Conformer Preferences in Aralkyl Chloro-sulphides

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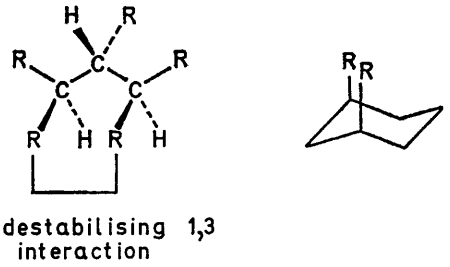
Conformational preferences of the four isomers of 1-α-chlorobenzyl-2-phenylpropyl 2,4-dinitrophenyl sulphide are approximated from vicinal n.m.r. coupling constants. The ordering of groups at the carbons bearing chlorine and sulphur dominates the conformation of the entire molecule. The data are consistent with a possible attractive chlorine–hydrogen interaction when the bonds to carbon of these two groups are parallel. The reactivity of the four isomers is briefly discussed.

CONFORMATIONAL studies of acyclic molecules having three asymmetric centres are simplified by the fact that only two conformers usually need be considered. Other conformers are destabilized by repulsions of large groups at C-1 and C-3, similar to the interaction of diaxial substituents in a cyclohexane system (Scheme 1).[1-8] In

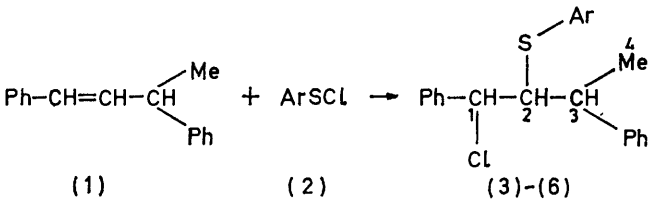
[1] A. Dempster, K. Price, and N. Sheppard, *Chem. Comm.*, 1968, 1457.
[2] P. E. McMahon and W. C. Tincher, *J. Mol. Spectroscopy*, 1965, **15**, 180.
[3] T. Shimanouchi and M. Tasumi, *Spectrochim. Acta*, 1961, **17**, 755.
[4] D. Doskocilova and B. Schnieder, *Coll. Czech. Chem. Comm.*, 1964, **29**, 2290.
[5] C. G. Overberger and T. Kurtz, *J. Org. Chem.*, 1966, **31**, 288.
[6] C. Kingsbury and D. C. Best, *J. Org. Chem.*, 1968, **33**, 3252.
[7] F. A. Bovey, 'Nuclear Magnetic Resonance Spectroscopy,' Academic Press, London, 1969, p. 167.
[8] T. Shimanouchi, *Pure Appl. Chem.*, 1966, **12**, 287.

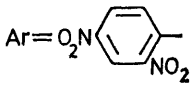
these acyclic molecules, an internal competition exists between groups at C-1 and groups at C-3 for the most



SCHEME 1

comfortable orientation with respect to the groups at C-2. It is of interest to see which centre dominates the conformation.[6]

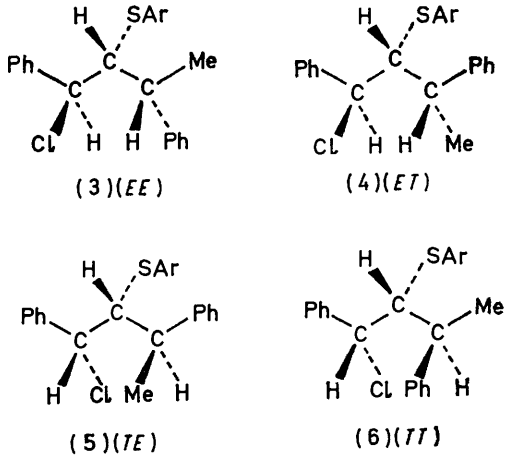




SCHEME 2

The compounds of interest (3)—(6) result from addition of 2,4-dinitrobenzenesulphenyl chloride (2) to the *cis*- and *trans*-alkenes (1) (Scheme 2).[9] The isomer having the *erythro*-configuration at C-1 and C-2, and the *threo*-configuration at C-2 and C-3 is termed *ET*. The other isomers, *EE*, *TE*, and *TT*, follow the same convention.

Table 1 lists the n.m.r. parameters for isomers (3)—(6), and the parameters for several comparison molecules (7)—(13). These parameters were established by trial and error variation of input data until the computer-generated plot of the spectrum was superimposable on the original spectrum.[10] Usually the line separations were very close to the actual coupling constants.



SCHEME 3

The addition of (2) to *trans*- (1) was accompanied by very little asymmetric induction.[11,12] The diastereomeric adducts, m.p.s 166 and 155°, were found in 43 and 57% relative yields. Both diastereomers have large coupling constants $J_{1,2}$ (*ca.* 10 Hz), and small coupling constants $J_{2,3}$ (*ca.* 3 Hz), indicative of predominately *trans* and *gauche* sets of hydrogens respectively.[13,14]

TABLE 1

60 MHz N.m.r. spectral parameters [a] for compounds (3)—(13)

$PhC^{1}HClC(SAr)H^{2}CHR^{2}R^{3}$

Compound	Isomer	M.p. (°C)	R^2	R^3	$J_{1,2}$/Hz	$J_{2,3}$/Hz	δ_1	δ_2	δ_3
(3)	*EE*	166	Me	Ph	10·4	3·4	4·64	3·93	4·14
(4)	*ET*	155	Me	Ph	10·8	3·0	5·01	3·87	4·15
(5)	*TE*	166	Me	Ph	3·3	9·5	5·59	3·77	3·35
(6)	*TT*	193	Me	Ph	4·2	8·4	4·88	3·84	3·23
(7)	*erythro*	144	Me	H	8·6		4·96	3·82	
(8)	*threo*	127	Me	H	4·8		5·27	3·87	
(9)	*erythro*	133	H	Ph	8·4	*b*	5·05	4·02	3·65 [d]
(10)	*threo*	153	H	Ph	3·8	*c*	5·25	3·99	2·94 [d]
(11)	*erythro*	162	Me	Me	10·7	2·4	4·90	3·78	*ca.* 2·9
(12)	*threo*	138	Me	Me	6·1	6·2	5·32	3·77	*ca.* 2·0
(13)	*erythro*	175	Ph	Ph	7·8	7·1	5·20	4·57	4·65

[a] All spectra were run on a Varian A-60D instrument for *ca.* 10% w/v solutions in deuteriochloroform. [b] Coupling constants of 3·4 and 10·4 Hz were observed between 2-H and 3-H_a. [c] Coupling constants of 6·1 and 8·5 Hz were observed between H-2 and 3-H_a. [d] The other benzylic hydrogen occurs at δ 2·96 (*erythro*-isomer) and 3·37 (*threo*-isomer).

Structures (3) and (4) (Scheme 3) show the possible configurations for these diastereomers. Molecular models show that H-1 of (3) lies over the face of the phenyl group at C-3. Strong shielding of H-1 due to the aromatic

[9] (*a*) N. Kharasch, *J. Chem. Educ.*, 1956, **33**, 585; (*b*) G. H. Schmid and V. M. Csizmadia, *Canad. J. Chem.*, 1966, **44**, 1338; (*c*) W. H. Mueller and P. E. Butler, *J. Amer. Chem. Soc.*, 1968, **90**, 2075; (*d*) F. T. Bond, *ibid.*, 1968, **90**, 5326; (*e*) C. Brown and D. R. Hogg, *J. Chem. Soc.* (*B*), 1968, 1262, and references therein.

[10] A. A. Bothner-By and S. Castellano, *J. Chem. Phys.*, 1964, **41**, 3863.

[11] J. D. Morrison and H. S. Mosher, 'Asymmetric Organic Reactions,' Prentice-Hall, Englewood Cliffs, 1971, p. 219.

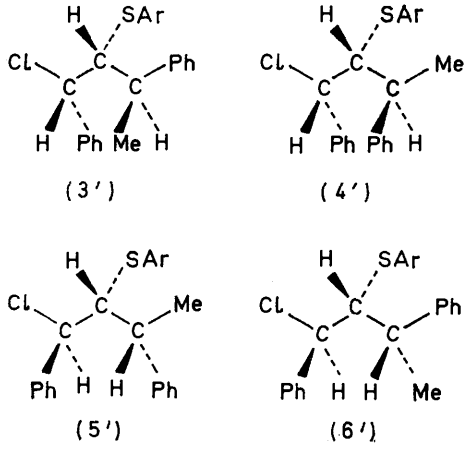
[12] D. J. Abbot and C. J. M. Stirling, *Chem. Comm.*, 1971, 472.

[13] M. Karplus, *J. Amer. Chem. Soc.*, 1963, **85**, 2870.

[14] A. A. Bothner-By, *Adv. Magnetic Resonance*, 1965, **1**, 195.

ring current should be observed for this isomer.[15-17] Table 1 shows that this expectation is met for the compound of m.p. 166° and not for that of m.p. 155°. The former is thus assigned the *EE* configuration (3) and the latter the *ET* configuration (4).

Addition of (2) to *cis*-(1) again showed little asymmetric induction. Relative yields of 55% of an adduct of m.p. 166°, and 45% of an adduct of m.p. 193° were observed. Both adducts show small values for $J_{1,2}$ (*ca.* 4 Hz) and large values for $J_{2,3}$ (*ca.* 9 Hz). Qualitatively, the magnitudes of these coupling constants are indicative of a lower degree of conformational purity than that present in (3) and (4). Isomers of the *threo*-configuration rather commonly are more conformationally mixed than isomers of the *erythro*-configuration.[18,19] A high degree of shielding of H-1 would be expected for (6). Shielding is in fact observed for the isomer of m.p. 193°, which is assigned the *TT* configuration. In (5) and (6), molecular models suggest that H-3 lies over the face of the SPh group in one important conformation of this group. The chemical shift of H-3 in (5) and (6) indeed lies *ca.* 0·8 p.p.m. upfield from H-3 of (3) and (4) in which H-3 and SPh have no interaction.



SCHEME 4

It is evident that the ordering of groups at C-1 and C-2 dominates the conformation of (3)—(6). An interchange of phenyl and methyl groups at C-3 has little effect on general conformational purity. Thus, (3) and (4) prefer a conformer having *trans*-hydrogens at C-1 and C-2, and *gauche*-hydrogens at C-2 and C-3. On the other hand, an interchange of phenyl and chlorine groups at C-1 strongly affects conformation. Thus, (3) prefers *trans*-hydrogens at C-1 and C-2, but (5) prefers *gauche*-hydrogens at the same centres.

It is instructive to consider the seemingly stable, but relatively unpopulated conformers (3′)—(6′) (Scheme 4), which have the same configuration as (3)—(6) respectively. If the *gauche*-interactions in (3′)—(6′) are listed with those in (3)—(6) equivalent interactions may cancel. These interactions cannot be responsible for the importance of (3)—(6) relative to (3′)—(6′). This cancellation procedure assumes similar dihedral angles and similar steric interactions in the cancelled *gauche*-interactions. This is only approximately correct due to buttressing effects and other second-order effects.

TABLE 2

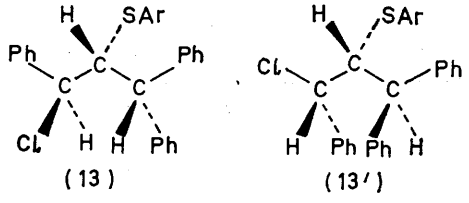
Non-cancellable *gauche*-interactions in (3)—(6) and (3′)—(6′)

(3)	(3′)	(4)	(4′)
R–Cl	Cl–SAr	H–Ph	Cl–SAr
SAr–CH_3	R–Ph	R–Cl	R–Ph
R^1–Ph	R^1–CH_3	R^1–CH_3	R^1–Ph
		SAr–Ph	H–CH_3
(5)	**(5′)**	**(6)**	**(6′)**
Ph–SAr	Cl–H	R–Cl	Cl–H
R–Cl	R–Ph	R^1–Ph	R–Ph
H–Ph	SAr–CH_3	H–CH_3	R^1–CH_3
R^1–CH_3	R^1–Ph		

R = CHMePh, R^1 = CHClPh.

The *gauche*-interactions that remain after cancellation are shown in Table 2. One structural feature is present in all populated conformers but absent in all unpopulated conformers, *i.e.* the R–Cl interaction (R = CHMePh). One interaction is common to all conformers having a low population, *i.e.*, the R–Ph interaction. This interaction is very likely repulsive. We are hesitant to ascribe a dominating influence to this factor, since a similar interaction is also present in two of the highly populated conformers, (3) and (6). However, the apparent conformational purity of (3) and (6) is only slightly less than that of (4) and (5) in which this interaction is absent.

In the R–Cl interaction, the C–Cl bond axis is parallel to the C–H bond axis of the R group. This possibly attractive interaction[20-22] may be enhanced by the 3-phenyl group, since a much smaller degree of conformational purity is evident for the *threo*-isomers lacking the 3-phenyl groups. Thus, (5) and (6) show a stronger conformational preference than (12). Compound (10; R = benzyl) also shows a stronger preference for a



conformer in which the 1-chlorine and the 3-hydrogen are eclipsed than does (8; R = ethyl).

Compound (13) appears quite anomalous. It is

[15] F. A. Bovey, E. Hood, E. Anderson, and L. Snyder, *J. Chem. Phys.*, 1965, **42**, 3900.
[16] C. E. Johnson, jun., and F. A. Bovey, *J. Chem. Phys.*, 1958, **29**, 1012.
[17] H. O. House, R. Magin, and H. Thompson, *J. Org. Chem.*, 1963, **28**, 2403.
[18] C. Kingsbury and D. C. Best, *J. Org. Chem.*, 1967, **32**, 7.
[19] See, however, C. Kingsbury, *J. Org. Chem.*, 1970, **35**, 1379; G. H. Schmid, *Canad. J. Chem.*, 1968, **46**, 3415.
[20] R. J. Abraham and K. Perry, *J. Chem. Soc.* (*B*), 1970, 539.
[21] F. A. Momany, R. A. Bonham, and W. McCoy, *J. Amer. Chem. Soc.*, 1963, **85**, 3077.
[22] B. Hawkins, W. Bremser, S. Borcic, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1971, **93**, 4472.

generally less conformationally pure than (3), (4), and even (9). Molecular models give no hint as to why (13′) is able to compete with the seemingly more stable (13).

The rates of solvolysis of the various compounds were determined (Table 3) to see if any correlation between conformation and reactivity was evident.[23] No correlation was discernible. The solvolysis data are notable for the large difference in reactivity of (3)—(6), which have the same chemical constitution but different arrangements of atoms in space. Thus (3) is over 10^3 times more reactive than (6). Compound (6) is the only material that did not give products of retained configuration. The slowness of the solvolysis of (6) is probably the result of three factors. (*a*) The 3-phenyl group is in a less sterically hindered position with respect to the sulphide group in (6) compared to (5). Greater steric acceleration of synartetic assistance by sulphide results for (5). The conformation shown in Scheme 2, of course, is but one of many available to the molecule as it gains energy in its approach to the transition state. Observation of the most reasonable conformations still places the arylthio-group in a more hindered position in (5) than in (6). (*b*) The episulphonium ion intermediate is probably asymmetric.[24,25] The benzylic carbon, C-1, probably bears more of the positive charge than C-2. Thus, overlap of the 1-phenyl orbitals and the orbitals which bear the charge is important even in an episulphonium ion intermediate. Molecular models suggest that steric hindrance of effective overlap of the 1-phenyl is worse in (6) than in (5). (*c*) Steric hindrance to solvation of the leaving group seems worse in (6) than in (5). Compounds (3) and (4) solvolyse much more rapidly than (5) and (6). A *trans*-episulphonium ion intermediate is formed from (3) and (4) in which the 1-phenyl group is unhindered and capable of overlap with the orbitals which bear the charge.

TABLE 3

Solvolysis rates and activation parameters for (3)—(13) in 95% ethanol

Compound	$10^4 k_{obs}/s^{-1}$ 50·0°	60·0°	70·0°	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}
(3)	3·42 ± 0·06	8·17 ± 0·08	18·3 ± 0·1	17·9	−19
(4)	1·42 ± 0·01	3·90 ± 0·01	8·64 ± 0·04	19·2	−17
(5)	0·011 ± 0·001	0·028 ± 0·002	0·061 ± 0·001		
(6)	0·0014 ± 0·0007				
(7)	2·61 ± 0·01	6·15 ± 0·15	14·1 ± 0·1	17·9	−20
(8)	0·042 ± 0·001	0·11 ± 0·01	0·26 ± 0·01		
(9)	1·09 ± 0·01				
(10)			0·35 ± 0·01		
(11)	5·30 ± 0·08				
(12)	0·025 ± 0·001	0·062 ± 0·001	0·17 ± 0·01		
(13)	0·54 ± 0·01	1·30 ± 0·02	3·18 ± 0·03	18·7	−21

EXPERIMENTAL

General Method of Preparation of Alkenes using the Wittig Reaction.[26]—Enough dry dimethylformamide (DMF) was added to the appropriate phosphonium salt, anhydrous potassium iodide, if used, and aldehyde to make the resulting solution approximately 1M in each of the reactants. The solution was cooled to 0° under nitrogen and a solution of potassium t-butoxide (1M) in dry DMF was added dropwise with stirring at 0°. When the addition of base was complete, the mixture was stirred for 2 h without cooling, and then worked-up,[26] purified, and the isomers were separated by distillation.

Preparation of 1,3-*Diphenylpropenes.*—A solution of potassium t-butoxide (50 g, 0·268 mol) in DMF (350 ml) was added to an equimolar quantity of triphenyl-(2-phenylethyl)phosphonium bromide in cold benzaldehyde (26·5 g, 0·25 mol). Work-up and vacuum-distillation yielded an oil (20·3 g, 43%), b.p. 109—115° at 1·1 mmHg (lit.,[27] 103—104° at 1 mmHg). This oil was distilled, using a spinning band column, yielding 23 fractions (0·3—1·5 ml each) with the following b.p.s at *ca.* 3·2 mmHg: fractions 1—6, 124—139°; fractions 7—15, 141—143°; fractions 16 and 17, 143—150°; fractions 18—22, 150—153°; fractions 23—25, 154—167°. These fractions were analysed by g.l.c. using a QF-1 column (200°; 100 ml min^{-1} helium flow). The retention times of the *cis*- and *trans*-alkenes were 3·2 and 3·7 min, respectively. The n.m.r. spectra of the *cis*-alkene (fractions 7—15) and *trans*-alkene (fractions 18—22) agreed with those of Raunio and Bonner.[27]

Preparation of erythro-1-α-*Chlorobenzyl*-2-*phenylethyl* 2,4-*Dinitrophenyl Sulphide* (9).—To a solution of *trans*-1,3-diphenylpropene (1·92 g, 0·01 mol) in DMF (10 ml) was added the chloride (2) (2·60 g, 0·011 mol) which gave yellow *needles* (4·01 g, 93%), m.p. 132·5—133° (from dichloromethane–pentane), $\nu_{max.}$ 1592, *ca.* 1525, 1496, 1460, 1454, 1432, *ca.* 1340, 1241, 1146, 1100, 1048, 1040, 1032, 1028, 942, 929, 901, 891, 833, 827, 793, 773, 740, 731, 710, 701, 693, 663, 660, 618, 610, 592, 583, 531, 524, 489, 471, and 422 cm^{-1} (Found: C, 58·9; H, 4·0. $C_{21}H_{17}ClN_2O_4S$ requires C, 58·8; H, 4·0%).

Preparation of the threo-*Isomer* (10).—Similar treatment of *cis*-1,3-diphenylpropene gave *adduct* (10) (90%), m.p. 152·5—153° (from dichloromethane–pentane), $\nu_{max.}$ *ca.* 1590, *ca.* 1520, 1495, 1492, 1453, 1441, *ca.* 1340, 1240, 1210, 1181, 1142, 1100, 1085, 1045, 1030, 943, 917, 907, 833, 796, 765, 750, 743, 732, 725, 699, 691, 666, 650, 596, 573, 542, 428, 472, and 443 cm^{-1} (Found: C, 58·65; H, 4·05%).

Preparation of 1,3,3-*Triphenylpropenes.*—To a solution of benzyltriphenylphosphonium bromide (47·6 g, 0·11 mol)

[23] D. Y. Curtin, *Rec. Chem. Progr.*, 1954, **15**, 111.
[24] K. Gunderman, *Angew. Chem. Internat. Edn.*, 1963, **2**, 674.
[25] T. L. Jacobs and R. Macomber, *J. Amer. Chem. Soc.*, 1968, **33**, 2988.
[26] L. D. Bergelson and M. M. Shemyakin, *Tetrahedron*, 1963, **19**, 149.
[27] E. K. Raunio and W. A. Bonner, *J. Org. Chem.*, 1963, **28**, 372.

in DMF (250 ml), small portions of sodium methoxide (5·91 g, 0·11 mol total) and a solution of diphenylacetaldehyde (19·6 g, 0·11 mol) in DMF (100 ml) were alternately added. Work-up gave plates of the *trans*-olefin, m.p. 98·5—99·0° (from light petroleum). The residual liquid was vacuum-distilled, yielding an oil (8·7 g, 32%), b.p. 146—151° at 0·12 mmHg (lit.,[28] 200° at 2 mmHg). An n.m.r. spectrum of the distilled oil indicated that it consisted of a mixture of 82% *cis*- and 18% *trans*-alkene.

Preparation of erythro-2-α-*Chlorobenzyl*-1,1-*diphenylethyl* 2,4-*Dinitrophenyl Sulphide* (13).—To a solution of *trans* 1,3,3-triphenyl-1-propene (2·70 g, 0·01 mol) in DMF (10 ml) was added the chloride (2) (2·59 g, 0·011 mol) which gave yellow *crystals* (3·77 g, 75%), m.p. 174·5—175·0° (from dichloromethane–pentane). The n.m.r. spectrum of this compound was a complex ABX pattern, and it was necessary to obtain all n.m.r. parameters by computer simulation, $\nu_{max.}$ 1591, *ca.* 1520, 1492, 1451, *ca.* 1340, 1244, 1144, 1046, 1034, 1015, 914, 854, 832, 829, 792, 763, 754, 743, 733, 713, 702, 693, 664, 627, 614, 600, 574, 567, 552, 535, and 466 cm^{-1} (Found: C, 64·35, H, 4·05. $C_{27}H_{21}ClN_2O_4S$ requires C, 64·2; H, 4·2%).

Attempted Preparation of the threo-*Isomer of* (13).—To a solution of 1,3,3-triphenylpropene (1·35 g, 5·0 mmol; 82% *trans*, 18% *cis*) in DMF (5 ml) was added to the chloride (2) (1·30 g, 5·5 mmol). The solution was heated for 30 min and left at room temperature for 6 days. The n.m.r. spectrum of the product, after normal work-up, showed no desired *threo*-adduct. The reaction was repeated using the alkene mixture (3·20 g, 11·8 mmol) and compound (2) (4·00 g, 17 mmol) in dry acetic acid (10 ml). The solution was heated on the steam-bath for 8 h and left at room temperature for 8 days. The product again contained no *threo*-adduct, as shown by n.m.r. spectroscopy.

Preparation of 1,3-*Diphenylbut*-1-*enes*.—To a solution of 3-phenylpropanal (33·5 g, 0·25 mol) and benzyltriphenylphosphonium bromide (108·5 g, 0·25 mol) in DMF (300 ml) was added a solution of potassium t-butoxide (50 g, 0·268 mol), in DMF (250 ml). The isomers were separated by spinning-band distillation at 1·2 mmHg. Twenty-nine fractions were taken (1—2 ml each): fractions 2—12 b.p. 99—101°; fractions 13 and 14, b.p. 101·5—104°; fractions 15—29, b.p. 104—105°. The fractions were analysed by g.l.c. using a QF-1 column (195°; helium flow 65 ml min^{-1}). The retention times of the *cis*- and *trans*-alkenes were 3·0 and 4·5, respectively. Fractions 2—12 were *cis*-alkene of 99% purity, and fractions 15—29 were *trans*-alkene of 99% purity. The n.m.r. spectra were identical with those reported by Ela and Cram.[29]

Reaction of trans-1,3-*Diphenylbut*-1-*ene with the Chloride* (2).—To a solution of the alkene (4·16 g, 0·02 mol) in dry acetic acid (15 ml) was added the chloride (2) (5·25 g, 0·022 mol) which yielded a mixture (7·60 g, 87%), m.p. 143—148°, which consisted of 43% *EE*- and 57% *ET*-adducts, as determined by integration of the n.m.r. spectrum of the crude. The two diastereomers were separated by several recrystallizations from chloroform–pentane, the *EE*-diastereomer being the less soluble [*EE* (2·73 g, 31%), m.p. 166—167°; *ET* (4·22 g, 48%), m.p. 155·0—155·5°]. erythro-erythro-1-α-*Chlorobenzyl*-2-*phenylpropyl* 2,4-*dinitrophenyl sulphide* (3) had $\nu_{max.}$ (KBr) 1590, 1525, 1491, 1450, 1336, 1139, 1140, 1090, 1044, 1029, 914, 902, 831, 828, 801, 769, 755, 751, 741, 731, 726, 704, 698, 686, 674, 660, 611, 606, 593, 579, 540, 528, 471, and 430 cm^{-1} (Found: C, 59·6; H, 4·4; N, 6·5. $C_{22}H_{19}ClN_2O_4S$ requires C, 59·65; H, 4·3; N, 6·3%). The erythro-threo-*isomer* (4) had $\nu_{max.}$ (KBr) 1590, 1536, 1512, 1460, 1452, 1375, *ca.* 1340, 1243, 1160, 1150, 1093, 1045, 1038, 1030, 1024, 917, 911, 903, 842, 833, 831, 782, 777, 753, 731, 702, 692, 673, 662, 629, 595, 543, 530, 506, 497, 471, and 433 cm^{-1} (Found: C, 59·65; H, 4·25%).

Reaction of cis-1,3-*Diphenylbut*-1-*ene with the Chloride* (2).—To a solution of the *cis*-alkene (4·18 g, 0·02 mol) in DMF (15 ml) was added the chloride (2) (5·24 g, 0·022 mol) which yielded a mixture, (7·25 g, 82%), m.p. 153—163°, which consisted of 55% *TE*- and 45% *TT*-diastereomer, as determined by integration of the n.m.r. spectrum of the crude product. The two diastereomers were separated by several recrystallizations from dichloromethane–pentane in which the *TT*-isomer is much less soluble [*TE* (3·88 g, 44%), m.p. 166·0—166·5°; *TT* (3·21 g, 36%), m.p. 193·0—193·5°]. The threo-erythro-*isomer* (5) had $\nu_{max.}$ (KBr) 1593, 1583, 1529, 1510, 1493, 1453, *ca.* 1340, 1302, 1249, 1151, 1133, 1093, 1050, 1032, 1020, 920, 910, 841, 832, 823, 791, 753, 746, 733, 708, 700, 681, 666, 622, 609, 600, 581, 548, 535, and 473 cm^{-1} (Found: C, 59·6; H, 4·3; N, 6·15%). The threo-threo-*isomer* (6) had $\nu_{max.}$ 1591, *ca.* 1515, 1492, 1451, 1445, *ca.* 1340, 1240, 1131, 1087, 1050, 1030, 1013, 918, 911, 832, 812, 765, 744, 731, 702, 692, 676, 611, 586, 534, 488, and 459 cm^{-1} (Found: C, 59·65; H, 4·4%).

Solvolyses of the 2,4-*Dinitrophenylsulphenyl Chloride Derivatives of the* β-*Substituted Styrenes*.—The sulphenyl chloride derivatives of the β-substituted styrenes were solvolysed in aqueous ethanol (*ca.* 95%). Commercial absolute ethanol was distilled from magnesium ethoxide, taking the centre cut, and diluted to the desired density with deionized, triply distilled water. Rates were determined conductiometrically, using a calibrated Wheatstone bridge (Clough–Brengle). Powdered adduct (*ca.* 1—2 mg) was dissolved in the solvent (10 ml) (at the reaction temperature) and forced through fritted glass disc filter (25—50 pore diameter) directly into the conductivity cell containing solvent (50—70 ml) and immersed in a thermostatted bath at the desired temperature. After thorough shaking for *ca.* 1 min, the first reading was used for ' zero time '. Readings were taken continuously until the resistance showed no change over an extended period (' infinity point ') (*ca.* 12 h for *erythro*-compounds and 24 h for *threo*-compounds). The first-order rate constants were determined as usual.

For each compound, 2—7 rate determinations (each containing 30—100 data points) were made at each temperature. All calculations were accomplished by computer, using a linear least-squares program containing a provision for correction of the infinity point by incremental variation. The infinity point value used was that which allowed the smallest standard deviation from the least squares line. The maximum observed correction of infinity point, was 7·21%, with typical runs showing 0—1·5% correction. The linearity of each determination extended to only two or three half-lives.

Solvolysis Products from Compound (13).—The mixture consisted of 91% ether and 9% alcohol, m.p. 119—126°, δ* 0·95—1·30 (relative integration 2·73, *J* 7·0 Hz, OCH_2CH_3), 2·95—3·50 (1·82, m, OCH_2CH_3), 4·35—4·80 (1·91, m, 2-H of ether and alcohol and 1-H of ether), 5·06 (0·09, d, $J_{1,2}$ 4·6

* Primes refer to positions of the dinitrophenyl ring.

[28] N. Campbell and K. W. Delahunt, *J. Chem. Soc.* (*C*), 1966, 1811.

[29] S. W. Ela and D. J. Cram, *J. Amer. Chem. Soc.*, 1966, **88**, 5777.

Hz, 1-H of alcohol), 7·00—7·07 (6, m, Ph and 6′-H of ether and alcohol), 8·07 (1, dd, $J_{5',6'}$ 9·0, $J_{3',5'}$ 2·5 Hz, 5′-H, of ether and alcohol), and 8·55 (1, d, $J_{3',5'}$ 2·5 Hz, 3′-H of ether and alcohol).

Solvolysis Products from Compound (3).—The mixture consisted of 87% ether and 13% alcohol, m.p. 121—129°. The coupling constant $J_{1,2}$ of the ether product could not be obtained due to superimposition of peaks in that region. However, product ratios were easily obtained by integration over the methyl and methylene absorptions of the ethoxy-group and the 1-H and hydroxy-peaks of the alcohol, δ * 1·22 (relative integration 2·61, t, J 7·0 Hz, OCH_2CH_3), 1·63 (3, d, J 6·8 Hz, $CHCH_3$ of ether and alcohol), 2·36br (0·13, s, OH), 3·28 (1·64, q, J 7·0 Hz, OCH_2CH_3), 3·60—4·20 (1·87, m, 1- and 2-H of ether and 2-H of alcohol), 4·63 (0·13, d, $J_{1,2}$ 8·8 Hz, 1-H of alcohol), 6·90—7·60 (11, m, 2 × Ph and 6′-H of ether and alcohol), 8·02 (1, dd, $J_{5',6'}$ 9·0, $J_{3',5'}$ 2·5 Hz, 5′-H of ether and alcohol), and 8·53 (1, d, $J_{3',5'}$ 2·5 Hz, 3′-H of ether and alcohol).

Solvolysis Products from Compound (5).—The mixture consisted of 82% ether and 18% alcohol, oil, δ * 1·16 (relative integration 2·46, t, J 7·0 Hz, OCH_2CH_3), 1·45—1·75 (3, m, $CHCH_3$ of ether and alcohol), 2·33br (0·18 s, OH), 3·00—4·00 (3·64, m, OCH_2CH_3 and 2- and 3-H of ether and alcohol), 4·81 (0·82, d, $J_{1,2}$ 3·6 Hz, 1-H of ether), 5·29 (0·18, d, $J_{1,2}$ 3·4 Hz, 1-H of alcohol), 6·90—7·55 (6, m, Ph and 6′-H of ether and alcohol), 7·92 (1H, dd, $J_{5',6'}$ 9·0, $J_{3',5'}$ 2·5 Hz, 5′-H, of ether and alcohol), and 8·55 (1, d, $J_{3',5'}$ 2·5 Hz, 3′-H).

Products from the Reaction of Compound (6) *with Ethanol.*—The product, m.p. 125—136°, after 14 months reaction at 50·0°, consisted of 30% unchanged material, 38% normal *threo-threo*-ether, and 32% epimeric *erythro-threo*-ether. Separation of the mixture was attempted using a 1 × 22 cm silica gel column and eluting with successively richer mixtures of benzene in light petroleum. Little separation of the diastereomers occurred, although the starting material could be separated in this way. The chromatographic residues could not be crystallized.

[2/1530 *Received*, 30*th June*, 1972]

* See note on p. 951.