanston, Illinois 60201

Received September 25, 1967

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.

---

[1] National Institutes of Health Predoctoral Fellow, 1964–1966.

[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).

TABLE I

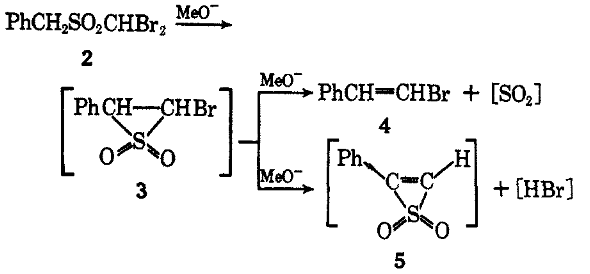
PRODUCTS FROM THE REACTIONS OF BENZYL DIBROMOMETHYL SULFONE (2) WITH BASES

Base	Temp, °C	$PhCH{=}CH_2$,[a] %	$PhC{\equiv}CH$ (6),[a] %	$PhCH{=}CHBr$ (4),[b] % trans	cis	$PhCH{=}CHSO_3H$ (8),[c] %
0.46 *M* NaOMe[d]	0	0	Trace	5	3	75
0.20 *M* NaOMe[d]	65	10	12	9	1	50
0.46 *M* NaOMe[d]	65	8	15	8	2	50
1.0 *M* NaOMe[d]	65	10	25	8	Trace	45
0.40 *M* NaOH[e]	0	10	20	0	0	55
0.20 *M* NaOH[e]	85	22	12	0	0	40
0.40 *M* NaOH[e]	85	15	35	Trace	0	35
0.80 *M* NaOH[e]	85	16	46	Trace	0	22
0.46 *M* *t*-BuOK	25	Trace	45	0	0	40
0.46 *M* *t*-BuOK	83	Trace	70	0	0	15
1.50 *M* *t*-BuOK	83	1	80	0	0	Trace
0.40 *M* NaOH 0.64 *M* Na_2SO_3	85	40	15	Trace	0	32

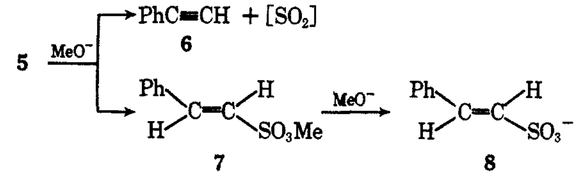
[a] Analyzed by vpc; the ratio of $PhC{\equiv}CH/PhCH{=}CH_2$ is not affected by heating with base. [b] Analyzed by vpc; the ratio of *cis*/*trans* is unaffected by 0.46 *M* methoxide ion methanol or 0.40 *M* hydroxide in 40% aqueous dioxane at 0°, but decreases in the refluxing base systems. [c] Isolated as the *p*-chlorobenzylthiiuronium salt. [d] In methanol. [e] In 40% (by volume) water in dioxane.

In a similar study with $PhCH_2SO_2CHCl_2$ and sodium hydroxide in 50% aqueous dioxane at 87° the products have been shown to be **6** (56%) and **8** (31%).[3b] With *t*-BuOK in *t*-BuOH the amount of **6** increased to 76% and **8** disappeared. This change was ascribed to a steric effect. The results of a product study of the reaction of **2** with various bases at two temperatures are summarized in Table I.

At 0° in methanol **2** reacts readily with methoxide ion to give *β*-bromostyrene (**4**, 5% *trans*, 3% *cis*), methyl *trans*-*β*-phenylethenesulfonate (**7**, 75%), but only a trace of phenylacetylene (**6**). This result is similar to that obtained with $(PhCHBr)_2SO_2$ under comparable conditions where methyl *cis*-2,3-diphenylethenesulfonate was the major product (84%) and diphenylacetylene was the minor product (16%).[2] No bromostilbenes (analogs of **4**) were produced under these conditions, but small amounts were observed when the reaction was run in aqueous dioxane.[2] At 65° in methanol or at 0° (or 85°) in 40% aqueous dioxane, **2** gave 8–22% of styrene; the amount was increased to 40% by including sodium sulfite in the reaction mixture (Table I).



(1)



(2)

$$\begin{array}{llll}
PhCH_2SO_2CHBr_2 & + SO_3^{2-} + HO^- \longrightarrow & [PhCH_2SO_2CH_2Br] & + SO_4^{2-} + Br^- \quad (3a)\\
[PhCH_2SO_2CH_2Br] & + 3HO^- \longrightarrow & PhCH{=}CH_2 & + SO_3^{2-} + Br^- + 2H_2O \quad (3b)\\
\hline
PhCH_2SO_2CHBr_2 & + 4HO^- \longrightarrow & PhCH{=}CH_2 & + SO_4^{2-} + 2Br^- + 2H_2O \quad (3c)
\end{array}$$

The formation of styrene from **2** in aqueous alkaline dioxane has been observed previously.[4] It no doubt arises, as was suggested,[4] by the reduction of **2** by sulfite ion (a reaction product) to $PhCH_2SO_2CH_2Br$, followed by a Ramberg–Bäcklund reaction on this bromide. The reduction may be formulated as a nucleophilic displacement on bromine initiated by sulfite ion ($SO_3^{2-} + Br_2CHSO_2CH_2Ph \rightarrow BrSO_3^- + BrCHSO_2CH_2Ph$). The over-all equations are 3a–c.

The proposed role of sulfite ion in the reaction is supported by the marked increase in the amount of styrene produced when sulfite is introduced as a reagent. Additional evidence was provided by the observation that dibromomethyl phenyl sulfone was reduced quantitatively to bromomethyl phenyl sulfone by sodium sulfite in refluxing aqueous dioxane within 2 hr. About 40% of reduction also occurred under similar conditions with sodium methoxide in methanol, indicating that methoxide ion can also bring about reduction by nucleophilic attack on bromine.

$$PhSO_2CHBr_2 + SO_3^{2-} + H_2O \xrightarrow{\text{dioxane}} PhSO_2CH_2Br + HSO_4^- + Br^- \quad (4)$$

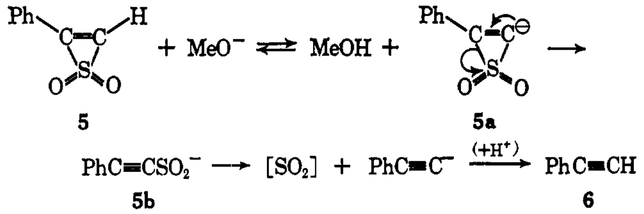
The ratio of phenylacetylene (**6**) to methyl *trans*-*β*-phenylethenesulfonate (**7**, isolated as **8**) was found to increase by as much as 50% by doubling the alkoxide ion concentration. This observation, which was made in all three base–solvent systems (Table I) differs somewhat from that made in the seemingly analogous reaction in which base reacts with **1** (or 2,3-diphenylthiirene 1,1-dioxide) to give comparable products (*e.g.*, diphenylacetylene and methyl *cis*-2,3-diphenylethenesulfonate from methoxide ion in methanol). In the latter reaction the ratio of products remains constant with changing base concentration, although there is an increase in the alkyne/alkene ratio with increasing temperature, as with **2** (Table I).[2] The ratio of **6** to **8** formed from 0.46 *M* *t*-BuOK in *t*-BuOH changes from 1.1:1 to 4.7:1 as the temperature is increased from 25 to 83°. When the concentration of *t*-BuOK was in-

---

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

creased to 1.5 *M*, the yield of **6** at 83° increased from 70 to 80% and no **8** could be detected (Table I). The latter result is comparable to that obtained with $PhCH_2SO_2CHCl_2$.[3b] Our results indicate, however, that temperature and concentration are more important than the nature of the base[3b] in determining the ratio of **6**/**8**.

There appear to be at least two mechanisms by which **6** may be formed from **5**. The methyl analog of **5**, 2-methylthiirene 1,1-dioxide, has been shown to react rapidly with base to give propynesulfinate ion, which decomposes to propyne.[5] The decomposition of **5** can no doubt take an analogous path (eq 5).



(5)

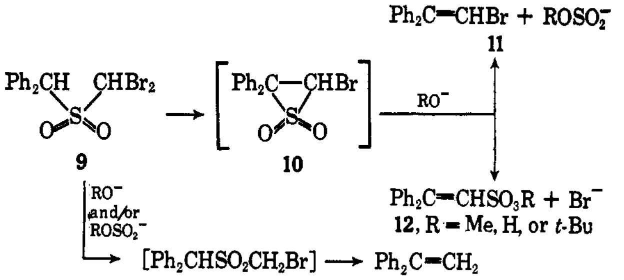
A second possibility is attack of methoxide ion on the sulfur atom of **5** in a mechanism comparable with that suggested in the previous paper for the formation of diphenylacetylene from 2,3-diphenylthiirene 1,1-dioxide.[2] (Small amounts of **6** also arise at higher temperatures by dehydrobromination of *cis*-, but not *trans*-, *β*-bromostyrene.)

The formation of **7** (methyl *trans*-*β*-phenylethenesulfonate) from **5** is expected by analogy with the conversion of 2,3-diphenylthiirene 1,1-dioxide to methyl *cis*-1,2-diphenylethenesulfonate.[2,6] The latter reaction is first order in methoxide ion,[2] and this is probably true also for the reaction **5** → **7**.

One observation not accounted for on the basis of the mechanisms proposed is the increase in the ratio of **6** to **7** with increased base concentrations. It would seem that each of the reactions by which **6** is formed should be first order in methoxide ion, as should the formation of **7** from **5**. For example, in the route **5** → **5a** → **5b** → **6** the concentration of **5a** should be very low, since sulfones are known to be very weak acids,[7] and the concentration of **5a** should, therefore, be directly related to the concentration of methoxide ion. If the decomposition of **5b** to $PhC\equiv C^-$ is rate determining and is first order in methoxide ion, this would explain an increase in the **6**/**7** ratio with increasing methoxide ion concentration, but it seems more likely that the decomposition of **5b** is a first-order process and does not require methoxide ion attack. Additional experimental work will be required to clarify this point.

The formation of small amounts of *β*-bromostyrenes from **2** in methanol no doubt occurs by attack of methoxide ion on 2-bromo-3-phenylthiirane 1,1-dioxide (**3**). Comparable decompositions of 2-phenyl- and *trans*-2,3-diphenylthiirane 1,1-dioxides to alkenes have been observed, and have been found to be first order in methoxide ion.[8] Dehydrobromination of **3** to **5** by methoxide ion is, however, a faster reaction.

The reaction of benzhydryl dibromomethyl sulfone (**9**) with methoxide or hydroxide ion was of interest because of the inability of the expected intermediate, 2-bromothiirane 1,1-dioxide (**10**, analog of **3**), formed in the first step to undergo dehydrobromination. The principal products from **9** were found to be **11** and **12**, together with the reduction product 1,1-diphenylethene (eq 6).



(6)

The distribution of products obtained from **9** and from the analogous dichloride (**13**) under various conditions are summarized in Tables II and III.

TABLE II

PRODUCTS FROM THE REACTION OF BENZHYDRYL DIBROMOMETHYL SULFONE (9) WITH BASES

Base	Temp, °C	$Ph_2C{=}CH_2$,[a] %	$Ph_2C{=}CHBr$ (**11**),[a] %	$Ph_2C{=}CHSO_3H$ (**12**),[b] %
0.15 *M* NaOMe[c]	0	5	30	60
0.46 *M* NaOMe[c]	0	Trace	22	73
1.4 *M* NaOMe[c]	0	Trace	18	80
0.15 *M* NaOMe[c]	65	20	80	Trace
0.46 *M* NaOMe[c]	65	3	65	30
1.4 *M* NaOMe[c]	65	Trace	30	65
0.40 *M* NaOH[d]	0	8	27	60
0.40 *M* NaOH[d]	85	30	45	20
0.46 *M* *t*-BuOK[e]	25	10	20	65
0.46 *M* *t*-BuOK[e]	83	15	25	58
0.40 *M* NaOH 0.64 *M* Na_2SO_3 }[d]	85	85	8	7

[a] Analyzed by vpc. [b] Isolated as the *p*-chlorobenzylthiuronium salt. [c] In methanol. [d] In 40% (by volume) water–dioxane. [e] In *t*-butyl alcohol.

TABLE III

PRODUCTS FROM THE REACTION OF BENZHYDRYL DICHLOROMETHYL SULFONE (13) WITH BASES

Base	Temp, °C	$Ph_2C{=}CH_2$,[a] %	$Ph_2C{=}CHCl$,[a] %	$Ph_2C{=}CHSO_3H$,[b] %
0.46 *M* NaOMe[c]	0	0	48	50
0.46 *M* NaOMe[c]	65	Trace	72	25
0.40 *M* NaOH[d]	0	0	43	55
0.40 *M* NaOH[d]	85	Trace	77	20
0.46 *M* *t*-BuOK[e]	25	0	35	60
0.46 *M* *t*-BuOK[e]	83	4	35	60

[a] By vpc analysis. [b] Isolated as the *p*-chlorobenzylthiuronium salt. [c] In methanol. [d] In 40% (by volume) water–dioxane. [e] In *t*-butyl alcohol.

Benzhydryl dibromomethyl sulfone (**9**) is more susceptible to reduction than is benzyl dibromomethyl sulfone (**2**) judging from the 85% yield of 1,1-diphenylethene obtained in the presence of sodium sulfite (Table II) compared with 40% of styrene from **2** (Table I). As would be expected, the corresponding dichloride (**13**) shows less tendency toward reduction (Table III).

The formation of **10** as an intermediate is expected from the earlier work,[2,3,8] and the formation of **11** and **12** is readily rationalized on this basis. Thiirane 1,1-dioxides are known to undergo rapid base-initiated decompositions to alkenes,[8] and this is the probable path

---

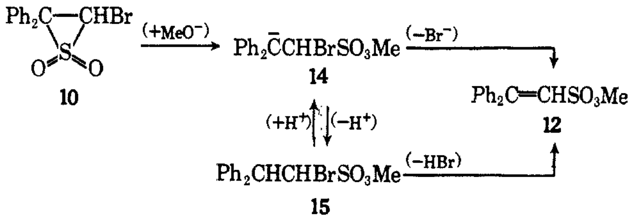
[5] L. A. Carpino and R. H. Rynbrandt, *J. Amer. Chem. Soc.*, **88**, 5682 (1966).

[6] L. A. Carpino and L. V. McAdams, III, *ibid.*, **87**, 5804 (1965).

[7] F. G. Bordwell, R. H. Imes, and E. C. Steiner, *ibid.*, **89**, 3905 (1967).

[8] F. G. Bordwell, J. M. Williams, Jr., E. B. Hoyt, Jr., and B. B. Jarvis, *ibid.*, **90**, 429 (1968).

for the conversion of **10** into **11**. The reaction **10** → **12** has no established precedent. However, chloromethyl ethyl sulfone reacts with hydroxide ion to give small amounts of isomeric propanesulfonates,[9] no doubt by way of 2-methylthiirane 1,1-dioxide.[10] An analogous reaction with **10** offers a reasonable path to **12** (eq 7).



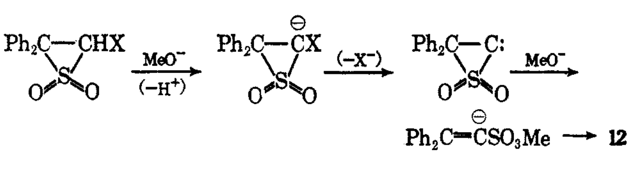
(7)

The formation of **12** as the major product from the reaction of 3-bromo-2,2-diphenylthiirane 1,1-dioxide (**10**) with sodium methoxide, sodium hydroxide, or potassium *t*-butoxide at low temperatures (0–25°) is in marked contrast to the behavior of other thiirane 1,1-dioxides (*e.g.*, 2-phenyl or 2,3-diphenyl[8]) which give only alkenes under these conditions. Apparently the presence of two phenyl groups on a single carbon atom greatly promotes the rate of the reaction to form the carbanion (**14**). Protonation of **14** should be very rapid, and it seems resaonable to expect **15** as an intermediate. Attempts to isolate **15** at low temperatures and at low base concentrations were unsuccessful, however. It was desirable to prepare **15** in order to measure its rate of conversion to **12**, but initial attempts to do so failed.

At temperatures of 65° at low base concentration (0.15 *M*) the amount of **11** formed from dibromide **9** increased to 80% (Table II); similar results were obtained from the corresponding dichloride **13** (Table III). For the dibromide this increase in **11** is accompanied by an increase in styrene (Table II) which indicates that sulfite ion, rather than methoxide ion, is the principal reducing agent.

The amount of **12** formed from dibromide **9** at 0° increases from 60 to 80% with a 9.3-fold increase in methoxide ion concentration; a somewhat larger increase is noted at 65°. This corresponds to a relatively small increase in rate and may be a salt effect.

Other pathways for the conversion of **10** into **12** can be imagined, for example



This pathway cannot be excluded by the data on hand, but the very slow rate of chloride loss from $t\text{-BuSO}_2\text{CH}_2\text{Cl}$ or $\text{PhSO}_2\text{CH}_2\text{Cl}$ under basic conditions makes it appear unlikely.[10]

Preliminary kinetic data obtained at 25° in methanolic sodium methoxide indicate that the rate of formation of **8** from **2** is about $5 \times 10^{-2}\ M^{-1}\ \text{sec}^{-1}$. This is about 50-fold faster than the rate observed for the corresponding monobromide, $\text{PhCH}_2\text{SO}_2\text{CH}_2\text{Br}$.[10] Under comparable conditions the rate of formation of **12** from **9** is about $2\ M^{-1}\ \text{sec}^{-1}$. More exact data will be given in a later paper, and the effect of bromine in accelerating the rate of the Ramberg–Bäcklund reaction will be discussed.

Experimental Section[11]

General Methods.—Vpc analyses were performed on an F & M Model 300 using a 5-ft (0.25-in. o.d.) copper tubing column of 12% SE-30 silicon gum rubber on Chromosorb W (60–80 mesh) support. The column temperature varied according to which materials were being analyzed, *viz.* phenylacetylene and styrene at 70°; bromostyrenes at 125°; 1,1-diphenylethylene, 1,1-diphenyl-2-bromoethylene, and 1,1-diphenyl-2-chloroethylene at 195°. The flow rate was constant within a run but varied from run to run. Because of this variance, the retention times are not given; they were, however, identical within each run with those of authentic samples.

The samples were prepared by diluting the resulting reaction mixture extracts to 5.0 ml. From these stock solutions 5 μl of sample was injected into the instrument. The peak areas for these samples were compared directly to those of standard samples of styrene, phenylacetylene,[12] 1,1-diphenylethylene[12] 1,1-diphenyl-2-bromoethylene,[13] bromostyrene,[14] and 1,1-diphenyl-2-chloroethylene.[15]

Benzyl Dibromomethyl Sulfone (2).—A 94% yield of benzylsulfonylacetic acid, mp 136–138° (lit.[16] mp 135–137°), was obtained from 50 g (0.40 mole) of phenylmethanethiol[17] by reaction with aqueous sodium chloroacetate followed by oxidation with 30% hydrogen peroxide in acetic acid–acetic anhydride solution. To a solution containing 15.0 g (70.1 mol) of benzylsulfonylacetic acid dissolved in 250 ml of acetic acid and 100 ml of 10% potassium bromide in water was added 7 ml (135 mmol) of bromine. This mixture was stirred at room temperature for 30 min, and was then warmed to *ca.* 50° with a heat lamp. After standing at 50° for 3 hr, it was poured into 200 ml of water. The water solution was extracted with two 100-ml portions of methylene chloride which were combined, washed with 5% sodium bicarbonate solution until basic, and dried over anhydrous magnesium sulfate. The methylene chloride was removed *in vacuo*, and the resulting solid was recrystallized from methylene chloride–hexane to give 20.7 g (90%) of **2**, mp 125–126° (lit.[4] mp 123–124°).

Methyl *trans*-2-Phenylethenesulfonate (7).—To a solution containing 3.3 g (10 mmol) of **2** in 500 ml of methanol was added 5.4 g (100 mmol) of solid sodium methoxide. This solution was stirred at 0° for 2 hr and acidified with concentrated hydrochloric acid the major portion of methanol was removed by distillation. The remaining methanolic solution, *ca.* 50 ml, was poured into 100 ml of water and extracted well with ether. The ether extracts were combined and dried with anhydrous magnesium sulfate. The ether was removed *in vacuo* resulting in an oil which solidified on standing. The solid was recrystallized from benzene to give 1.55 g (78%) of **7**, mp 68–69° (lit.[18] mp 68.0–68.7°).

Diphenylmethylmercaptoacetic Acid.—A solution containing 36.8 g (0.20 mol) of benzhydrol, 24 ml of 48% hydrobromic acid, and 16.5 g (0.22 mol) of thiourea in 400 ml of benzene was stirred at room temperature for 20 hr. The resulting precipitate was collected on a filter and washed with 200 ml of benzene. The solid was transferred to a flask containing 32 g of sodium hydroxide and 18.8 g (0.20 mol) of chloroacetic acid dissolved in 400 ml of water. This mixture was held at reflux for 3 hr, cooled, and acidified to pH 2 with concentrated hydrochloric acid. The acidified mixture was extracted well with ether and the ether extracts were combined and washed with saturated salt solution

---

[9] B. Bäcklund, Ph.D. Dissertation, Uppsala, Sweden, 1945.

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

[11] Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill.

[12] Aldrich Chemicals Co., Milwaukee, Wis.

[13] F. G. Bordwell and M. L. Peterson, *J. Amer. Chem. Soc.*, **81**, 2000 (1959).

[14] Eastman Chemicals, Rochester, N. Y.

[15] D. Y. Curtin and E. W. Flynn, *ibid.*, **81**, 4714 (1959).

[16] J. Tsung and J. Y. Chi, *Hua Hsueh Hsueh Pao*, **26**, 31 (1960); *Chem. Abstr.*, **55**, 17635*f* (1960).

[17] We wish to thank Evans Chemetics, Inc., New York, N. Y., for a generous supply of phenylmethanethiol.

[18] C. S. Rondestvedt and J. C. Wygant, *J. Amer. Chem. Soc.*, **73**, 5785 (1951).

prior to drying with anhydrous magnesium sulfate. Filtration followed by concentration *in vacuo* gave a solid which was recrystallized from carbon tetrachloride to give 41.5 g (80%) of material, mp 127–129.[16]

Diphenylmethylsulfonylacetic Acid.—To a suspension of 10.3 g (40.0 mmol) of diphenylmethylmercaptoacetic acid in 50 ml of acetic acid and 10 ml of acetic anhydride was added 14 ml of 30% hydrogen peroxide. The mixture warmed spontaneously to *ca.* 50° yielding a solution. The mixture was then cooled in a water bath until the reaction was no longer strongly exothermic and then stirred at room temperature overnight. The excess hydrogen peroxide was reduced with sodium bisulfite, and then the reaction mixture was concentrated *in vacuo*. The residue was taken up in water–methylene chloride, and the aqueous phase extracted well with methylene chloride. The extracts were combined, washed with saturated salt solution, and dried with anhydrous magnesium sulfate. Filtration followed by concentration *in vacuo* of the filtrate gave a solid which was recrystallized from benzene to give 9.8 g (85%) of the desired compound, mp 142–144°, with decarboxylation.[16]

Benzyhydryl Dibromomethyl Sulfone (9).—Diphenylmethylsulfonylacetic acid (3.48 g, 12 mmol) was suspended in 60 ml of acetic acid and 30 ml of water, and while cooling in an ice bath, 1.4 ml of bromine (27 mmol) in 15 ml of 30% potassium bromide was added dropwise with stirring. After stirring at room temperature overnight, the mixture was concentrated *in vacuo* to give a residue which was transferred with water and methylene chloride to a separatory funnel. The aqueous phase was extracted well with methylene chloride, and the combined extracts were washed with sodium bicarbonate and saturated salt solution and dried over anhydrous magnesium sulfate. Concentration gave 4.5 g of material, which was recrystallized from chloroform–hexane to give an 80% yield of crystals in two crops, mp 202–203° dec and 197–199° dec. A portion recrystallized for analysis melted at 203–204° dec.

Anal. Calcd for $C_{14}H_{12}Br_2O_2S$: C, 41.60; H, 2.99. Found: C, 41.61; H, 2.98.

Reaction of Benzhydrol Sulfone (9) with Bases. A. With Methoxide in Methanol. 1.—To a solution containing 2.5 g of sodium methoxide in 100 ml of methanol (0.46 *M* in methoxide ion) was added 1.50 g (3.71 mmol) of 9. This mixture was stirred at 0° for 1 day. It was then heated at reflux[19] for 2 hr, poured into 200 ml of water, and extracted well with ether. The aqueous portion was saved. The ether was washed with water and saturated salt solution, and dried with anhydrous magnesium sulfate. The ether was removed *in vacuo*, and the resulting oil was diluted with ether in a volumetric flask to 5.0 ml. This mixture was then analyzed at 195° by vpc (see Table II). The aqueous layer was concentrated to *ca.* 25 ml and 750 mg of *p*-chlorobenzylthiuronium chloride dissolved in 5 ml of water was added. The resulting precipitate was collected and washed with water; 1.25 g (73%) of *p*-chlorobenzylthiuronium 2,2-diphenylethylenesulfonate, mp 181–183°,[13] was collected.

2.—To a solution containing 2.5 g of sodium methoxide in 100 ml of methanol heated at reflux (65°) under nitrogen was added 1.50 g (3.71 mmol) of 9. This solution was stirred at reflux for 2 hr and was worked up as before (see Table II).

Treatment of 9 with varying concentrations of sodium methoxide in methanol either at 0 or 65° was carried as above. The reaction times were decreased or increased appropriately according to the base concentration. The data are given in Table II.

B. Reaction of 9 with Sodium Hydroxide in 40% Dioxane. 1.—To a solution containing 1.6 g of sodium hydroxide in 60 ml of water and 25 ml of dioxane was added 1.50 g (3.71 mmol) of 9 dissolved in 15 ml of dioxane (0.40 *M* in hydroxide ion). This mixture stirred at 0° for 20 hr and then worked up as usual (see Table II).

2.—To a solution containing 1.6 g of sodium hydroxide dissolved in 60 ml of water and 40 ml of dioxane was added 1.50 g of 9. This mixture was stirred under nitrogen at 87° for 2 hr. The mixture was worked up as usual (see Table II).

3.—When the above reaction was repeated in the presence of 680 mg (5.0 mmol) of sodium sulfite, the reaction mixture consisted of 87% 1,1-diphenylethylene, 9% 1,1-diphenyl-2-bromoethylene, and 4% 1,1-diphenylethylenesulfonic acid (isolated as the *p*-chlorobenzylthiuronium salt).

C. Reaction of 9 with Potassium *t*-Butoxide in *t*-Butyl Alcohol. 1.—To a solution containing 9.0 g of potassium *t*-butoxide in 80 ml of *t*-butyl alcohol was added 1.30 g (3.21 mmol) of 9 dissolved in 120 ml of *t*-butyl alcohol. This mixture was stirred at room temperature (25°) for 2 days. *n*-Pentane was used in the work-up (see Table II).

2.—To a solution containing 9.0 g of potassium *t*-butoxide dissolved in 100 ml of *t*-butyl alcohol was added quickly 1.00 g (2.48 mmol) of 9 dissolved in 100 ml of hot *t*-butyl alcohol. This mixture was stirred at reflux (83°) under nitrogen for 1.5 hr. The reaction mixture was worked up as before (see Table II).

Reactions of Benzyl Dibromomethyl Sulfone (2) with Bases.—Treatment of 2 with sodium methoxide in methanol, sodium hydroxide in aqueous dioxane, and potassium *t*-butoxide in *t*-butyl alcohol was carried out in the same manner as in the case of 9 (see Table I).

Treatment of 2.70 g (8.24 mmol) of 2 with 1.40 g (11.1 mmol) of sodium sulfite with 0.40 *M* sodium hydroxide in 60% aqueous dioxane at 87° under nitrogen for 2 hr, gave 42% styrene, 15% phenylacetylene (vpc analysis), and 36% 2-phenyl-1-ethylenesulfonic acid (isolated as the *p*-chlorobenzylthiuronium salt) (see Table I).

Benzhydryl Dichloromethyl Sulfone (13).—Chlorine gas was slowly passed through a solution containing 10.0 g (34.5 mmol) of diphenylmethylsulfonylacetic acid dissolved in 180 ml of acetic acid and 90 ml of water. The resulting saturated chlorine mixture was stirred at 30–40° for 4 hr. This mixture was then poured into 200 ml of water, which was extracted with three 100-ml portions of ether. The ether extracts were combined and washed with 5% sodium bicarbonate and saturated salt solutions. After drying with anhydrous magnesium sulfate, the ether was removed *in vacuo* to give a solid which was recrystallized from carbon tetrachloride to give 4.1 g (38%) of 13, mp 157–161°. This was recrystallized from ethanol, mp 161–163°.

Anal. Calcd for $C_{14}H_{12}Cl_2O_2S$: C, 53.34; H, 3.84; Cl, 22.50. Found: C, 53.59; H, 3.93; Cl, 22.47.

Reactions of α,α-Dichloro Sulfone 13 with Bases.—The reactions of 13 with sodium methoxide in methanol, sodium hydroxide in 60% aqueous dioxane, and with potassium *t*-butoxide in *t*-butyl alcohol were carried out in precisely the same manner as for the dibromo analog 9. The usual amount of 13 used in the runs was 1.20 g (3.81 mmol). The results are shown in Table III.

Phenyl Dibromomethyl Sulfone.—To a solution containing 4.0 g (20 mmol) of phenylsulfonylacetic acid[20] and 2.0 g of potassium bromide dissolved in 70 ml of acetic acid and 35 ml of water at room temperature was added 2 ml of bromine dissolved in 5 ml of acetic acid. A heat lamp was shown on the stirring solution, and the temperature rose to 70°. This mixture was then stirred at 60–70° for 3 hr. The reaction was worked up by pouring into water and extracting well with ether. The ether extracts were combined and washed 10% sodium sulfite solution, 5% sodium bicarbonate solution, and saturated salt solution followed by drying with anhydrous magnesium sulfate. The ether was removed *in vacuo*, and the resulting oil was crystallized from hexane–ether to give 5.6 g (90%) of phenyl dibromomethyl sulfone, mp 71–74°. This was recrystallized from hexane, mp 82–83°.

Anal. Calcd for $C_7H_6Br_2O_2S$: C, 26.77; H, 1.93; Br, 50.90. Found: C, 26.90; H, 2.07; Br, 50.76.

Treatment of Phenyl Dibromomethyl Sulfone with Reducing Agents.—A solution containing 1.50 g (4.78 mmol) of phenyl dibromomethyl sulfone dissolved in 100 ml of 0.37 *M* sodium methoxide in methanol was held at reflux for 2 hr. After allowing the solution to cool to room temperature, water was added, and this mixture was extracted well with ether which was then dried with anhydrous magnesium sulfate. The ether was removed *in vacuo*, and a pmr spectrum of the resulting oil showed the product to be a mixture of starting material (60%) and phenyl bromomethyl sulfone (40%).

Treatment of phenyl dibromomethyl sulfone with 0.08 *M* sodium sulfite in 60% aqueous dioxane at 87° for 2 hr gave a quantitative conversion to phenyl bromomethyl sulfone, mp 50–52°.[21]

---

[19] This converts methyl *trans*-2-phenylethenesulfonate (7) into the sulfonate 8 which stays in the aqueous layer and is analyzed separately from the other organic reaction products. This treatment at reflux temperature does not affect the per cent of 1,1-diphenylethylene and 1,1-diphenyl-2-bromoethylene.

[20] G. Kresze, W. Schramm, and G. Cleve, *Chem. Ber.*, **94**, 2060 (1961).

[21] Undepressed on admixture with an authentic sample furnished by D. Schexnayder.

Methyl 2,2-Diphenylethylenesulfonate (12).—To a solution containing 8.0 g (19.9 mmol) of 9 dissolved in 120 ml of tetrahydrofuran and 250 ml of methanol at −10° was added 15.0 g of sodium methoxide. This mixture stirred at −10° for 2 hr. The usual water work-up with ether extraction gave a solid which was recrystallized from hexane–carbon tetrachloride to give 3.8 g (70%) of 12, mp 95–96°.

Anal. Calcd for $C_{15}H_{14}O_3S$: C, 65.67; H, 5.14. Found: C, 66.00; H, 5.11.

Registry No.—2, 16003-63-7; 9, 16003-62-6; 12, 16003-64-8; 13, 16003-65-9; phenyldibromomethyl sulfone, 16003-66-0.

Acknowledgment.—We are grateful to the National Science Foundation (NSF GP-4208) for support of this work.

Alumina: Catalyst and Support. XXXVII.[1] Mechanism of Dehydration of *cis*- and *trans*-2-Alkyl-, -2-Phenyl-, and -3-*t*-Butylcyclohexanols over Alumina Catalysts[2,3]

EDWARD J. BLANC[3] AND HERMAN PINES

The Ipatieff High Pressure and Catalytic Laboratory, Department of Chemistry, Northwestern University, Evanston, Illinois 60201

Received November 27, 1967

The mechanism of dehydration of the stereoisomers of 2-alkyl-, 2-phenyl-, and 3-*t*-butylcyclohexanols over alumina, prepared from aluminum isopropoxide, was studied by the micropulse technique at atmospheric pressure and at temperatures of 200–350°. The preferred mode of dehydration was found to be *trans* elimination. The *cis*-2-substituted cyclohexanols gave the 1-substituted cyclohexenes as the major product, whereas the 3-substituted cyclohexenes were the major products from the *trans*-2-substituted cyclohexanols. This *trans* elimination may be pictured as taking place between two surfaces of alumina, such as in a crevice or pore. Thus a basic site could abstract a proton on one side of the alcohol molecule, while an acidic site was attacking a hydroxyl group on the opposite side. This explanation is consistent with the concept of alumina acting as a "pseudo-solvent." Treatment of the catalyst with pyridine and extrapolation of the plots of per cent composition *vs.* per cent conversion to zero conversion showed the 4- and the 1-substituted cyclohexenes from the *trans*-2-substituted cyclohexanols to be initial products. A 1,3 elimination and an E1 process, respectively, were proposed as the mechanistic pathways to these olefins. The dehydration of *cis*- and *trans*-2-methylcyclohexanol-2-*d* was consistent with the concept of concerted *trans* elimination as the preferred mode of dehydration. However, the results also suggested that 1-methylcyclohexene from *trans*-2-methylcyclohexanol was produced *via* an E1 process. Variances in product distribution with the position, size, and nature of the group suggested that steric and polar factors play a role in determining the product distribution.

Recently the concept of alumina acting as a "pseudo-solvent" has been proposed by Pines and Manassen.[4] This "solvating" action of alumina is considered to arise from an acidic site attacking the hydroxyl group of the alcohol while a basic site abstracts a proton from the opposite side of the molecule. Thus *trans* elimination, similar to E2 reaction in solution, is the preferred mode of dehydration.

This concept has been used to explain the results or dehydration of menthol and neomenthol,[5] 2-*exo*- and 2-*endo*-bornanol,[6] and the four stereoisomers of 1-decalol.[7] In all of these cases products other than those which arise from *trans* elimination were also found. These were products of *cis* and γ or 1,3 elimination.

In the present study the dehydration of a series of *cis*- and *trans*-substituted cyclohexanols was investigated in order to evaluate the effect of steric and polar factors on the product distribution. The alcohols studied were *cis*- and *trans*-2-methyl-, 2-isopropyl-, 2- and 3-*t*-butyl-, and 2-phenylcyclohexanol. The dehydration of *cis*- and *trans*-2-methylcyclohexanol-2-*d* was also studied in order to shed more light on the formation of the 1-R-cyclohexenes which cannot be formed by *trans* elimination of *trans*-2-R-cyclohexanols.

The alcohols were prepared by hydrogenation of the corresponding alkylphenols, and the isomers were separated by preparative gas chromatography or by chromatography over alumina.

The dehydrations were made using the micropulse technique, which was first applied by Emmett and coworkers[8] and modified by Steingaszner and Pines.[9] Schappell and Pines[7] showed that the micropulse technique used for dehydration over alumina gave results similar with those obtained in a flow system. The reactions were carried out at atmospheric pressure and at temperatures of 200–350°.

Alumina prepared from aluminum isopropoxide was used in amounts of 2–16 mg. The catalyst was of 20/40 mesh size and was supported between zones of glass beads of the same mesh.

To each of the alcohols a known amount of an internal standard was added. This standard, a hydrocarbon which was stable under the reaction conditions, was used to calculate the conversion into olefins and the relative retention times of the olefins. The solid alcohols were dissolved in cyclohexane to form a 10–20 mol % solution. The sample sizes were 5–10 μl.

The reaction products were analyzed by gas chromatography and identified by comparison of their relative retention times with those of known samples.

---

[1] For paper XXXVI, see W. F. Fry and H. Pines, *J. Org. Chem.*, **33**, 602 (1968).

[2] Paper XIV of the series of Dehydration of Alcohols. For Paper XIII, see N. C. Sih and H. Pines, *ibid.*, **31**, 4092 (1966).

[3] (a) This research was supported in part by the Atomic Energy Commission Contract AT(11-1) 1096. (b) The following terminology was used in this paper: "2-R-cyclohexanols," "2-R-cyclohexenes," etc. R stands for the substituent groups methyl, isopropyl, *t*-butyl, and phenyl.

[4] H. Pines and J. Manassen, *Advan. Catal.*, **16**, 49 (1966).

[5] H. Pines and C. N. Pillai, *J. Amer. Chem. Soc.*, **83**, 3270 (1961).

[6] K. Watanabe, C. N. Pillai, and H. Pines, *ibid.*, **84**, 3934 (1962).

[7] F. G. Schappell and H. Pines, *J. Org. Chem.*, **31**, 1735 (1966).

[8] R. J. Kokes, H. Tobin, Jr., and P. H. Emmett, *J. Amer. Chem. Soc.*, **77**, 5860 (1955).

[9] P. Steingaszner and H. Pines, *J. Catal.*, **5**, 356 (1966).