# Mechanisms of Elimination Reactions. XXV. Stereoconvergent Elimination from the Diastereoisomeric 2-*p*-Toluenesulfonyl-1,2-diphenyl-1-chloroethanes[1]

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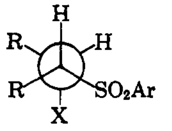
*Received November 19, 1962*

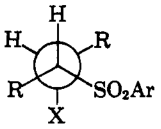
The diastereoisomeric 2-*p*-toluenesulfonyl-1,2-diphenyl-1-chloroethanes have been subjected to base-promoted dehydrochlorination. The *erythro* isomer eliminates cleanly *trans;* the *threo* isomer eliminates cleanly *cis;* thus both give α-*p*-toluenesulfonyl-*cis*-stilbene. This unsaturated sulfone and the corresponding *trans*-stilbene derivative have been prepared by straightforward syntheses; the latter rearranges to the former much more slowly than the former is produced in the elimination reactions. The results are consistent with a concerted elimination for the *erythro* isomer and a carbanion-intermediate process for the *threo* isomer.

In general it has been observed that bimolecular elimination from acyclic diastereoisomeric halides or sulfonate esters leads by *trans* elimination to isomeric olefins.[2] *trans*-Stereospecific elimination has even been observed in base-promoted elimination from *dl-erythro*- and *dl-threo*-3-*p*-toluenesulfonyl-2-butyl *p*-bromobenzenesulfonates[3] and the corresponding isomers of 3-benzenesulfonyl-2-butyl iodides,[4] where activation of the proton by the sulfonyl group might have been anticipated to lead to nonstereoselective carbanionic elimination.[5–8]

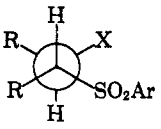
*trans*-Elimination from these *erythro* and *threo* chlorosulfones may be assumed to have transition states with conformations related to the structures I and II, respectively, which would lead (with loss of H and X) to the sulfonyl *cis* olefins IV and *trans* olefins V, respectively.



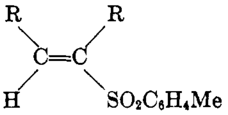
I
(a) R = $CH_3$
(b) R = Ph



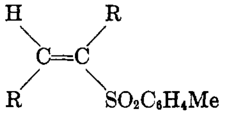
II
(a) R = $CH_3$
(b) R = Ph



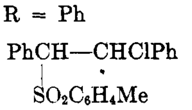
III
(a) R = $CH_3$
(b) R = Ph



IV
(a) R = Ph

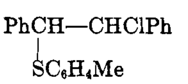


V
(a) R = Ph



$\underset{SO_2C_6H_4Me}{PhCH}\text{—}CHClPh$

VI



$\underset{SC_6H_4Me}{PhCH}\text{—}CHClPh$

VII

Of these processes, the one for the *erythro* isomers I has the advantage that presumed energy gain for the *trans* concerted process[5,9] is not compensated for by the large increase in steric strain to be anticipated by the nonbonding interaction between the large arenesulfonyl group and the R group. This interaction occurs in the corresponding *trans* elimination from the *threo* isomers in conformation II. For this reason it was tempting to predict that increasing the size of the R groups and/or increasing their ability to stabilize a negative charge might lead to a carbanionic process with the *threo* isomers. These would then presumably react *via* the more stable conformation III, and thus result in the formation of the more stable arenesulfonyl *cis* olefin IV. We, therefore, decided to prepare and study the diastereoisomeric 2-*p*-toluenesulfonyl-1,2-diphenyl-1-chloroethanes (VI), anticipating that the extra delocalization energy in a carbanion stabilized by a phenyl group as compared with a methyl group as well as the extra steric interaction might suffice. This, in fact, resulted, as is discussed subsequently.

As the desired compounds were unknown, the preparations of the chlorosulfones and of the corresponding olefins were undertaken. Addition of *p*-toluenesulfenyl chloride to *trans*- and to *cis*-stilbene led to diastereoisomeric chlorothioethers. These are *erythro*- and *threo*-2-*p*-toluenethio-1,2-diphenyl-1-chloroethanes (VII), respectively, assuming *trans* addition[10] to each olefin. Both chlorides solvolyzed in acetic acid and in ethanol, with the *erythro* isomer reacting more rapidly than the *threo* isomer.[11] Oxidation of these thioethers led to the corresponding β-chloro sulfones VI. Both sulfones reacted very rapidly with ethanolic sodium hydroxide to give, in substantially quantitative yield, α-*p*-toluenesulfonyl-*cis*-stilbene (IVa), the product of *trans* elimination from *erythro*-VI, but of *cis* elimination from *threo*-VI. The elimination proceeded at a rate possible to measure using ordinary techniques with the *threo* isomer at 10°, but too fast to measure in this way even at 0° with the *erythro* isomer; the fact that the eliminations were base-promoted was shown by the fact that both isomers could be recrystallized from ethanol without difficulty.

Proof of structure of the resulting olefin IVa was essential; its preparation and that of its isomer V were, therefore, carried out by alternative syntheses. Treatment of the *erythro* and *threo* isomers of VII with potassium *t*-butoxide in dimethyl sulfoxide and *t*-butyl alcohol gave α-*p*-thiocresoxy-*cis*-stilbene (VIII) and α-*p*-thiocresoxy-*trans*-stilbene (IX), respectively, as-

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(1) (a) Previous paper in series, S. J. Cristol and D. I. Davies, *J. Org. Chem.*, **27**, 293 (1962). This paper was presented before the Division of Organic Chemistry at the 140th National Meeting of the American Chemical Society in Chicago, Ill., September, 1961; (b) The term "stereoconvergent" to describe a reaction in which diastereoisomeric reagents lead to a single stereoisomeric product or to identical mixture of isomers has been suggested by P. L. Southwick, A. K. Colter, R. J. Owellen, and Y.-C. Lee, *J. Am. Chem. Soc.*, **84**, 4299 (1962).

(2) References to many such reactions have been given recently. See S. J. Cristol and R. S. Bly, Jr., *ibid.*, **82**, 142 (1960).

(3) F. G. Bordwell and P. S. Landis, *ibid.*, **79**, 1593 (1957).

(4) P. S. Skell and J. H. McNamara, *ibid.*, **79**, 85 (1957).

(5) S. J. Cristol, *ibid.*, **69**, 338 (1947).

(6) F. G. Bordwell and J. Kern, *ibid.*, **77**, 1141 (1955).

(7) H. L. Goering, D. I. Relyea, and K. L. Howe, *ibid.*, **79**, 2502 (1957).

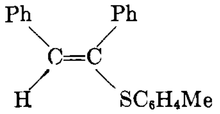
(8) S. J. Cristol and R. P. Arganbright, *ibid.*, **79**, 3441 (1957).

(9) S. J. Cristol, N. L. Hause, and J. S. Meek, *ibid.*, **73**, 674 (1951).

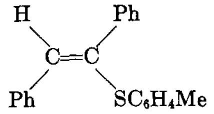
(10) (a) N. Kharasch, H. L. Wehrmeister, and H. Tigerman, *ibid.*, **69**, 1612 (1947); (b) D. J. Cram, *ibid.*, **71**, 3883 (1949); (c) N. Kharasch and A. J. Havlik, *ibid.*, **75**, 3734 (1953); (d) W. S. Orr and N. Kharasch, *ibid.*, **75**, 6030 (1953).

(11) P. G. Papathanassiou, Ph.D. thesis, University of Colorado, 1961.

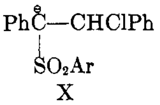
suming that both eliminations are *trans*. Oxidation of VIII and IX with hydrogen peroxide in acetic acid gave isomeric unsaturated sulfones. Of these, that from VIII was identical with the sulfone IV obtained by the dehydrochlorination of *erythro*- and *threo*-VI; the other isomer was thus the *trans*-stilbene V. The structural assignments were confirmed by the preparation of the thioethers VIII and IX by treatment with *p*-toluenesulfenyl chloride of $\alpha$-lithio-*cis*-stilbene[12] and $\alpha$-lithio-*trans*-stilbene,[12] respectively. These reactions should be expected to go with retention[3,12] and, in fact, were stereospecific.



VIII



IX



$$Ph\underset{SO_2Ar}{\overset{\ominus}{C}}-CHClPh$$

X

Before one may assume that both *erythro*- and *threo*-VI give IVa directly upon dehydrochlorination, it is, of course, necessary to show that Va is not an intermediate in one or both eliminations. The base-catalyzed rate of isomerization of Va to IVa was readily followed spectrophotometrically. The rate of isomerization of Va to IVa was shown to be very slow compared to the dehydrochlorination reaction, being approximately one-thirtieth that of elimination of the *threo* isomer at a temperature about 60° higher. Thus, IVa is the direct product from both isomers of VI.

The *trans* eliminations observed with *erythro*-VI, as well as with the *erythro* and *threo* butane derivatives,[3,4] Ia and IIa, are consistent with a concerted dehydrochlorination,[5,9] while the *cis* elimination observed with *threo*-VI may be readily rationalized by assuming a carbanion-intermediate mechanism.[13]

A transition state configurationally related to conformation Ib for elimination from *erythro*-VI is not in steric difficulty if one (or both) of the phenyl groups is rotated slightly out of the plane.[15] Such a conformation allows for the departing hydrogen and chlorine atoms to have the *trans* coplanarity required for concerted elimination. Conformation IIb is required for *threo*-VI in order to accommodate the proper geometry of hydrogen and chlorine for *trans* coplanar elimination. The steric overlap[16] between the *cisoid* phenyl group and the bulky elliptical *p*-toluenesulfonyl group is very substantial and cannot be removed completely in any orientation of the phenyl group when these groups are eclipsed. Thus steric strain may be expected to lower the reactivity of *threo*-VI compared with that of the *erythro* isomer by a concerted process.

The formation of carbanion X should not have a marked geometric requirement, and the most stable conformation IIIb for *threo*-VI should be suitable for reaction. Resonance stabilization of X by the conjugated phenyl and sulfone groups should enhance its rate of formation, and the decomposition of X into olefin IVb and chloride ion is unremarkable.[17]

The results observed then bear out the prediction that even with acyclic systems, when steric strains make the geometry required for *trans* coplanar elimination difficult to attain, resonance stabilization of a carbanion intermediate results in a fairly facile *cis* elimination.

Our results are related to those reported recently by Southwick and his co-workers[1b] in a carbonyl-activated system where a pair of diastereoisomeric halides gave largely one isomeric olefin. The term "stereoconvergent," which they have used to describe such a result, seems to us to be a particularly apt one.

## Experimental[19]

***erythro*-2-*p*-Thiocresoxy-1,2-diphenyl-1-chloroethane** (*erythro*-**VII**).—*p*-Toluenesulfenyl chloride[20] (17.2 g., 0.11 mole) was added in the dark to a solution of 20.0 g. (0.11 mole) of *trans*-stilbene in 110 ml. of carbon tetrachloride; the reaction mixture was heated at reflux until the red color disappeared (about 8 hr.). The mixture was cooled to room temperature and allowed to stand overnight. The crystals which separated were recrystallized from ethyl ether to give 26.3 g. (72%) of *erythro*-VII, m.p. 129–130°.

*Anal.* Calcd. for $C_{21}H_{19}ClS$; C, 74.42; H, 5.60. Found: C, 74.69; H, 5.79.

***erythro*-2-*p*-Toluenesulfonyl-1,2-diphenyl-1-chloroethane** (*erythro*-**VI**).—A solution containing 2.0 g. (5.9 mmoles) of *erythro*-VII and a large excess of peroxyphthalic acid in 300 ml. of ethyl ether was placed in a refrigerator for 24 hr. The solvent was then removed by distillation, and the remaining solid was dissolved in a mixture of 100 ml. of chloroform and 200 ml. of water and heated at reflux for 2 hr. The insoluble phthalic acid was removed by filtration and the chloroform layer was separated and dried over anhydrous magnesium sulfate. The solvent was removed by distillation after filtration of the desiccant. Recrystallization from ethanol gave 1.48 g. (66%) of *erythro*-VI, m.p. 182.5–184°.

*Anal.* Calcd. for $C_{21}H_{19}O_2ClS$: C, 68.00; H, 5.17. Found: C, 68.16; H, 5.15.

**Preparation of $\alpha$-*p*-Toluenesulfonyl-*cis*-stilbene (IVa) from *erythro*-VI.**—Two grams (5.5 mmoles) of *erythro*-VI was dissolved in 50 ml. of ethanol and treated with 20 ml. of 0.3 *N* ethanolic sodium hydroxide. The reaction mixture stood for a few minutes at room temperature. The solvent was removed and the remaining precipitate was washed once with water and recrystallized from alcohol. The yield was 1.65 g. (92%) of IVa, m.p. 179–180°.

*Anal.* Calcd. for $C_{21}H_{18}O_2S$: C, 75.41; H, 5.38. Found: C, 75.43; H, 5.25.

**Preparation of $\alpha$-*p*-thiocresoxy-*cis*-stilbene (VIII) by Dehydrochlorination.**—Three grams (8.9 mmoles) of *erythro*-VII was dissolved in 75 ml. of dimethyl sulfoxide, and then 45 ml. of 0.2 *M*

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[12] D. Y. Curtin and E. E. Harris, *J. Am. Chem. Soc.*, **73**, 4519 (1951).

[13] Evidence and discussions regarding the existence of carbanion intermediates in bimolecular elimination reactions where the geometry is unfavorable to a concerted elimination mechanism have been given in a large number of the papers in this series, dating from 1947. For a recent discussion of *cis* elimination in sulfones, see ref. 14.

[14] J. Hine and O. B. Ramsay, *J. Am. Chem. Soc.*, **84**, 973 (1962).

[15] The transition state, if *trans* concerted elimination is involved, will have the phenyl–phenyl steric strain intermediate between that in Ib and that in the olefin IVa.

[16] The transition state, if *trans* concerted elimination is involved, will have the phenyl–arenesulfonyl steric strain intermediate between that in IIb and that in Va.

[17] An attempt to find evidence for the intermediacy of X by partial dehydrochlorination and deuterium exchange in O-deuterated ethanol was unsuccessful, within the limits of infrared analysis. As pointed out before,[18] such negative evidence is consistent with a carbanion mechanism in which the reverse rate of the carbanion formation (reprotonation of the carbanion) is much smaller than loss of halide ion and formation of olefin.

[18] Deuterium-exchange experiments in eliminations with relatively simple alkyl halides or arenesulfonates have been routinely unsuccessful, except for an experiment with $\beta$-benzene hexaachloride, where the rate of reaction of the carbanion with deuterioethanol was approximately 0.7% of that of loss of chloride ion. This value was too small to observe by infrared techniques. S. J. Cristol and D. D. Fix, *J. Am. Chem. Soc.*, **75**, 2647 (1953). Such results are also compatible with concerted *cis* eliminations. See C. H. DePuy, R. D. Thurn, and G. F. Morris, *ibid.*, **84**, 1316 (1962), and ref. 14.

[19] Analyses are by Galbraith Laboratories.

[20] H. Lecher, R. Holschneider, K. Köberle, W. Speer, and P. Stöcklin, *Ber.*, **58**, 423 (1925).

potassium *t*-butoxide in *t*-butyl alcohol was added. The reaction mixture was heated for 30 min. on a steam bath, at the end of which time the reaction mixture was neutral to pH paper. The solvent was then distilled under reduced pressure. The remaining precipitate was washed once with water and dissolved in pentane. The hydrocarbon solution was extracted twice with water and was then separated and dried over anhydrous magnesium sulfate. The solvent was evaporated; recrystallization from ethanol gave 2.37 g. (90%) of VIII, m.p. 83–84°.

*Anal.* Calcd. for $C_{21}H_{18}S$: 83.40; H, 6.00. Found: C, 83.19; H, 5.76.

**Preparation of α-*p*-Toluenesulfonyl-*cis*-stilbene (IVa) from α-*p*-Thiocresoxy-*cis*-stilbene (VIII).**—α-*p*-Thiocresoxy-*cis*-stilbene, 400 mg. (1.32 mmoles), was dissolved in 25 ml. of glacial acetic acid. The solution was brought to boiling and 3 ml. of 30% hydrogen peroxide was added. The solution was boiled for 1 min., was allowed to stand for 1 hr., and then poured over crushed ice. The product was separated by filtration and recrystallized from ethanol. There was obtained 320 mg. (73%) of IVa, m.p. 179–180°.

**Preparation of α-*p*-Toluenesulfonyl-*cis*-stilbene (IVa) from α-Bromo-*cis*-stilbene.**—In 40 ml. of a 40% benzene–ethyl ether mixture was dissolved 1.5 g. (5.8 mmoles) of α-bromo-*cis*-stilbene.[21] The solution was cooled to −30°, and to the cold solution was added 6.4 ml. of 1.1 *M* *n*-butyllithium in ethyl ether.[12] After 20 min. there was added 800 mg. (5.8 mmoles) of *p*-toluenesulfenyl chloride, and the whole reaction mixture was maintained for 1.5 hr. at −30°. The solution was filtered and the solvent was removed. The remaining precipitate was washed once with water and was then dissolved in glacial acetic acid where it was brought to boiling and treated with 10 ml. of 30% hydrogen peroxide. The reaction mixture was then poured over crushed ice and the product was separated. After several recrystallizations from ethanol, it melted at 177–179° and weighed 1.12 g. (57%). This material was identical (melting point, mixture melting point, and infrared spectra) with IVa prepared by the alternative procedures.

***threo*-2-*p*-Thiocresoxy-1,2-diphenyl-1-chloroethane (*threo*-VII).**—Eight grams (44 mmoles) of *cis*-stilbene[22] was dissolved in 120 ml. of glacial acetic acid, warmed over a steam bath, and to the warm solution was added 7.50 g. (44 mmole) of *p*-toluenesulfenyl chloride. The *p*-toluenesulfenyl chloride was added quite rapidly and, as soon as the solution was colorless, the reaction was poured over crushed ice. The product was separated by filtration and recrystallized from ethyl ether or ethanol. There was obtained 9.67 g. (69%) of *threo*-VII, m.p. 69–70°.

*Anal.* Calcd. for $C_{21}H_{19}ClS$: C, 74.42; H, 5.60. Found: C, 74.19; H, 5.60.

**2-*p*-Toluenesulfonyl-1,2-diphenyl-1-chloroethane (*threo*-VI).**—Nine grams (27 mmoles) of *threo*-VII was dissolved in 100 ml. of glacial acetic acid and the solution was brought to boiling quite rapidly. Fifteen milliliters of 30% hydrogen peroxide was added and the solution was brought to boiling for 1 min. The solution was cooled to room temperature and poured over crushed ice. The product was separated by filtration and recrystallized from ethanol. The yield of *threo*-VI was 4.8 g. (49%), m.p. 151–152°. If this experiment were repeated, it would seem advisable to conduct the oxidation at lower temperatures or in a nonprotonic solvent to minimize solvolysis.

*Anal.* Calcd. for $C_{21}H_{19}O_2ClS$: C, 68.00; H, 5.17. Found: C, 68.10; H, 5.27.

**Elimination of Hydrogen Chloride from *threo*-VI.**—Two grams (5.5 mmoles) of *threo*-VI was dissolved in 50 ml. of ethanol and treated with 20 ml. of 0.30 *N* ethanolic sodium hydroxide. The reaction mixture was heated at reflux for 1 hr. The precipitated sodium chloride was removed by filtration and the solvent was removed by evaporation. The precipitated compound was washed once with water and recrystallized from ethanol. There was obtained 1.50 g. (84%) of IVa, m.p. 179–180°, which had the same infrared spectrum in carbon disulfide solution as the olefin obtained from the *erythro* isomer. A mixture melting point showed no depression. Similar results obtained when the dehydrochlorination was conducted for 6 hr. at 10°.

Reaction-rate studies were carried out at 10.2° using sodium hydroxide in ordinary (92.6 wt. %) ethanol, following the reaction by titrating the chloride ion formed with silver nitrate. Duplicate runs with 0.005 *M* *threo*-VI and 0.015 *M* sodium hydroxide gave $k_2 = 6.9 \times 10^{-2}$ l./sec./mole; with 0.010 *M* sodium hydroxide $k_2 = 7.1 \times 10^{-2}$ l./sec./mole. Average $k_2 = 7.0 \times 10^{-2}$ l./sec./mole.

**α-*p*-Thiocresoxy-*trans*-stilbene (IX).**—This was prepared from 1.0 g. (3.0 mmoles) of *threo*-VII as described previously for the *erythro* isomer. There was obtained 0.78 g. (88%) of IX, m.p. 52–53°.

*Anal.* Calcd. for $C_{21}H_{18}S$: C, 83.40; H, 6.00. Found: C, 83.52; H, 6.08.

**α-*p*-Toluenesulfonyl-*trans*-stilbene (Va).**—This was prepared from 650 mg. (2.1 mmoles) of IX as described previously for the *cis*-stilbene isomer. The yield of Va was 450 mg. (72%), m.p. 148.5–149.5°.

*Anal.* Calcd. for $C_{21}H_{18}O_2S$: C, 75.41; H, 5.38. Found: C, 75.43; H, 5.52.

**Preparation of α-*p*-Toluenesulfonyl-*trans*-stilbene Va from α-Bromo-*trans*-stilbene.**—This preparation used 670 mg. (2.5 mmoles) of α-bromo-*trans*-stilbene.[21] Treatment with butyllithium[12] and with *p*-toluenesulfenyl chloride was conducted substantially as described before for the *cis* isomer. There was obtained 350 mg. (43%) of Va, m.p. 146–148°. This material was identical with the sample described in the preceding paragraph.

**Isomerization of α-*p*-Toluenesulfonyl-*trans*-stilbene (Va) to α-*p*-Toluenesulfonyl-*cis*-stilbene (IVa).**—In a 50-ml. flask containing 10 ml. of ethanol was dissolved 85 mg. of Va. The solution was treated with 5 ml. of 0.19 *M* ethanolic sodium hydroxide and heated at reflux over a steam bath for 6 hr. The solution was allowed to stand at room temperature for a few hours. Crystals separated whose melting point (179–180°) and infrared spectrum were identical with those of IVa.

The rate of this reaction was measured at 71.9° with 0.01 *M* Va and 0.05 *M* sodium hydroxide in ordinary ethanol, following the reaction by the change in extinction coefficient at 275 mμ. Va has ε 13,700 and IVa has ε 22,400 at this wave length. Duplicate runs gave $k_2 = 2.7 \times 10^{-3}$ l./sec./mole. Va has $\lambda_{max}$ at 270 mμ (ε 13,800) while $\lambda_{max}$ for IVa is 275 mμ.

**Acknowledgment.**—The authors are indebted to the National Science Foundation for generous support of this work.

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[21] P. Pfeiffer, *Z. physik. Chem.*, **48**, 40 (1904).

[22] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1957, p. 180.