Mechanistic Study of *syn*- and *anti*-Elimination from Diastereoisomeric Halogenosulphonylethanes

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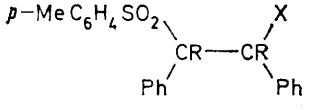
The reactions of *erythro*- and *threo*-1-chloro- and -1-bromo-1,2-diphenyl-2-*p*-tolylsulphonylethanes (I_H)—(IV_H) and of the 1,2-dideuterio-derivatives (I_D)—(IV_D) with methoxide ion in methanol and with triethylamine in benzene have been followed kinetically. For methoxide ion the reactions of the *erythro*-isomers (*anti*-elimination) are much faster than those of the *threo*-derivatives (*syn* + *anti*-elimination). The sensitivity to the leaving group is rather modest for both isomers whereas reaction rates are markedly influenced by isotopic substitution. In the reactions with amine the $k_{erythro} : k_{threo}$ ratios become much smaller and $k_{Br} : k_{Cl}$ values close to unity are observed for the latter isomer. Isotope effects are higher for *syn*- than for *anti*-elimination. These and related observations are evaluated in terms of an *E*2 mechanism involving a small degree of C–X breakage in the transition state or an *E*1cB mechanism of irreversible type.

RECENTLY [1] we reported results concerning the stereochemical course of the dehydrohalogenation of *erythro*- and *threo*-1-chloro- and -1-bromo-1,2-diphenyl-2-*p*-tolylsulphonylethanes (I_H)—(IV_H) promoted by a broad spectrum of solvent–base pairs. At the same time work of



(I_H) *erythro*, R = H, X = Cl (II_H) *threo*, R = H, X = Cl
(I_D) *erythro*, R = D, X = Cl (II_D) *threo*, R = D, X = Cl
(III_H) *erythro*, R = H, X = Br (IV_H) *threo*, R = H, X = Br
(III_D) *erythro*, R = D, X = Br (IV_D) *threo*, R = D, X = Br

relevant interest on this topic has been performed in other laboratories by using different sulphones.[2] The main conclusion which can be reached by combining the results of these and previous investigations [3-5] is that the stereochemical course of the elimination in open chain sulphonyl derivatives may vary anywhere from 100% *anti*- to 100% *syn*-stereospecificity depending upon the nature of the substrate and of the promoting reagent.

Against this background, attempts to reveal mechanistic variations associated with different contributions of the stereochemical pathways appear to deserve considerable attention.[6,7] We report now the results of a kinetic study performed on the diastereoisomeric sulphones (I_H)—(IV_H) and on the deuterio-counterparts (I_D)—(IV_D).

[1] V. Fiandanese, C. V. Maffeo, G. Marchese, and F. Naso, *J.C.S. Perkin II*, 1975, 221.

[2] J. C. Philips, M. Aregullin, M. Oku, and A. Sierra, *Tetrahedron Letters*, 1974, 4157.

[3] (*a*) V. Fiandanese, G. Marchese, F. Naso, and O. Sciacovelli, *J.C.S. Perkin II*, 1973, 1336; (*b*) V. Fiandanese, G. Marchese, and F. Naso, *J.C.S. Chem. Comm.*, 1972, 250.

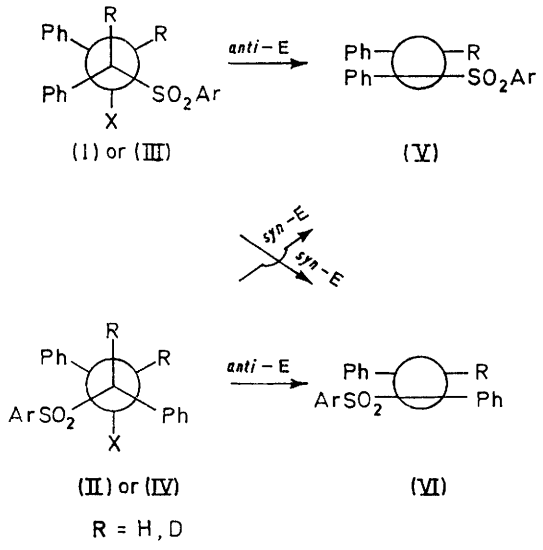
[4] S. J. Cristol and P. Pappas, *J. Org. Chem.*, 1963, **28**, 2066.

[5] R. Andrisano, A. S. Angeloni, and A. Fini, *Tetrahedron*, 1972, **28**, 2681; P. S. Skell and J. H. McNamara, *J. Amer. Chem. Soc.*, 1957, **79**, 85; F. G. Bordwell and P. S. Landis, *ibid.*, p. 1593; M. Rossetti, M. Tiecco, and A. Tundo, *Boll. sci. Fac. Chim. ind. Bologna*, 1964, **22**, 7.

[6] For recent reviews on elimination reactions see, A. F. Cockerill 'Elimination Reactions,' in 'Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1973; R. A. More O'Ferrall, 'Eliminations Reactions in Solution,' in 'The Chemistry of the Carbon–Halogen Bond,' ed. S. Patai, Wiley, New York, 1973, ch. 9; W. H. Saunders, jun., and A. F. Cockerill, 'Mechanisms of Elimination Reactions,' Wiley, New York, 1973; M. Schlosser in 'Methoden der Organischen Chemie,' Houben–Weyl–Muller, Thieme Verlag, Stuttgart, 1972, Band V/1b, p. 9; 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, D. V. Banthorpe in 'Studies on Chemical Structure and Reactivity,' ed. J. H. Ridd, Methuen, London, 1966, ch. 3; J. F. Bunnett, in 'Survey of Progress in Chemistry,' ed. A. F. Scott, Academic Press, New York, vol. 5, 1969; C. K. Ingold, *Proc. Chem. Soc.*, 1962, 265.

[7] For kinetic studies on elimination from halogenosulphonylethanes see V. Fiandanese, G. Marchese, and F. Naso, *J.C.S. Perkin II*, 1973, 1538 and references therein.

Methoxide ion in methanol and triethylamine in benzene were chosen as bases, due to their different stereochemical behaviour.[1]



SCHEME

RESULTS

Stereochemical Course.—Compounds (I_D)—(IV_D) were subjected to the action of bases as previously described for the corresponding isotopically normal compounds. The analysis of the resulting olefin which permits investigation of the stereochemical course (see Scheme) was performed by i.r. and n.m.r. spectroscopy. In the case of reactions of *threo*-isomers with methoxide ion deuteriation was found to cause a slight increase in the extent of the *syn*-pathway. The results of experiments performed at 25° are in Table 1. The variations observed in the temperature range 15—35° were within experimental error.

Kinetic Measurements.—Second-order kinetics (first order in base and in substrate) were obeyed for the reactions with methoxide ion in methanol. However, increase in base concentration was found to cause a small increase in the rate coefficients even working at relatively low methoxide ion concentration.[8] Reactions performed in the presence of added salt ($NaClO_4$) suggested that the trend could be due at least in part to a positive salt effect. For this reason isotope effects and activation parameters were measured at the same concentration. The relevant data are in Tables 2 and 3.

In the case of the *threo*-derivatives (II) and (IV) dissection of the overall rate coefficients into k_{syn} and k_{anti} values can be easily obtained by combining the data of Tables 1 and 2. The resulting $k_H : k_D$ ratios and activation parameters for the two stereochemical components are reported in Table 3 together with data for *anti*-elimination from the *erythro*-isomers (I) and (III). The reason for the large error limit in the isotope effects for compounds (II) and (IV) can be easily explained by taking into account the fact that they are derived from four independent experiments (two kinetic measurements for k_H and k_D and two stereochemical experiments for ascertaining the extent of *syn*- and *anti*-pathways for both isotopically normal and deuteriated substrates). No induction time was observed in the reactions of the deuterio-derivatives in alcohol thus suggesting a lack of H–D exchange during the elimination process.[9] In the case of the *threo*-bromo-derivative the same conclusion was also reached by analysing the recovered starting material.

A sealed ampoule technique was used in the reactions with triethylamine in benzene. The relevant data are reported in Table 4. No *threo* ⟶ *erythro* isomerization was observed during elimination, as shown by n.m.r. analysis of prematurely quenched reactions.

TABLE 1

Stereochemical course in the base-promoted dehydrohalogenation of *threo*-isomers [a] (II) and (IV)

Substrate [b]	Base	10[Base]/M	Solvent	t/°C	Method	Elimination (%) [c] *anti*	*syn*
(II_H)	MeONa	0.2	MeOH	25	I.r.	39	61
					N.m.r.	38	62
(II_D)	MeONa	0.2	MeOH	25	I.r.	28	72
					N.m.r.	28	72
(IV_H)	MeONa	0.2	MeOH	25	I.r.	34	66
					N.m.r.	33	67
(IV_D)	MeONa	0.2	MeOH	25	I.r.	27	73
					N.m.r.	26	74
(II_H)	Et_3N	6.0	C_6H_6	65	I.r.	0	100
(II_D)	Et_3N	6.0	C_6H_6	65	I.r.	0	100
(IV_H)	Et_3N	6.0	C_6H_6	65	I.r.	8	92
(IV_D)	Et_3N	6.0	C_6H_6	65	I.r.	13	87

[a] *erythro*-Isomers (I) and (III) gave 100% *anti*-elimination (see ref. 1). [b] Concentration of substrate was 3×10^{-3}M in the reactions with methoxide ion and 3×10^{-2}M in the reactions with Et_3N. [c] Maximum standard deviation from repeated analyses, ±1.5%.

DISCUSSION

Reactions with Methoxide Ion in Methanol.—When methoxide ion is used as base the lack of H–D exchange rules out an *E*1cB mechanism involving a free carbanion which can be captured by a solvent molecule. On the other hand the values of the isotope effect, which should be considered largely of the primary kind with a small, if any, contribution from a secondary effect, seem sufficiently high to rule out the intervention of internal re-

[8] On the dependence between elimination rates and methoxide ion concentration see (*a*) R. A. More O'Ferrall, *J.C.S. Perkin II*, 1972, 976; (*b*) D. J. McLennan and R. J. Wong, *ibid.*, 1974, 1373; (*c*) A. B. N. Gray and D. J. McLennan, *ibid.*, p. 1377.

[9] R. A. More O'Ferrall and S. Slae, *J. Chem. Soc.* (*B*), 1970, 260.

TABLE 2

Rate coefficients [a] for the methoxide ion promoted dehydrohalogenation of compounds (I)—(IV)

Substrate	10^2[MeONa]/ M	10^2[$NaClO_4$]/ M	t/°C	10^2k/ 1 mol^{-1} s^{-1}
(I_H)	8.70		18	281
(I_H)	4.40		25	412
(I_H)	4.40	4.35	25	459
(I_H)	8.80		25	470
(I_D)	8.60		25	69.4
(I_H)	8.80		35	1 090
(II_H)	2.10		16	1.88
(II_H)	2.20		25	4.35
(II_H)	2.00		25	4.40 [b]
(II_H)	4.30		25	4.37
(II_H)	4.10		25	4.38 [b]
(II_H)	6.40		25	4.70
(II_H)	6.00		25	4.65 [b]
(II_H)	8.00		25	4.90 [b]
(II_D)	2.20		25	1.04
(II_H)	2.10		35	11.10
(III_H)	8.70		18	491
(III_H)	4.40		25	686
(III_H)	4.40	4.35	25	755
(III_H)	8.80		25	840
(III_D)	8.90		25	117
(III_H)	8.75		35	1 800
(IV_H)	2.25		16	4.06
(IV_H)	2.15		25	9.04
(IV_H)	2.15	3.90	25	9.58
(IV_D)	2.10		25	1.83
(IV_H)	4.30		25	9.60
(IV_H)	4.30	1.77	25	9.84
(IV_H)	6.05		25	9.90
(IV_H)	2.15		35	21.3

[a] Probable error for k values is 2%. Unless otherwise indicated the data have been obtained by using an u.v. spectrophotometer (*threo*-isomers) or a stopped-flow instrument (*erythro*-isomers). The concentration of substrate was 4.25×10^{-5}M in the first case and 1.40×10^{-5}M in the second. [b] Volhard method. Concentration of substrate 3.0×10^{-3}M.

turn.[7,10] We are then left with two possibilities, an $E2$ process or an $E1cB$ mechanism involving a rate-determining ionization.[6] Therefore, the assumptions previously made for explaining the stereochemical course now find experimental support.[1]

In principle, further narrowing of the possibilities could be sought in the leaving group effect. However, our data show that the $k_{Br} : k_{Cl}$ ratios are ambiguously small (*ca.* 2) leaving aside the configuration of the substrate and the stereochemical pathway involved. This leaving group effect does not allow a distinction to be made between an $E2$ mechanism where the C–X bond is broken only to a small extent and an $E1cB$ mechanism where C–X bond breakage is not involved at all in the rate-determining step. A variety of factors are involved in establishing the $k_{Br} : k_{Cl}$ ratios in nucleophilic substitution at saturated carbon.[11] The problem is more complex in an elimination reaction [12] where other factors such as the influence of the leaving halogen atom upon the proton abstraction process and the stability of the resulting (incipient) carbanion [13] must also be taken into account.

A similar situation was faced in the elimination from the related 1-halogeno-2-phenylsulphonylethanes [7] where, without ruling out a stepwise process, a preference for the concerted mechanism was expressed on the basis of the trend observed in the isotope effects. In fact, this was in the order Br > Cl > F as expected on the basis of leaving group abilities.[6] In the present investigation we find a more complex picture since the isotope effects are similar in the case of the *erythro*-isomers (*anti*-elimination) whereas the order is $(k_H : k_D)_{Br} > (k_H : k_D)_{Cl}$ for the *threo*-isomers (*anti*- + *syn*-elimination). Therefore, we hesitate to tilt the balance in favour of the concerted process and prefer to discuss the results obtained in terms of both mechanisms. It should be borne in mind that the two types of process can merge with each other and making a distinction between a mechanism with a C–X bond ' completely unbroken ' and one where the same bond is ' *almost* completely unbroken ' is an uphill task.[14,15]

TABLE 3

Isotope effects and activation parameters [a] for the methoxide ion promoted dehydrohalogenation of compounds (I)—(IV) in methanol

Substrate	Stereochemical component	k_H/k_D (at 25°)	E_a/ kcal mol^{-1}	$\Delta H^{\ddagger}_{25}$°/ kcal mol^{-1}	$\Delta S^{\ddagger}_{25}$°/ cal mol^{-1} K^{-1}
(I_H)	*anti*	6.7 ± 0.3	14.3	13.7	−9.6
(II_H)	*anti*	5.8 ± 0.6 [b]	16.6 [c]	16.0 [c]	−12.9
(II_H)	*syn*	3.6 ± 0.3 [b]	16.6 [c]	16.0 [c]	−12.2
(III_H)	*anti*	7.2 ± 0.3	13.6	13.0	−10.7
(IV_H)	*anti*	6.3 ± 0.8 [d]	15.5 [c]	14.9 [c]	−15.6
(IV_H)	*syn*	4.5 ± 0.4 [d]	15.5 [c]	14.9 [c]	−14.3

[a] Probable errors are ±0.5 kcal mol^{-1} for E_a and $\Delta H^{\ddagger}$, and ±1.5 cal mol^{-1} K^{-1} for $\Delta S^{\ddagger}$. [b] Considering the overall elimination process $k_H/k_D = 4.2 \pm 0.2$. [c] A similar temperature dependence is assumed for the *syn*- and *anti*-components (see text). [d] Considering the overall elimination process $k_H/k_D = 5.0 \pm 0.2$.

Transition states which could occur in the $E2$ processes have been previously suggested.[1] According to this hypothesis the $(k_{erythro} : k_{threo})_{anti}$ ratio (*ca.* 300) is

[10] D. J. Cram, ' Fundamentals of Carbanion Chemistry,' Academic Press, New York, 1965; D. J. Cram and A. S. Wingrove, *J. Amer. Chem. Soc.*, 1964, **86**, 5490; H. M. Walborksky and J. M. Motes, *ibid.*, 1970, **92**, 2445; J. A. Zoltewicz and L. S. Helmick, *ibid.*, p. 7547; W. K. Kwok, W. G. Lee, and S. I. Miller, *ibid.*, 1969, **91**, 468; E. Lord, M. P. Naan, and C. D. Hall, *J. Chem. Soc.* (*B*), 1971, 220; C. W. Rigby, E. Lord, M. P. Naan, and C. D. Hall, *ibid.*, p. 1192; D. J. McLennan and R. J. Wong, *J.C.S. Perkin II*, 1974, 526; see, however, A. Streitwieser, jun., P. H. Owens, G. Sonnichsen, W. K. Smith, G. R. Ziegler, H. M. Niemeyer, and T. L. Kruger, *J. Amer. Chem. Soc.*, 1973, **95**, 4254.

[11] R. Bird and C. J. M. Stirling, *J.C.S. Perkin II*, 1973, 1221.

[12] A. F. Cockerill, *Tetrahedron Letters*, 1969, 4913.

[13] On the influence of β-halogens on the stability of carbanions see Z. Rappoport, ' Nucleophilic Vinylic Substitution,' in 'Advances in Physical Organic Chemistry,' ed. V. Gold, Academic Press, London, 1969, vol. 7, p. 21; D. Daloze, H. G. Viehe, and G. Chiurdoglu, *Tetrahedron Letters*, 1969, 3925.

[14] F. G. Bordwell, *Accounts Chem. Res.*, 1970, **3**, 281; F. G. Bordwell, D. A. R. Happer, and G. D. Cooper, *Tetrahedron Letters*, 1972, 2759.

[15] P. F. Cann and C. J. M. Stirling, *J.C.S. Perkin II*, 1974, 820.

TABLE 4

Rate coefficients and activation parameters [a] for the triethylamine-promoted dehydrohalogenation of compounds (I)—(IV) in benzene

Substrate	$10^4\ k$/l mol^{-1} s^{-1} 50°	65°	80°	E_a/ kcal mol^{-1}	$\Delta H^{\ddagger}_{50°}$/ kcal mol^{-1}	$\Delta S^{\ddagger}_{50°}$/ cal mol^{-1} K^{-1}	k_H/k_D (at 65°)
(I_H)	3.02	5.55	9.58	8.7	8.1	−49.8	1.7
(II_H)	0.52	1.21	2.79	12.6	12.0	−41.2	5.1
(III_H)	14.8	26.6	46.7	8.7	8.1	−46.7	1.9
(IV_H)	0.85	1.71	3.47	10.6 [b]	10.0 [b]	−46.5 [b]	4.3 [c]

[a] Probable errors are 2% for k, ±0.5 kcal mol^{-1} for E_a and $\Delta H^{\ddagger}$, ±1.5 cal mol^{-1} K^{-1} for $\Delta S^{\ddagger}$, and 5% for k_H/k_D values. [b] Apparent values. A small contribution of the *anti*-component is present in these runs (see Table 1). [c] The measured value (4.1) has been corrected for the participation of the *anti*-pathway.

easily explained in the partial eclipsing [4,16] between the bulky $ArSO_2$ and the Ph group which would occur during formation of the *trans*-olefin (VI). Furthermore, the lower isotope effects of the *syn*-pathway could reflect a higher degree of carbanionic character in the transition state.[6]

According to the *E*1cB hypothesis,[1] if ionization is rate determining the high $k_{erythro} : k_{threo}$ ratio should be attributed to the lower energy of the carbanion deriving from the *erythro*-isomer and of the transition state leading to it.[17] Indeed, *E*1cB reactions of the reversible type in similar sulphones involving phenoxy as the leaving group have been studied by Redman and Stirling and the rates were found to be strongly dependent upon the configuration of the substrate, the *erythro*-isomer being more reactive than the *threo*.[17,18] Furthermore, the difference in the sensitivity to isotope substitution observed for the two stereochemical pathways occurring in isomers (II) and (IV) suggests that they should not necessarily possess a common carbanionic intermediate [1] and different transition states could be involved for the two proton abstraction processes.

Reactions with Triethylamine in Benzene.—The data of Table 4 concerning the title reactions reveal some interesting differences in respect to the behaviour observed with the alkoxide–alcohol pair. The $k_{erythro} : k_{threo}$ ratio is much smaller and for the chloro-derivatives a value of *ca.* 4 is observed. The isotope effects are higher for the *threo*-compounds which react predominantly or exclusively *via syn*-elimination than for the *erythro*-isomers which follow the *anti*-pathway. This result appears rather unexpected when one considers that lower values are often associated with *syn*-elimination both in olefin-[19] and acetylene-forming [20] eliminations. On the other hand the *erythro*-derivatives show a higher sensitivity to the leaving group than the *threo*-isomers, the $k_{Br} : k_{Cl}$ ratios being respectively *ca.* 5 and 1.2 at 80°. The latter figure becomes slightly smaller when it is taken into account that the *syn*-pathway in the case of the *threo*-bromo-derivative represents 90% of the overall process.

At this point it is tempting to accommodate all these facts by assuming that the *erythro*-isomers follow an *E*2 mechanism with a high degree of carbanionic character in the transition state, whereas an irreversible *E*1cB mechanism is utilized by the *threo*-isomers. The latter substrates in an *anti*-*E*2 transition state would suffer a severe energetic penalty particularly if a considerable amount of carbon–carbon double bond has developed. Therefore, a rate-determining ionization is preferred and this is monitored by the high isotope effects and the very low leaving group effect.

However, following the same approach used for the reactions in the protic solvent it seems more convenient to comment upon the various mechanistic possibilities rather than attempt to formulate a precise mechanistic diagnosis.

In principle, the isotope effect measured for the *erythro*-derivatives could be also consistent with an *E*1cB mechanism involving internal return.[21] However, it is worth recalling here that fluorosulphonylethanes which react through an *E*1cB mechanism involving ion pairs have isotope effects as low as 0.8.[3b,7] Furthermore, assuming that internal return is important for the *erythro*-isomers one would expect a similar situation for the *threo*-derivatives. At variance with this expectation for the latter isomers the high $k_H : k_D$ values do not suggest the intervention of internal return.

On the other hand, for reasons stated above in the case of the *threo*-compounds a mechanism involving only a very small degree of C–X breakage cannot be completely ruled out. This may be particularly valid in the case of the bromo-derivative (IV) for which the isotope effect is lower than for the chloro-analogue. In principle, on the basis of the irreversible *E*1cB hypothesis closer values would be expected. The unusual trend could be explained by invoking a significant contribution from the *E*2 mechanism which, according to the data for the *erythro*-isomers, could be characterized by low isotope effects. The variation in the activation parameters on changing the leaving group could also fit the hypothesis of a variation in mechanism. However, comparison of these data is complicated by the intervention of the *anti*-component in the reactions of the bromo-derivative (IV).

In conclusion, the results of the present investigation

[16] D. J. Cram, F. D. Greene, and C. H. DePuy, *J. Amer. Chem. Soc.*, 1956, **78**, 790.

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

[18] R. P. Redman and C. J. M. Stirling, unpublished results cited in ref. 15. We thank Professor C. J. M. Stirling for valuable information concerning elimination from phenoxysulphones.

[19] J. L. Coke, 'Stereochemistry of Hofmann Elimination,' in 'Selective Organic Transformations,' ed. B. S. Thyagarajan, Wiley–Interscience, New York, 1972, vol. 2, p. 269; K. C. Brown and W. H. Saunders, jun., *J. Amer. Chem. Soc.*, 1970, **92**, 4292; D. S. Bayley and W. H. Saunders, jun., *ibid.*, p. 6904.

[20] G. Marchese, G. Modena F. Naso, and N. Tangari, *J. Chem. Soc.* (*B*), 1970, 1196; *Boll. sci. Fac. Chim. ind. Bologna*, 1968, **26**, 209.

[21] F. G. Bordwell, *Accounts Chem. Res.*, 1972, **5**, 374.

support the view [7] that halogenosulphonylethanes are a flexible system where structural and environmental factors determine the nature of the stereochemical course and the mechanism. Concerted and stepwise processes are both available. This proposition can be considered of general validity by extension to a variety of olefin-[1,3,7,8b,c,15,22] and acetylene-forming [20,23] eliminations involving relatively acidic leaving protons.

EXPERIMENTAL

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

Materials.—Bases and solvents were prepared and purified as previously described.[7] Sodium perchlorate was dried by heating under vacuum at 130° for 24 h.

Compounds (I_H)—(IV_H) were prepared according to previously described procedures [1,4] which, by using dideuteriostilbenes [24] as starting materials, could also be used for the synthesis of the deuteriated counterparts (I_D)—(IV_D). A brief description of the methods is given below.

erythro-1-*Chloro*-1,2-*dideuterio*-1,2-*diphenyl*-2-p-*tolylsulphonylethane* (I_D). Addition of toluene-*p*-sulphenyl chloride to *trans*-dideuteriostilbene [24] yielded *erythro*-1-chloro-1,2-dideuterio-1,2-diphenyl-2-*p*-tolylthioethane,[4] m.p. 129—130° (from ethyl ether). Oxidation of the sulphide with perphthalic acid yielded compound (I_D),[4] m.p. 183—184° (from ethanol).

threo-1-*Chloro*-1,2-*dideuterio*-1,2-*diphenyl*-2-p-*tolylsulphonylethane* (II_D). Addition of toluene-*p*-sulphenyl chloride to *cis*-1,2-dideuteriostilbene [24] yielded *threo*-1-chloro-1,2-dideuterio-1,2-diphenyl-2-*p*-tolylthioethane,[4] m.p. 69—70° (from ethanol). Oxidation of the sulphide with perphthalic acid yielded compound (II_D),[4] m.p. 151—152° (from ethanol).

erythro-1-*Bromo*-1,2-*dideuterio*-1,2-*diphenyl*-2-p-*tolylsulphonylethane* (III_D). Sodium toluene-*p*-thiolate was treated with *trans*-1,2-dideuteriostilbene oxide [25] to give *erythro*-1,2-dideuterio-1,2-diphenyl-2-*p*-tolylthioethanol,[1] m.p. 96—98° (from n-hexane). Oxidation with peracetic acid yielded *erythro*-1,2-dideuterio-1,2-diphenyl-2-*p*-tolylsulphonylethanol,[1] m.p. 156—157° (from ethanol). The alcohol was treated with PBr_3 to obtain compound (III_D),[1] m.p. 205—206° (from ethanol).

threo-1-*Bromo*-1,2-*dideuterio*-1,2-*diphenyl*-2-p-*tolylsulphonylethane* (IV_D). Toluene-*p*-thiolate was treated with *cis*-1,2-dideuteriostilbene oxide.[25] The resulting 1,2-dideuterio-1,2-diphenyl-2-*p*-tolylthioethanol,[1] m.p. 74—75° (from n-hexane) was treated with PBr_3 to give *threo*-1-bromo-1,2-dideuterio-1,2-diphenyl-2-*p*-tolylthioethane,[1] m.p. 88—89° (from acetone–water). Oxidation of this halide with perphthalic acid gave compound (IV_D),[1] m.p. 134—135° (from ethanol).

N.m.r. analysis performed on compounds (I_D)—(IV_D) showed the presence of two deuterons in each case.

Reactions.—The stereochemical course was followed by i.r. analysis as previously described.[1] Identical experimental conditions were employed for isotopically normal and deuteriated substrates. α-*p*-Tolylsulphonyl-*cis*-stilbene (V_H),[4] the *trans*-isomer (VI_H),[4] and the corresponding *deuterio-derivatives* (V_D) and (VI_D) presented bands in the region 650—760 cm^{-1} which permitted the accurate use of standardization plots. The i.r. analysis was complemented with n.m.r. analysis which was based on the comparison of the area of the methyl protons, the chemical shift in $CDCl_3$ being τ 7.7 for the *cis*-derivatives (V) and τ 7.8 for the *trans*-isomers (VI).

Kinetic Measurements.—The reactions of the *erythro*- and *threo*-isomers with methoxide ion were followed spectrophotometrically at 275 nm respectively by means of a Durrum–Gibson stopped-flow instrument and by means of a Zeiss DMR 21 instrument. In the latter case some runs were also followed by Volhard titration of the produced halide ion. The same titration was used in the case of the reactions with triethylamine.[7]

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