Dehydrohalogenation of *threo*- and *erythro*-1-Chloro- and 1-Bromo-1,2-diphenyl-2-*p*-tolylsulphonylethanes. A Survey of the Stereochemical Course

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The stereochemical course of the dehydrohalogenation of the diastereoisomeric 1-chloro- and 1-bromo-1,2-diphenyl-2-*p*-tolylsulphonylethanes (I)—(IV) has been studied. A broad spectrum of base–solvent pairs has been employed. For all the reagents used the *erythro*-isomers (I) and (III) invariably gave *anti*-elimination. The *threo*-isomers (II) and (IV) followed a course strongly dependent upon the nature of the base. In reactions promoted by anionic bases the importance of the *syn*-component increased with the strength of the reagents. Addition of a crown ether did not cause a significant effect. When amines were used the stereochemical outcome was influenced by the nature of the leaving group, of the solvent, and of the attacking base. The observations are briefly discussed in the light of current views concerning elimination reactions. The use of diethylaminomethylpolystyrene as a dehydrohalogenating agent has been also tested.

THE stereochemical course of the 1,2-elimination process is attracting interest.[1,2] The great majority of published studies deal with alkyl chains of varying degrees of complexity, but a relatively small number of other derivatives have been also investigated.[1,2]

We have recently explored the stereochemical course of the dehydrohalogenation of deuterium labelled 1-fluoro-2-phenylsulphonyl-1-phenylthioethanes and the first case of complete *syn*-stereospecificity in an *E*1cB process was found.[3] Furthermore, the stereochemical outcome appeared to be influenced by the nature of the base.[4] In the present investigation DL-*erythro*- and DL-*threo*-1-chloro- and -1-bromo-1,2-diphenyl-2-*p*-tolylsulphonylethanes (I)—(IV), were used as substrates and their reactions with a broad spectrum of base–solvent pairs were explored with the aim of gaining a deeper insight into the factors governing the *syn*–*anti*-dual pattern in systems of this kind. In one case,

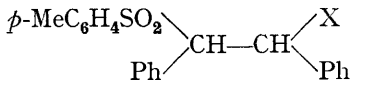
[1] (*a*) A. F. Cockerill, 'Elimination Reactions,' in 'Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1973; (*b*) R. A. More O'Ferrall, 'Elimination Reactions in Solution,' in 'The Chemistry of the Carbon–Halogen Bond,' ed. S. Patai, Wiley, New York, 1973, ch. 9; (*c*) W. H. Saunders, jun., and A. F. Cockerill, 'Mechanisms of Elimination Reactions,' Wiley, New York, 1973; (*d*) M. Schlosser in 'Methoden der Organischen Chemie,' Houben–Weyl–Müller, Thieme Verlag, Stuttgart, 1972, Band V/1b, p. 9; (*e*) C. J. M. Stirling, 'Elimination Reactions,' in 'Essays in Chemistry,' eds. J. N. Bradley, R. D. Gillard, and R. F. Hudson, Academic Press, London, 1973, vol. 5; for earlier reviews see (*f*) D. V. Banthorpe in 'Studies on Chemical Structure and Reactivity,' ed. J. H. Ridd, Methuen, London, 1966, ch. 3; (*g*) J. F. Bunnett, in 'Survey of Progress in Chemistry,' ed. A. F. Scott, Academic Press, New York, vol. 5, 1969; (*h*) C. K. Ingold, *Proc. Chem. Soc.*, 1962, 265.

[2] J. Sicher, *Angew. Chem. Internat. Edn.*, 1972, **11**, 201.

[3] V. Fiandanese, G. Marchese, and F. Naso, *J.C.S. Chem. Comm.*, 1972, 250.

[4] V. Fiandanese, G. Marchese, F. Naso, and O. Sciacovelli, *J.C.S. Perkin II*, 1973, 1336.

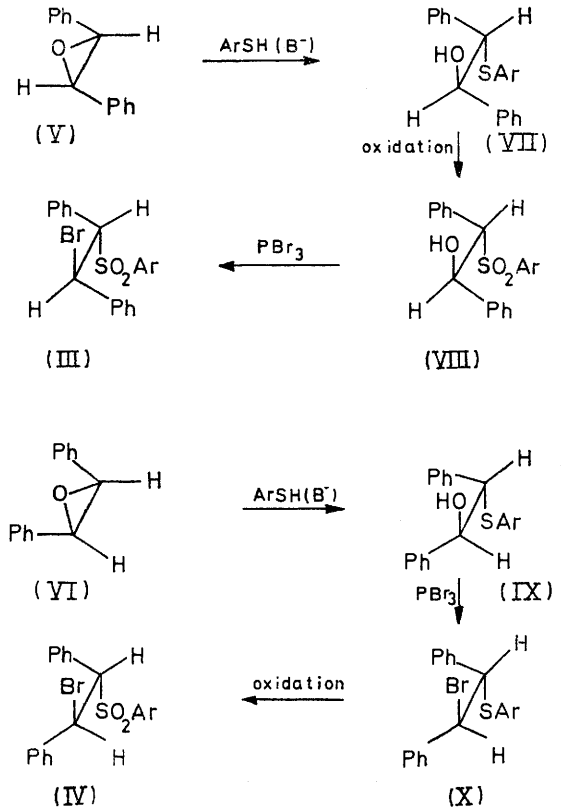
namely for the reactions of the chloro-compounds (I) and (II) with sodium hydroxide in ethanol, the stereochemical course was known from the work of Cristol and Pappas.[5]



(I) *erythro*, X=Cl (II) *threo*, X=Cl
(III) *erythro*, X=Br (IV) *threo*, X=Br

RESULTS AND DISCUSSION

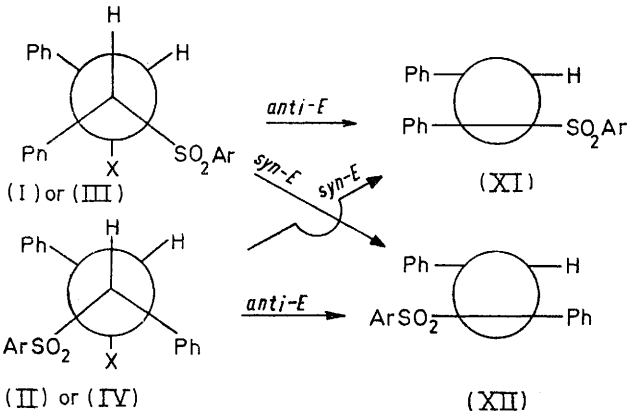
Substrates.—The synthesis of the chloro-compounds (I) and (II) has been reported.[5] The corresponding bromo-derivatives (III) and (IV) were prepared in a stereospecific manner starting with the reaction between *trans*- (V) or *cis*- (VI) stilbene oxide and toluene-*p*-thiolate ion followed by halogenation and oxidation. The sequence is presented in Scheme 1.



SCHEME 1 Ar = *p*-MeC_6H_4

Stereochemical Course.—(a) *Reactions with anionic bases.* The title reactions reached completion upon mixing or after a few minutes and the *threo*-derivatives appeared to be slower reacting.[5] In the case of the reactions of these isomers with methoxide ion in methanol or with nitrophenoxide ion in dimethyl sulphoxide longer reaction times (a few hours) were required.

Scheme 2 shows that the stereochemical course can be easily established by analysing the configuration of the olefin produced.



SCHEME 2

The stereochemical results reported in Table 1 reveal several features of interest. (i) Both *erythro*-isomers (I) and (III) give complete *anti*-elimination inde-

TABLE 1

Stereochemical course in the reactions of compounds (I)—(IV) with anionic bases at 25°

Substrate [a]	Base	10^2[Base]/ M	Elimination (%) *anti*	*syn*
Solvent C_6H_6				
(I)	Bu^tOK	*b*	100	0
(II)	Bu^tOK	*b*	0	100
Solvent C_6H_6–Bu^tOH (80 : 20)				
(I)	Bu^tOK	1·0	100	0
(II)	Bu^tOK	1·0	0	100
(III)	Bu^tOK	1·0	100	0
(IV)	Bu^tOK	1·0	0	100
Solvent EtOH [c]				
(I)	NaOH		100	0
(II)	NaOH		0	100
Solvent MeOH				
(I)	MeONa	0·2	100	0
(II)	MeONa	1·0	40	60
(III)	MeONa	0·2	100	0
(IV)	MeONa	1·0	35	65
Solvent DMSO				
(I)	MeONa [d]	0·5	100	0
(II)	MeONa [d]	0·5	0	100
(I)	PhOK	0·7	100	0
(II)	PhOK	0·7	72	28
(III)	PhOK	0·7	100	0
(IV)	PhOK	0·7	65	35
(II)	*p*-$NO_2C_6H_4ONa$	1·5	90	10
(IV)	*p*-$NO_2C_6H_4ONa$	1·5	93	7
(I)	$MeCO_2Na$	*b*	100	0
(II)	$MeCO_2Na$	*b*	100	0
(III)	$MeCO_2Na$	*b*	100	0
(IV)	$MeCO_2Na$	*b*	100	0
Solvent MeCN				
(I)	$Et_4N^+F^-$	1·4	100	0
(II)	$Et_4N^+F^-$	1·4	100	0

[a] Concentration of substrates ranged between 0·2 and 1·3 × 10^{-2}M. [b] Owing to the low solubility of the base heterogeneous conditions were used. [c] Data taken from ref. 5. Participation of EtO^- is likely to occur in these reactions (see ref. 1*c*, p. 92). [d] In order to prevent intervention of DMSO anion and to increase the solubility of the alkoxide, 2% MeOH was present in these runs (see A. Giametta, G. Marchese, and F. Naso, *Gazzetta*, 1971, **101**, 247).

[5] S. J. Cristol and P. Pappas, *J. Org. Chem.*, 1963, **28**, 2066.

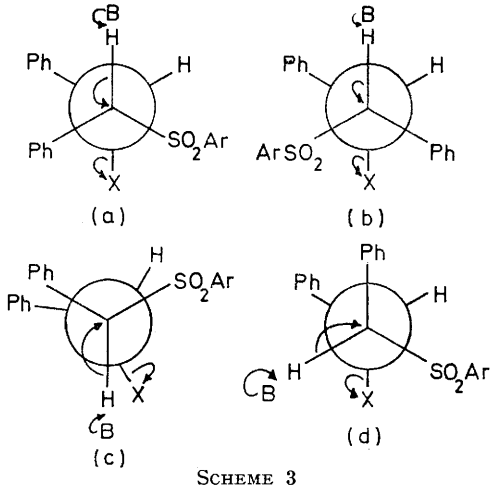
pendent of the nature of the promoting base. (ii) In contrast with the behaviour of the *erythro*-compounds (I) and (III) the *threo*-isomers (II) and (IV) follow a stereochemical course which is strongly influenced by the nature of the reagent. Systems of high basicity give complete *syn*-elimination. A decrease in the strength of the base leads to an *anti*-stereochemical course. Examples of this behaviour are the fluoride and the acetate ions in dipolar aprotic solvents. A mixture of *syn*- and *anti*-components is observed in some cases where bases of intermediate strength are used. In the reactions with methoxide ion in methanol the *syn*-component predominates, whereas the reverse is true for the phenoxide ion promoted processes. (iii) No significant difference is observed on changing the leaving group from chlorine to bromine.

A rationale of the observations made would require knowledge of the mechanism operating in each case. On the basis of the large difference of reactivity observed between the reactions of (I) and (II), both leading to the *cis*-stilbene derivative (XI), an *E*2 process was suggested for the *erythro*-isomer whereas an *E*1cB mechanism was postulated as operating for the *threo*-compound.[5] In fact, it was thought that an *anti*-*E*2 transition state in the latter substrate would be energetically unfavourable because of eclipsing between the Ph and the $ArSO_2$ groups. Furthermore, the lack of H–D exchange pointed to the irreversibility of the proposed intermediate.[5] On the other hand, we have shown recently [6] that 1-bromo- and 1-chloro-2-phenylsulphonyl ethanes follow an *E*2 process involving a transition state in which C–H bond breakage occurs first whereas the C–X bond is stretched only to a small extent. An irreversible *E*1cB process was considered less likely although it was not possible to rule it out completely. Summing up our and others' experience we can tentatively restrict the mechanistic possibilities to an *E*2 mechanism involving a low degree of C–X bond cleavage or we can assume that rupture of this bond is not involved at all in the transition state, which would lead to a rapidly collapsing carbanion.

According to the first hypothesis the transition state for the *anti*-processes may be periplanar as depicted in the Newman projections (a) and (b) (Scheme 3) whereas two limiting possibilities can be envisaged for the *syn*-component, *i.e.* a fully eclipsed synperiplanar (c) or a synclinal (d) transition state.

Within this framework the increasing importance of the *syn*-component with the basicity of the reagent can be explained by the view [1b,g,7] that a stronger base leads to a higher degree of carbanionic character which has to be developed at C_β in order to permit the so-called ' double inversion mechanism.' [1h,2,7]

An alternative view [1b,c,8,9] on the effect of the basic strength in *E*2 processes suggests that the higher reactivity associated with the stronger base could influence both C–H and C–X cleavages and as a consequence a more reactant-like transition state would result. In a similar situation the advantage accruing from anti-periplanarity is not decisive [1c,8] and consequently the *threo*-isomers could react with the stronger bases (Bu^tO^- or MeO^- in DMSO) through a *syn*-pathway to give the more stable olefin. By choosing the synclinal transition state (d) the molecules could avoid ' partial eclipsing ' between the $ArSO_2$ and Ph groups and ' full eclipsing ' between the two phenyl groups which would occur in (b) and (c) respectively. Weaker bases



SCHEME 3

would involve a higher degree of C=C bond formation and the stereoelectronic factor [1c,8] would become of importance, thus shifting the stereochemistry toward the more usual *anti*-process.

According to the *E*1cB hypothesis, the stereochemical course could be explained as proposed by Stirling in a similar case.[10] The *anti*-component in the *erythro*-isomer should arise from proton abstraction in conformation (a). The intermediate carbanion would present an ideal situation for the elimination of the leaving group. In the case of the *threo*-isomer the stereochemistry would still be of the *anti*-type when hydrogen abstraction occurs from conformation (b). However, since the *trans*-olefin (XII) would be formed in this process, rotation of the intermediate could also occur and it would lead to the *syn*-component with formation of the more stable *cis*-stilbene derivative (XI).[10]

Although the above reasoning is based in terms of *E*2 or *E*1cB mechanisms it is possible that, depending on the substrate configuration and on the base–solvent pair used, either one or the other is actually operating. Indeed, our recent work [6] has suggested that sulphonylhalogenoethanes can be classified as reacting at the border between concerted and stepwise mechanisms.

[6] V. Fiandanese, G. Marchese, and F. Naso, *J.C.S. Perkin II*, 1973, 1538.

[7] J. Sicher and J. Závada, *Coll. Czech. Chem. Comm.*, 1968, **33**, 1278.

[8] D. S. Bayley and W. H. Saunders, jun., *J. Amer. Chem. Soc.*, 1970, **92**, 6904.

[9] (*a*) G. Marchese, G. Modena, F. Naso, and N. Tangari, *J. Chem. Soc.* (*B*), 1970, 1196; (*b*) G. Marchese, F. Naso, and V. Sgherza, *Gazzetta*, 1971, **101**, 251.

[10] C. J. M. Stirling, *Internat. J. Sulfur Chem.* (*C*), 1971, **6**, 41.

A final point concerning the stereochemical course of the reactions with anionic bases is the lack of any significant base–leaving group interaction suggested by the absence of the 'crown ether effect' [4,11,12] (see Table 2). As far as the reactions with phenoxide ion in dioxan are concerned these results are at variance with the behaviour observed in the case of 1-fluoro-2-phenylsulphonyl-1-phenylthioethane, where the addition of dicyclohexyl-18-crown-6 did cause a marked effect.[4] This suggests the conclusion that in the present cases it is more difficult to obtain pseudocyclic transition states probably because of the high degree of eclipsing due to the large substituents.

TABLE 2

Stereochemical course in the reactions of compounds (II) and (IV) with various bases in the presence of dicyclohexyl-18-crown-6

Substrate [a]	Base	10^3[Base]/ M	Elimination (%) *anti*	*syn*
Solvent C_6H_6				
(II)	Bu^tOK	*b*	0	100
(II)	Bu^tOK crown ether [c]	*b*	0	100
Solvent C_6H_6–Bu^tOH (80 : 20)				
(II)	Bu^tOK	4·0	0	100
(II)	Bu^tOK crown ether [c]	4·0	0	100
Solvent dioxan				
(II)	PhOK	5·5	88	12
(II)	PhOK crown ether [d]	5·5	87	13
(IV)	PhOK	5·5	84	16
(IV)	PhOK crown ether [d]	5·5	87	13

[a] Concentration of substrates was in the range 3·5—5·0 × 10^{-3}M. [b] Under heterogeneous conditions. [c] Concentration of crown ether was 5·5 × 10^{-3}M. [d] Concentration of crown ether was 9·0 × 10^{-3}M.

(b) *Reactions with amines.* The stereochemical course of the title reactions is reported in Table 3. It can be observed that as in the previous cases the *erythro*-isomers invariably follow the *anti*-pathway. In contrast the *threo*-compounds follow a stereochemical course which is influenced by the nature of the reacting amine, of the solvent, and of the leaving group. The extent of *syn*-component measured in the case of the reactions with triethylamine, particularly in benzene, is higher than expected considering the basicity and the low reactivity of the reagent.[3,6] In fact, the behaviour is rather similar to that observed with the highly basic and reactive systems of Table 1. Probably, pseudocyclic transition states become important when neutral bases are used. The interaction between the (incipient) positive charge on nitrogen and the leaving group could lead to a preference for the *syn*-component.[3] Factors which would affect the nature of the transition states would also affect this interaction, thus influencing the stereochemical course. Eventually, we observe the result of a fine balance between basicity, reactivity, medium, and steric [13] effects.

TABLE 3

Stereochemical course in the reactions [a] of compounds (I)—(IV) with triethylamine (Et_3N), piperidine ($C_5H_{10}NH$), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)

Substrate [b]	Amine	10^2[Amine]/ M	*t*/°C	Elimination (%) *anti*	*syn*
Solvent MeCN					
(I)	Et_3N	6·0	80	100	0
(II)	Et_3N [c]	6·0	80	30	70
(III)	Et_3N	6·0	80	100	0
(IV)	Et_3N	6·0	80	57	43
(II)	$C_5H_{10}NH$	1·8	80	22	78
(IV)	$C_5H_{10}NH$	1·8	80	35	65
(II)	DBU	2·2	25	88	12
(IV)	DBU	2·2	25	85	15
Solvent C_6H_6					
(I)	Et_3N	6·0	80	100	0
(II)	Et_3N	6·0	80	0	100
(III)	Et_3N	2·5	80	100	0
(IV)	Et_3N	3·5	80	8	92
(II)	$C_5H_{10}NH$	2·8	80	*ca.* 3	97
(IV)	$C_5H_{10}NH$	2·8	80	10	90
(I)	DBU	3·7	25	100	0
(II)	DBU	6·5	25	53	47
(III)	DBU	3·7	25	100	0
(IV)	DBU	6·5	25	62	38

[a] Reaction times were 15—90 h for Et_3N, 1 h for $C_5H_{10}NH$, and 10 min for DBU. [b] Concentration of substrates ranged between 1·7 and 4·9 × 10^{-2}M. [c] The use of DMSO as solvent gave 80% *syn*- and 20% *anti*-elimination.

However, some of the changes reported could be explained without invoking cyclic transition states. For instance, the higher degree of carbanionic character which is associated with the chloro-compounds relative to the bromo-derivatives,[1a–c,6,9] could be responsible for the higher extent of *syn*-component observed in most reactions of substrate (II). Similar considerations would apply to the changes observed on going from acetonitrile to benzene, which has been found to shift the mechanism toward the carbanionic side.[6]

A final point of interest is the use of diethylaminomethylpolystyrene [14] (see Table 4) which is a novel reagent for elimination processes. Owing to the low solubility of the base in all the solvents tested the reactions were performed under heterogeneous condi-

TABLE 4

Stereochemical course in the reactions † of compounds (II)—(IV) with diethylaminomethylpolystyrene at 80°

Substrate	Solvent	Elimination (%) *anti*	*syn*
(II)	MeCN	32	68
(III)	MeCN	100	0
(IV)	MeCN	40	60
(II)	C_6H_6	0	100
(IV)	C_6H_6	14	86

† Performed by stirring polymer (0·5 g) in solution (10 ml) of substrate.

[11] F. Naso and L. Ronzini, *J.C.S. Perkin I*, 1974, 340.
[12] C. J. Pedersen and H. K. Frensdorff, *Angew. Chem. Internat. Edn.*, 1972, **11**, 16; J. Závada, M. Svoboda, and M. Pánková, *Tetrahedron Letters*, 1972, 711; R. A. Bartsch and K. E. Wiegers, *ibid.*, p. 3819; D. H. Hunter and D. J. Shearing, *J. Amer. Chem. Soc.*, 1973, **95**, 8333; D. H. Hunter, Y.-T. Lin, A. L. McIntyre, D. J. Shearing, and M. Zvagulis, *ibid.*, p. 8327.
[13] J. Weinstock, R. G. Pearson, and F. G. Bordwell, *J. Amer. Chem. Soc.*, 1956, **78**, 3473. See also ref. 1*a*, pp. 225—226.
[14] M. Roth, P. Dubs, E. Götschi, and A. Eschenmoser, *Helv. Chim. Acta*, 1971, **54**, 710.

tions. Dehydrohalogenation was effected and the stereochemical preference for the *syn*-pathway shown again. The use of this reagent is of considerable interest from the synthetic and mechanistic points of view.[15]

EXPERIMENTAL

N.m.r. spectra were recorded with a Varian HA 100 spectrometer. I.r. spectra were taken in carbon disulphide with a Perkin-Elmer model 257 instrument.

Bases and Solvents.—1,8-Diazabicyclo[5.4.0]undec-7-ene, sodium acetate, and diethylaminomethylpolystyrene (Fluka) were pure commercial compounds. Piperidine was distilled over potassium hydroxide. *p*-Nitrophenoxide [16] and phenoxide [17] were prepared according to known procedures. The purification of the other bases, solvents, and of dicyclohexyl-18-crown-6 ether has been described elsewhere.[6,11]

Substrates.— *erythro*-1-Chloro-1,2-diphenyl-2-*p*-tolylsulphonylethane (I), m.p. 183—184° (from ethanol), and the corresponding *threo*-isomer (II), m.p. 151—152° (from ethanol), were prepared according to the procedure of Cristol and Pappas.[5]

erythro-1,2-*Diphenyl*-2-*p*-*tolylthioethanol* (VII). Water (15 ml) containing sodium toluene-*p*-thiolate ($4\cdot0 \times 10^{-2}$ mol) was added to a solution of *trans*-stilbene oxide (8 g, $4\cdot0 \times 10^{-2}$ mol) (V) [18] in acetone (150 ml). The reaction mixture was refluxed for 6 h, the solvent was then removed, and the mixture was diluted with water and extracted with ether. The extract was evaporated and the residual oil was crystallized from n-hexane to give the *alcohol* (VII) (10·5 g, 80%), m.p. 96—98° (Found: C, 78·2; H, 6·2; S, 10·0. $C_{21}H_{20}OS$ requires C, 78·7; H, 6·3; S, 10·0%), τ ($CDCl_3$) 5·1 and 5·7 (*J* 5 Hz, CH–CH) and 7·8 (CH_3).

erythro-1,2-*Diphenyl*-2-p-*tolylsulphonylethanol* (VIII). *Compound* (VIII) was prepared in quantitative yield by oxidation of the alcohol (VII) with peracetic acid; m.p. 156—157° (from ethanol) (Found: C, 71·5; H, 5·7; S, 9·0. $C_{21}H_{20}O_3S$ requires C, 71·6; H, 5·7; S, 9·1%), τ ($CDCl_3$) 4·1 and 5·9 (*J* 2 Hz, CH–CH) and 7·7 (CH_3).

erythro-1-*Bromo*-1,2-*diphenyl*-2-p-*tolylsulphonylethane* (III). PBr_3 (2·85 g, 1×10^{-2} mol) in $CHCl_3$ (10 ml) was added to a solution of the alcohol (VIII) (3·0 g, $8\cdot5 \times 10^{-3}$ mol) in $CHCl_3$ (40 ml). After 10 h at room temperature the solution was washed with aqueous sodium hydrogen carbonate (5%) and water and dried (Na_2SO_4). After the solvent had been removed the residue was crystallized from ethanol to give *product* (III) (2·3 g, 65%), m.p. 205—206° (Found: C, 60·4; H, 4·6; Br, 19·2; S, 7·7. $C_{21}H_{19}BrO_2S$ requires C, 60·7; H, 4·6; Br, 19·2; S, 7·7%), τ [$(CD_3)_2SO$] 4·0 and 4·3 (*J* 11 Hz, CH–CH) and 7·7 (CH_3).

threo-1,2-*Diphenyl*-2-p-*tolylthioethanol* (IX). The title *compound* was prepared in 80% yield as described for the *erythro*-isomer and using *cis*-stilbene oxide (VI) [18] as substrate. The crude material was obtained as an oil which solidified on treatment with n-hexane; m.p. 74—75° (Found: C, 78·2; H, 6·1; S, 10·0. $C_{21}H_{20}OS$ requires C, 78·7; H, 6·3; S, 10·0%), τ ($CDCl_3$) 5·2 and 5·8 (*J* 8 Hz, CH–CH) and 7·8 (CH_3). The n.m.r. spectrum revealed contamination by the *erythro*-isomer (VII). Repeated crystallizations from n-hexane did not improve the isomeric purity.

threo-1-*Bromo*-1,2-*diphenyl*-2-p-*tolylthioethane* (X). The title *compound* was obtained in 75% yield by treating the alcohol (IX) with PBr_3 for 1 h and following the procedure described for the preparation of (III); m.p. 88—89° (from acetone–water) (Found: C, 66·1; H, 4·8; Br, 20·8; S, 8·4. $C_{21}H_{19}BrS$ requires C, 65·8; H, 5·0; Br, 20·8; S, 8·4%), τ ($CDCl_3$) 4·7 and 5·3 (*J* 7 Hz, CH–CH) and 7·8 (CH_3).

threo-1-*Bromo*-1,2-*diphenyl*-2-p-*tolylsulphonylethane* (IV). The title *compound* was prepared in quantitative yield by oxidation of the sulphide (X) with perphthalic acid as described for a similar case; [5] m.p. 134—135° (from ethanol) (Found: C, 61·0; H, 4·7; Br, 19·2; S, 7·7. $C_{21}H_{19}BrO_2S$ requires C, 60·7; H, 4·6; Br, 19·2; S, 7·7%), τ ($CDCl_3$) 4·0 and 5·1 (*J* 7 Hz, CH–CH) and 7·8 (CH_3).

Reactions.—The reactions were performed under the conditions indicated in the Tables and followed by t.l.c. [silica gel PF_{254}; light petroleum (b.p. 60—70°)–diethyl ether (7 : 3) as eluant]. After completion the mixture was diluted with water and extracted with $CHCl_3$. Evaporation yielded quantitatively α-*p*-tolylsulphonyl-*cis*-stilbene (XI), m.p. 179—180° (from ethanol) [5] and/or α-*p*-tolylsulphonyl-*trans*-stilbene (XII), m.p. 148·5—149·5°.[5] The crude material was subjected to i.r. analysis. For this determination standardization plots were obtained by using mixtures of known composition. Comparison of bands in the region 660—760 cm^{-1} reduced the error to *ca.* 3%.

Control experiments performed with most of the bases used ruled out the intervention of *trans–cis*-isomerization under the reaction conditions. Furthermore, within the time employed for performing the experiments, no significant reaction was detected in the absence of base.

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[15] C. G. Overberger and K. N. Sannes, *Angew. Chem. Internat. Edn.*, 1974, **13**, 99.

[16] H. E. Zaugg and A. D. Schaefer, *J. Amer. Chem. Soc.*, 1965, **87**, 1857.

[17] N. Kornblum and A. P. Lurie, *J. Amer. Chem. Soc.*, 1959, **81**, 2705.

[18] D. Y. Curtin and D. B. Kellom, *J. Amer. Chem. Soc.*, 1953, **75**, 6011.