# A Base-induced Elimination Reaction of Phenylsulfonylacetates. I. General Aspect and Stereochemistry

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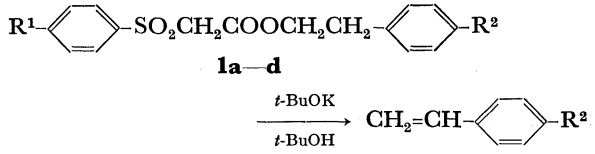
(Received December 27, 1973)

Esters of phenylsulfonylacetic acid were found to undergo a base-induced $\beta$-elimination reaction with *t*-butoxide in *t*-butyl alcohol. The intervention of a carbanion as an intermediate of the elimination was proposed. The stereochemistry of the elimination was examined by the use of *erythro*- and *threo*-2-deuterio-1,2-diphenylethyl phenylsulfonylacetates. From the deuterium content in a product, *i.e.*, *trans*-stilbene, the elimination was found to occur predominantly in a *syn* fashion.

The pyrolytic elimination reaction of acetates has been investigated extensively, and it is well known that almost all of the reactions proceed through a cyclic six-membered transition state.[1] However, little is known about the base-induced $\beta$-elimination reaction of the acetates in solution.[2,3] Curtin and Kellom[3] observed that 1,2-diphenylethyl acetate predominantly undergoes a *syn* elimination with potassium amide in liquid ammonia to give stilbene. With *t*-butoxide in *t*-butyl alcohol, however, no elimination was observed. In a previous paper,[4] we reported that 1,2-diphenylethyl phenylsulfonylacetate produces *trans*-stilbene and methyl phenyl sulfone upon treatment with *t*-butoxide in *t*-butyl alcohol.[5] Experiments with a deuterium-labeled diastereoisomeric pair of the ester suggested that the stereochemistry of the reaction was a *syn* elimination. The present paper will be concerned with a more detailed investigation of the mechanism of this and related base-induced *syn* elimination reactions.

## Results and Discussion

In order to shed light on the mechanism of elimination reactions of phenylsulfonylacetates, we first employed 2-phenylethyl phenylsulfonylacetate (**1a**). This ester did not react when heated in diphenyl ether (259 °C). Thus, we anticipated that no thermal elimination operated below this temperature. On the other hand, it was found that the ester gives methyl phenyl sulfone on treatment with potassium *t*-butoxide in *t*-butyl alcohol (reflux) or on treatment with sodium methoxide in diphenyl ether (reflux). Because the presence of a styrene-forming elimination reaction with bases had been suggested, kinetic studies of the base-induced elimination reactions were performed for *para*-substituted 2-phenylethyl phenylsulfonylacetates (**1a**—**d**) using potassium *t*-butoxide in absolute *t*-butyl alcohol. The rates of the olefin-forming elimination reactions from **1** were followed spectrophotometrically by means of the characteristic absorption of the styrenes produced. An excess of the base was required to bring



**1a—d**



**a**, $R^1=H$, $R^2=H$; **b**, $R^1=H$, $R^2=CH_3$; **c**, $R^1=H$, $R^2=Cl$; **d**, $R^1=CH_3$, $R^2=H$

Table 1. Pseudo-first-order rate constants and activation parameters for eliminations from arylsulfonylacetates (**1a—d**) and 2-methyl-2-(phenylsulfonyl)propanoate (**2**) with *t*-butoxide in *t*-butyl alcohol

| Substrate | Temp.[a] (°C) | $k\times10^6$ ($s^{-1}$)[b,c] | $\Delta H^{\neq}$[d] (kcal·mol$^{-1}$) | $\Delta S^{\neq}$[d] (e.u.) |
|---|---|---|---|---|
| **1b** | 40.0 | 0.899±0.038 | | |
| **1b** | 50.0 | 2.25 ±0.01 | 19.8 | −23.2 |
| **1b** | 60.0 | 6.49 ±0.03 | | |
| **1a** | 40.0 | 2.15 ±0.02 | | |
| **1a** | 50.0 | 6.39 ±0.03 | 21.4 | −16.1 |
| **1a** | 60.0 | 18.0 ±0.4 | | |
| **1c** | 40.0 | 7.62 ±0.08 | | |
| **1c** | 50.0 | 20.9 ±0.2 | 20.9 | −15.5 |
| **1c** | 60.0 | 60.8 ±0.6 | | |
| **1d** | 40.0 | 1.98 ±0.01 | | |
| **1d** | 50.0 | 6.00 ±0.05 | 21.5 | −16.1 |
| **1d** | 60.0 | 16.8 ±0.2 | | |
| **2** | 40.0 | 0.679±0.026 | | |
| **2** | 50.0 | 1.28 ±0.04 | 11.6 | −49.7 |
| **2** | 60.0 | 2.24 ±0.26 | | |

a) Bath temperature was kept within ±0.05 °C. b) Initial concentrations; [substrate]=$5.00\times10^{-3}$M, and [base]=1.00 M. c) Deviations listed are standard deviations. d) At 50.0 °C.

about the elimination reaction of **1** effectively. The pseudo-first-order rate constants and the other thermodynamic data for the eliminations from **1a—d** are given in Table 1. In the reaction of **1a** with an excess amount of potassium *t*-butoxide in *t*-butyl alcohol, the reaction mixture was quenched by hydrochloric acid-*d* at an appropriate stage of the reaction, and the recovered starting material was submitted to NMR examination. The NMR spectra of the recovered **1a** showed that the methylene hydrogen atoms positioned $\alpha$ to the sulfonyl group were considerably displaced by deuterium atoms.[4] This observation suggests that a large portion of **1** must be converted into its conjugate base (carbanion) under the above conditions. Numerous examples illustrating the base-induced hydrogen exchange of methylene hydrogens positioned $\alpha$ to a sulfonyl group have been reported, and they have been explained on the basis of the formation of a carbanion stabilized by a strongly electron-withdrawing inductive effect of the sulfonyl group and a 3d-orbital resonance

with the adjacent sulfur atom.[6]

Since 2-phenylethyl 2-methyl-2-(phenylsulfonyl)propanoate (**2**) has no methylene hydrogens positioned α to the sulfonyl group, it is unlikely to anticipate **2** to

$$PhSO_2-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-COOCH_2CH_2Ph$$

**2**

give a carbanion similar to that of **1**. Accordingly, the reaction of **2** with potassium *t*-butoxide in absolute *t*-butyl alcohol was examined. The rate data and the activation parameters for the elimination reaction from **2** are also given in Table 1. As is shown in Table 1, the rate constant for the elimination from **2** is smaller than that for the elimination from **1a**. The values of the activation enthalpy and entropy for the elimination from **2** are quite different from those for the eliminations from **1a—d**. These results imply that the reaction mechanism of the elimination from **2** differs from that of **1**. It should be emphasized that a rapid formation of the carbanion occurs in the reaction of **1**, but not in the reaction of **2**. Judging from the facts described above, it is likely that the carbanion plays an important role in the olefin-forming elimination reaction of **1**. The carbanionic center thus formed in **1** should considerably lower the leaving ability of the leaving group ($ArSO_2CH_2COO^-$), thus decreases the rate of the E2 reaction of **1**. However, this is not the case. An alternative possibility is that the carbanionic center acts intramolecularly as an attacking base against β-hydrogen to promote the elimination; that is, an intramolecular carbanionic elimination takes place in the present case. A carbanionic mechanism has frequently been supposed to account for the *syn* eliminations in the systems where the favored *anti* co-planarity can not be readily attained.[7] However, the role of the carbanionic center in the present reaction is apparently distinct from those described in the literature.[7] It seems to act as a base to abstract β-hydrogen through a six-membered cyclic transition state. If so, the elimination should proceed in a *syn* fashion. Consequently, the stereochemistry of the elimination reaction was examined. The substrates used were two deuterium-labeled diastereoisomers of 1,2-diphenylethyl phenylsulfonylacetate (**3**)—that is, *dl-erythro-* and *dl-threo-*2-deuterio-1,2-diphenylethyl phenylsulfonylacetates (**4e** and **4t**).

$PhSO_2CH_2COOCHPhCH_2Ph$

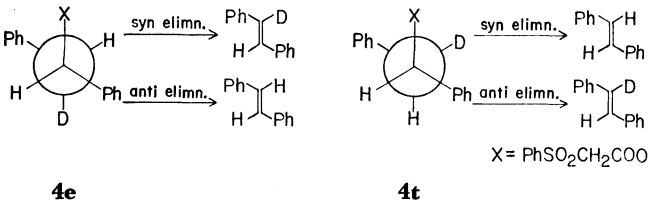
**3**

$PhSO_2CH_2COOCHPhCHDPh$

**4e, t**

**e**, *erythro-*; **t**, *threo-*

The products resulting from the reaction of **3** or **4** with potassium *t*-butoxide in absolute *t*-butyl alcohol were found by gas chromatography to be *trans*-stilbene, 1,2-diphenylethanol, and methyl phenyl sulfone. No *cis*-stilbene was detected; that is, this elimination is stereoselective. Under the conditions employed, no isomerization from **4e** to **4t** or the reverse occurred, as checked by NMR. Both *trans*-stilbene and 1,2-diphenylethanol were quite stable under the conditions employed, as checked by gas chromatography. Furthermore, **4e** or **4t** recovered from the reaction mixture was found to retain its deuterium atom, as checked by NMR and mass spectrometries; that is, no D–H exchange was present. Also, no hydrogen exchange of *trans*-stilbene was observed with potassium *t*-butoxide in *t*-butyl alcohol-*O-d*. These observations clearly show that the stereochemistry of the elimination can be elucidated by examining the deuterium content of *trans*-stilbene obtained from **4e** and **4t**.




**4e** **4t**

Scheme 1.

From a consideration of a stereo-model of **4**, the most favorable conformations are those depicted in Scheme 1. If the elimination occurred in a *syn* fashion, **4e** should give *trans*-stilbene-α-*d*, while if it occurred in an *anti* fashion, **4e** should give *trans*-stilbene with no deuterium. On the other hand, **4t** should give *trans*-stilbene with no deuterium in a *syn* elimination, while in an *anti* elimination **4t** should give *trans*-stilbene-α-*d*. The deuterium contents of *trans*-stilbene obtained from the reactions of **4e** and **4t** with potassium *t*-butoxide in *t*-butyl alcohol were determined by mass spectrometry. The results are shown in Table 2. It is quite clear

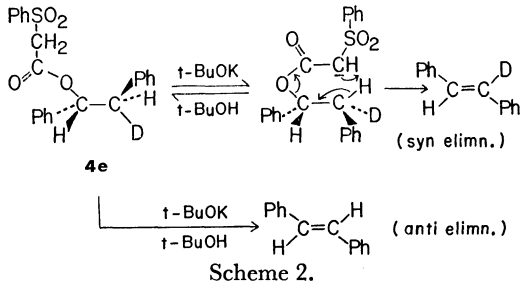
Table 2. Deuterium contents of *trans*-stilbene obtained from *erythro-* and *threo*-2-deuterio-1,2-diphenylethyl phenylsulfonylacetates (**4e** and **4t**) with *t*-butoxide in *t*-butyl alcohol[a]

| [*t*-BuOK] (M) | Deuterium content of *trans*-stilbene[c] | |
|---|---|---|
| | from **4e**[b] (%) | from **4t**[b] (%) |
| 0.10 | 84.2±1.9 | 29.5±2.5 |
| 0.30 | 82.6±2.0 | 50.1±2.3 |
| 0.50 | 82.0±2.0 | 50.8±1.7 |
| 0.70 | 81.8±0.7 | 53.0±1.2 |
| 1.00 | 82.6±2.4 | 53.9±1.1 |
| 1.30 | 82.4±0.8 | 53.1±2.5 |

a) Reaction temperature was 90.0 °C. b) Initial concentration was [substrate]$=5.00\times10^{-3}$M. c) Deviations listed are standard deviations.

that the stereochemically-favored course of the elimination from **4** is *syn*, but the predominance of *syn* elimination is not overwhelming. It seems that a dual mechanism is operating in these eliminations—a predominant *syn* elimination accompanied by a concomitant *anti* elimination. The deuterium content of *trans*-stilbene obtained from the elimination of **4e** is almost independent of the concentration of the base, while that obtained from **4t** increases with an increase in the concentration of the base.

From these results, it can be concluded that the carbanion, the conjugate base of the substrate, is




Scheme 2.

rapidly formed as an intermediate which successively undergoes the *syn* unimolecular elimination reaction through a six-membered cyclic transition state (Ei), as is depicted in Scheme 2. An *anti* elimination also occurs concomitantly with a *syn* elimination. A possible alternative may be a *syn* E2 mechanism. However, it is unlikely that a *syn* concerted bimolecular elimination occurs predominantly in the present case.[8]

Previously, Curtin and Kellom[3] treated *erythro*- and *threo*-2-deuterio-1,2-diphenylethyl acetates with potassium amide in liquid ammonia and explained their results in terms of the *syn* elimination mechanism. They proposed the cyclic mechanism, which had been rejected by Hauser, Shivers, and Skell[2] because an excess amide ion was required to convert 2-phenylethyl acetate into styrene. Our observations are compatible with Curtin's cyclic intramolecular mechanism for the *syn* elimination.[3] That the presence of the excess base is necessary to bring about the reaction effectively indicates that the excess base is required to displace the equilibrium toward carbanion formation.[4] As is shown in Scheme 2, in the *syn* elimination from **4e** to give *trans*-stilbene-α-*d* the β-proton should be abstracted by a base, the carbanionic center in **4e**. On the other hand, in the corresponding *anti* elimination from **4e** the β-deuteron should be abstracted by an external base, *t*-butoxide. The reverse operates in the elimination reaction from **4t**. Thus, the kinetic isotope effect may be thought to be responsible for the apparently higher *syn* path: *anti* path ratio for **4e** than for **4t** (Table 2). An increase in the fraction of a bimolecular elimination, which results from an increase in the base concentration, should be more significant in the reaction of **4t** than in that of **4e**, because the value of the primary kinetic isotope effect ($k_H/k_D$) for the *anti* elimination reaction of **4** must be appreciably higher than unity. Table 2 indicates that this is the case. Especially, a change in the base concentration from 0.1 to 0.3 M gives rise to a considerable increase in the fraction of *anti* elimination from **4t**; whereas the corresponding increase is not so significant in the case of **4e**. However, a leveling effect upon the change in deuterium content is observed with a further increase in the base concentration. This effect suggests a possibility of the contribution of ion pairs. A study of the effect of ion pairs will be presented elsewhere.

The *syn* elimination mechanism described above resembles the so-called α′,β-elimination mechanism. Both reactions include the preliminary abstraction of hydrogen in the leaving groups, and both proceed through cyclic transition states. However, the α′,β-elimination is mainly a reaction of an 'onium salt with an organometallic compound[9] and necessarily includes an ylide intermediate, which leads inevitably to a five-membered transition state; this is in contrast with the elimination from phenylsulfonylacetates with alkoxides described in the present paper.

## Experimental

All the melting points are uncorrected. The NMR spectra were taken on a JEOL JNM-PS-100 spectrometer, using tetramethylsilane as the internal standard, and the UV spectra on a Shimadzu UV-200 double-beam spectrophotometer. The gas chromatographic analyses were performed by means of a JEOL JGC-20K (f.i.d.) gas chromatograph. The mass spectra were recorded on a Hitachi RMS-4 mass spectrometer connected with a Hitachi K-53 gas chromatograph.

*Materials.* All the carboxylic esters were prepared in the usual way from the corresponding acid chlorides and the alcohols. These alcohols and carboxylic acids were prepared using methods reported in the literature.

*2-Phenylethyl Phenylsulfonylacetate (**1a**).* Recrystallized from ethanol; mp 81.0—81.5 °C; NMR ($CDCl_3$) δ 2.78 (t, 2H), 4.06 (s, 2H), 4.21 (t, 2H), and 7.01—7.90 (m, 10H). Found: C, 62.99; H, 5.34%. Calcd for $C_{16}H_{16}O_4S$: C, 63.14; H, 5.30%.

*2-(p-Tolyl)ethyl Phenylsulfonylacetate (**1b**).* Recrystallized from ethanol; mp 76.0—76.5 °C; NMR ($CDCl_3$) δ 2.25 (s, 3H), 2.73 (t, 2H), 4.05 (s, 2H), 4.18 (t, 2H), 7.01 (s, 4H), and 6.91—7.91 (m, 5H). Found: C, 64.20; H, 5.69%. Calcd for $C_{17}H_{18}O_4S$: C, 64.13; H, 5.70%.

*2-(p-Chlorophenyl)ethyl Phenylsulfonylacetate (**1c**).* Recrystallized from ethanol; mp 56 °C; NMR ($CDCl_3$) δ 2.76 (t, 2H), 4.08 (s, 2H), 4.20 (t, 2H), 7.03 (d, 2H), 7.16 (d, 2H), and 7.36—7.89 (m, 5H). Found: C, 56.77; H, 4.45%. Calcd for $C_{16}H_{15}ClO_4S$: C, 56.72; H, 4.46%.

*2-Phenylethyl p-Tolylsulfonylacetate (**1d**).* Recrystallized from ethanol; mp 63.5—64.0 °C; NMR ($CDCl_3$) δ 2.39 (s, 3H), 2.80 (t, 2H), 4.04 (s, 2H), 4.22 (t, 2H), 7.03—7.32 (m, 7H), and 7.74 (d, 2H). Found: C, 64.37; H, 5.66; S, 10.19%. Calcd for $C_{17}H_{18}O_4S$: C, 64.13; H, 5.70; S, 10.07%.

*2-Phenylethyl 2-Methyl-2-(phenylsulfonyl)propanoate (**2**).* Purified by column chromatography on silica gel, with chloroform as the eluent. Viscous sirup; $n_D^{25}$ 1.5510; NMR ($CCl_4$) δ 1.48 (s, 6H), 2.75 (t, 2H), 4.14 (t, 2H), and 6.97—7.76 (m, 10H). Found: C, 64.92; H, 6.07%. Calcd for $C_{18}H_{20}O_4S$: C, 65.04; H, 6.06%.

*1,2-Diphenylethyl Phenylsulfonylacetate (**3**).* Recrystallized from ethanol; mp 97.0—97.5 °C; NMR ($CDCl_3$) δ 3.10 (seven lines, 2H), 4.05 (s, 2H), 5.90 (t, 1H), and 6.99—7.79 (m, 15H). Found: C, 69.28; H, 5.32%. Calcd for $C_{22}H_{20}O_4S$: C, 69.45; H, 5.30%.

dl-erythro-*2-Deuterio-1,2-diphenylethanol.* This alcohol was prepared from *trans*-stilbene oxide by treatment with lithium aluminum deuteride, and was then recrystallized from hexane; mp 66—67 °C (lit,[3] 64.4—65.4 °C); NMR ($CDCl_3$) δ 2.43 (s, 1H), 2.77 (d, $J$=8 Hz, 1H), 4.51 (d, $J$=8 Hz, 1H), and 6.80—7.04 (m, 10H).

dl-threo-*2-Deuterio-1,2-diphenylethanol.* This alcohol was prepared from *cis*-stilbene oxide by treatment with lithium aluminum deuteride, and was then recrystallized from hexane; mp 66—67 °C (lit,[3] 64.4—65.4 °C); NMR ($CDCl_3$) δ 2.53 (s, 1H), 2.85 (d, $J$=5 Hz, 1H), 4.68 (d, $J$=5 Hz, 1H), and 7.00—7.28 (m, 10H).

dl-erythro-*2-Deuterio-1,2-diphenylethyl Phenylsulfonylacetate (**4e**).* Recrystallized from ethanol; mp 97.0—97.5 °C;

NMR ($CDCl_3$) $\delta$ 3.13 (d, $J$=8 Hz, 1H), 4.03 (s, 2H), 5.83. (d, $J$=8 Hz, 1H), and 6.94—7.74 (m, 15H).

dl-threo-*2-Deuterio-1,2-diphenylethyl Phenylsulfonylacetate (**4t**)* Recrystallized from ethanol; mp 97.0—97.5 °C; NMR ($CDCl_3$) $\delta$ 2.98 (d, $J$=6.5 Hz, 1H), 4.03 (s, 2H), 5.87 (d, $J$=6.5 Hz, 1H), and 6.97—7.80 (m, 15H).

*Solvent and Base.* *t*-Butyl alcohol was distilled twice from clean metallic sodium under anhydrous conditions. Potassium metal was cut clean of all oxides and rinsed in purified *t*-butyl alcohol. The metal was immediately transferred into an appropriate amount of anhydrous *t*-butyl alcohol and allowed to dissolve under anhydrous conditions.

*Kinetic Measurements.* The reactions of **1a—d** and **2** with potassium *t*-butoxide in *t*-butyl alcohol were carried out in a 20 ml flask. The initial concentration of the substrate was $5.00\times10^{-3}$ M, while that of the base was 1.00 M. Runs were carried out in a thermostatted bath. The temperature was controlled within $\pm$0.05 °C. At appropriate intervals of time, 2 ml aliquots were withdrawn from the flask and quenched in ethanol—water (1 : 1 by volume) in a 25 ml volumetric flask. The volumetric flask was filled to the mark with the ethanol—water mixture and shaken. The concentration of olefin in this solution was measured spectrophotometrically. The pseudo-first-order rate constants were obtained from the measured absorbances at the absorption maximum of styrene or substituted styrenes. Each rate constant was calculated by following the reaction till 10—15% completion; after that time a concomitant alcohol-forming reaction caused it to give complex kinetics. The molar extinction coefficients in ethanol—water (1 : 1 by volume) are as follows: styrene, $\lambda_{max}$ 248 nm ($\varepsilon$, $1.42\times10^4$); *p*-methylstyrene, $\lambda_{max}$ 252 nm ($\varepsilon$, $1.66\times10^4$); and *p*-chlorostyrene, $\lambda_{max}$ 253 nm ($\varepsilon$, $1.84\times10^4$).

*Product Analysis.* To a 20ml solution of potassium *t*-butoxide in absolute *t*-butyl alcohol, we added 0.100 mmol of the substrate. After having been maintained at 90.0 °C for 1 hr, the mixture was poured into water and extracted with ether. The ethereal solution was washed with water, dried, and analyzed by gas chromatography using a 2 m column of 2% PEG 20 M on Celite 545 (60—80 mesh) at 200 °C. The reaction products detected were *trans*-stilbene and 1,2-diphenylethanol.

*Deuterium Analysis.* To a 20 ml solution of potassium *t*-butoxide in absolute *t*-butyl alcohol, we added 0.100 mmol of the substrate (**4e** or **4t**). The mixture in a sealed ampoule was maintained at 90.0 °C for 1 hr and then treated in a manner similar to that above. The deuterium content of *trans*-stilbene was determined by mass spectrometry using a mass spectrometer connected with a gas chromatograph. The ionizing energy used for the analyses was 70 eV. The deuterium content was evaluated from the intensities of the corresponding mass peaks, corrected for the natural abundances of isotopes. The calculation method was based on the assumptions that hydrogen randomization precedes the formation of $M^+-H\cdot$ species from the stilbene molecular ion and that the value of the deuterium isotope effect ($k_H/k_D$) on fragmentation is unity.[10]

*Control Experiments.* When *cis*-stilbene was treated with potassium *t*-butoxide in *t*-butyl alcohol at 90.0 °C for 1.5 hr, it showed no detectable isomerization to *trans*-stilbene as checked by gas chromatography.

*trans*-Stilbene and 1,2-diphenylethanol were treated with potassium *t*-butoxide as has been described above. No detectable change was observed, as checked by gas chromatography.

The NMR spectrum of *trans*-stilbene treated with potassium *t*-butoxide in *t*-butyl alcohol-*O-d* as described above showed no H–D exchange. *t*-Butyl alcohol-*O-d* was prepared from potassium *t*-butoxide and deuterium oxide using a modification of a method described in the literature.[11] The isotopic purity of this alcohol was checked by NMR before use.

The starting ester (**4e** or **4t**) recovered from the reaction mixture showed neither interconversion into the corresponding epimer nor H–D exchange, as checked by NMR and mass spectrometries.

We wish to express our appreciation to Dr. Tamio Ueno, Kyoto University, and the staff of Hitachi, Ltd., for their valuable comments and co-operation in the mass spectrometry.

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