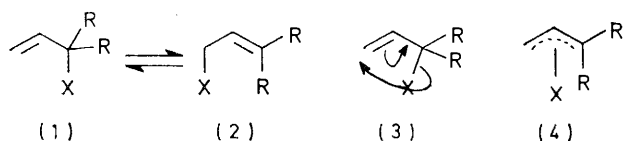


Mechanism of the [1,3] Phenylthio Shift in the Rearrangement of Allyl Sulphides

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Substituted allyl phenyl sulphides undergo a [1,3] allylic phenylthio shift by thermal, light-induced, and in some cases acid-catalysed pathways. Conditions are defined for causing or preventing the [1,3] shift and some of the factors which establish the position of equilibrium are identified. Crossover experiments suggest that the thermal and photochemical reactions occur by a radical chain mechanism and the acid-catalysed reaction *via* an allyl cation.

THE [1,3] allylic rearrangement ¹ [(1) \rightleftharpoons (2)] can occur as a concerted, thermally allowed process when X = CR₃, only by two unfavourable mechanisms: ² antarafacial migration with retention at X, or suprafacial migration with inversion at X (3) (the mechanism found by Berson ³



in his now classic example). The reaction is correspondingly rare, and this has sometimes concealed from organic chemists that the stable allyl compounds they customarily use (X = H, C, N, O, or F) occupy only an

¹ For a review see P. B. D. de la Mare in 'Molecular Rearrangements,' ed. P. de Mayo, Interscience, New York, 1963, vol. 1, pp. 27—110.

² R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 829; but see N. D. Epiotis, *J. Amer. Chem. Soc.*, 1973, **95**, 1206.

³ J. A. Berson and G. L. Nelson, *J. Amer. Chem. Soc.*, 1967, **89**, 5503; J. A. Berson, *Accounts Chem. Res.*, 1968, **1**, 152; H. A. Bampfield, P. R. Brook, and K. Hunt, *J.C.S. Chem. Comm.*, 1976, 146.

⁴ E. J. Lanpher, *J. Amer. Chem. Soc.*, 1957, **79**, 5578.

⁵ J. E. Nordlander and J. D. Roberts, *J. Amer. Chem. Soc.*, 1959, **81**, 1769; 1960, **82**, 6427; R. A. Benkeser, *Synthesis*, 1971, 347; D. A. Hutchinson, K. R. Beck, R. A. Benkeser, and J. B. Grutzner, *J. Amer. Chem. Soc.*, 1973, **95**, 7075.

'island of stability', since allyl compounds of most other elements carry out the [1,3] shift with great ease under a wide variety of conditions.

Allyl metal compounds can rearrange *via* an allyl anion (X = Na or K),⁴ or *via* the π -allyl complex (4), as for allyl Grignard reagents.⁵ For allyl transition metal complexes, this form (4) is often the stable structure rather than an intermediate.⁶ The more electronegative elements (*e.g.* halogens) can react by three other mechanisms: ⁷ a dissociative process (5) *via* an allyl cation ⁸ or radical,⁹ the S_N2' reaction (6), or an associative radical chain mechanism (7).⁹

Altogether the [1,3] allylic shift can occur by a remarkably wide variety of authentic mechanisms (Table 1), making prevention of the reaction difficult; and some synthetic intermediates, such as the allyl Grignard reagents ¹⁰ are notorious for giving unexpected products.^{5,11}

⁶ M. L. H. Green in 'Organometallic Compounds,' Chapman and Hall, London, 1968, vol. 2, pp. 39—64; M. L. H. Green and P. L. I. Nagy, *Adv. Organometallic Chem.*, 1964, **2**, 325; M. R. Churchill and R. Mason, *ibid.*, 1967, **5**, 105; M. Cooke, in 'Organometallic Chemistry,' Chem. Soc. Specialist Periodical Report, No. 4, 1975, pp. 336—352.

⁷ R. H. de Wolfe and W. G. Young, *Chem. Rev.*, 1956, **56**, 769.

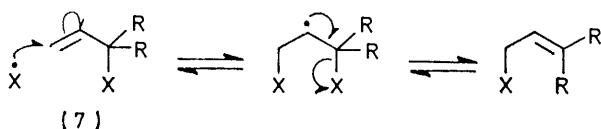
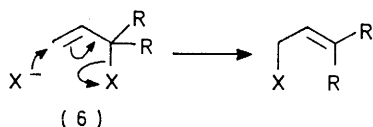
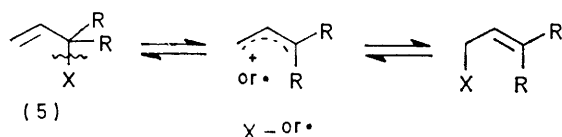
⁸ E. A. Braude, *Quart. Rev.*, 1950, **4**, 404.

⁹ J. W. Wilt in 'Free Radicals,' ed. J. K. Kochi, Wiley, New York, 1973, vol. 1, pp. 459—466.

¹⁰ R. H. de Wolfe and W. G. Young in 'The Chemistry of Alkenes,' ed. S. Patai, Interscience, London, 1964, pp. 688—731.

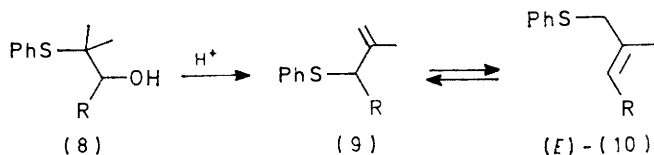
¹¹ Ref. 7, pp. 861—876; ref. 10, pp. 727—731.

Perhaps the only [1,3] shift to be put to much use in synthesis is the acid-catalysed rearrangement of allyl alcohols.^{8,12}



[1,3] Sulphur Shifts.—[1,3] Sulphur shifts are known in allyl sulphoxides¹³ and allyl sulphones,¹⁴ though the mechanism is uncertain. Allyl sulphides sometimes undergo a [1,3] shift during the thio-Claisen rearrangement,¹⁵ and before and after alkylation with Meerwein reagents.¹⁶ The only mechanistic investigation, by Kwart and Johnson,¹⁷ suggests a concerted mechanism with a polar transition state, and defines two separate conditions for the reaction: photochemical (with a xenon arc), and thermal (neat, or in solvents, at 77–160 °C). One example of a [1,3] sulphur shift is thought to go by a dissociative radical mechanism,¹⁸ and others by the associative radical chain mechanism.¹⁹

We have recently found²⁰ that allyl sulphides (9), formed by the acid-catalysed rearrangement of 2-phenylthioalcohols (8), undergo the [1,3] shift (9) → (10) very



easily. At first we thought, like previous workers, that this was a thermal reaction, but we found that it did not occur in solution in benzene, ethanol, chloroform, or acetonitrile in the dark even under reflux. The thermal rearrangement occurred only when the neat allyl sulphides (9) were heated at 100–110 °C.

The [1,3] shift does occur in solution on exposure to light, even daylight diffused through the window and

¹² Ref. 7, pp. 711–716; ref. 10, pp. 801–808; H. Pommer and A. Nürrenbach, *Pure Appl. Chem.*, 1975, **43**, 527; see also B. M. Trost and J. L. Stanton, *J. Amer. Chem. Soc.*, 1975, **97**, 4018.

¹³ D. A. Evans and G. C. Andrews, *Accounts Chem. Res.*, 1974, **7**, 147; S. Braverman and Y. Stabinsky, *Chem. Comm.*, 1967, 270.

¹⁴ A. C. Cope, D. E. Morrison, and L. Field, *J. Amer. Chem. Soc.*, 1950, **72**, 59.

¹⁵ H. Kwart and M. H. Cohen, *Chem. Comm.*, 1968, 319; H. Kwart and T. J. George, *ibid.*, 1970, 433; Y. Makisumi and T. Sasatani, *Tetrahedron Letters*, 1969, 1975; J. Tanaka, T. Katagiri, K. Takabe, and S. Takeshita, *Yuki Gosei Kagaku Kyokai Shi*, 1971, **29**, 788 (*Chem. Abs.*, 1971, **75**, 140636k).

the Pyrex flask. It can be prevented simply by wrapping the flask in aluminium foil. It seems possible that previous results on the 'thermal' reaction in solution actually refer to this photochemical process. The reaction is faster when the flask is exposed to direct sunlight or to the u.v. radiation (254 nm) used to inspect t.l.c. plates.

TABLE I

Mechanisms for the [1,3] allylic shift (1) ⇌ (2)

Mechanism	Shown by element X
(a) Concerted	
Concerted: details unknown	B ^a
Suprafacial with inversion at X	C, ^b Si ^c
Suprafacial with retention at X	C ^d
via π (η ³)-allyl complex (4)	Mg, ^{e,f} Li ^g
S _N 2' (6)	Transition metals ^h
S _E 2' (6)	Halogens ⁱ
	None?
(b) Dissociative	
via an allyl anion	Na, ^j K, ^j Li, ^j C ^k
via an allyl cation	O, ^l halogens, ^m S ⁿ
via an allyl radical	C, ^o N, ^p S ^q
(c) Associative	
Radical chain mechanism (7)	Br, ^r S ^{n,s}
(d) Mechanism unknown	H, ^t P, ^u Se ^v

^a K. G. Hancock and J. D. Cramer, *J. Amer. Chem. Soc.*, 1973, **95**, 3425, 6463. ^b Ref. 3. ^c J. Slutsky and H. Kwart, *J. Amer. Chem. Soc.*, 1973, **95**, 8678. ^d G. R. Krow and J. Reilly, *J. Amer. Chem. Soc.*, 1975, **97**, 3837. ^e Ref. 5. ^f Ref. 7, pp. 861–876; ref. 10, pp. 727–731. ^g C. R. Johnson, M. A. Weiner, J. S. Waugh, and D. Seyferth, *J. Amer. Chem. Soc.*, 1961, **83**, 1306. ^h Ref. 6. ⁱ Ref. 7, pp. 688–693; ref. 10, pp. 769–784. ^j Ref. 4. ^k R. C. Cookson and J. E. Kemp, *Chem. Comm.*, 1971, 385; J. C. Dalton and H.-F. Chan, *Tetrahedron Letters*, 1973, 3145; J. C. Dalton and B. G. Stokes, *ibid.*, 1975, 3179. ^l Ref. 8. ^m Ref. 7, pp. 694–696; ref. 10, pp. 784–800. ⁿ This work. ^o R. J. Stoodley in 'Organic Reaction Mechanisms', 1971, eds. B. Capon and C. W. Rees, Interscience, London, 1972, pp. 224–226; '1972', 1973, pp. 235–236; F. L. Scott in *ibid.*, '1973', eds. A. R. Butler and M. J. Perkins, Wiley, London, 1975, pp. 438–439. ^p R. S. Atkinson and C. W. Rees, *Chem. Comm.*, 1967, 1232; A. Padwa and P. H. J. Carlsen, *J. Org. Chem.*, 1976, **41**, 180. ^q Ref. 18. ^r Ref. 21. ^s Ref. 19. ^t W. J. Bailey and R. A. Baylouny, *J. Org. Chem.*, 1962, **27**, 3476; P. J. Kropp, H. G. Fravel, and T. R. Fields, *J. Amer. Chem. Soc.*, 1976, **98**, 840. ^u M. P. Savage and S. Trippett, *J. Chem. Soc. (C)*, 1967, 1998; L. Horner, A. Rapp, H. Winkler, A. Mentrup, H. Hoffmann, and P. Beck, *Tetrahedron Letters*, 1961, 161; but see R. D. Baechler, W. B. Farnham, and K. Mislow, *J. Amer. Chem. Soc.*, 1969, **91**, 5686. ^v K. B. Sharpless and R. F. Lauer, *J. Org. Chem.*, 1972, **37**, 3973.

For the aryl-substituted allyl sulphides (9; R = Ar) the [1,3] shift also occurs in the dark under the conditions of the acid-catalysed rearrangement of the alcohols (8; R = Ar) (toluene-*p*-sulphonic acid in benzene under reflux). This [1,3] shift is much slower (by ca. 100) than the [1,2] shift which precedes it [(8) → (9)], and if the

¹⁶ J. E. Baldwin, R. E. Hackler, and D. P. Kelley, *J. Amer. Chem. Soc.*, 1968, **90**, 4758.

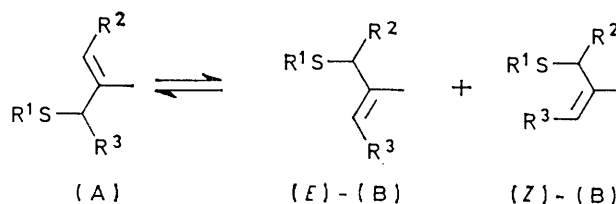
¹⁷ H. Kwart and N. Johnson, *J. Amer. Chem. Soc.*, 1970, **92**, 6064.

¹⁸ J. I. G. Cadogan and S. Kulik, *J. Chem. Soc. (C)*, 1971, 2621.

¹⁹ E. S. Huyser and R. M. Kellogg, *J. Org. Chem.*, 1965, **30**, 2867; S. J. Cristol and R. Kellman, *ibid.*, 1971, **36**, 1866; S. N. Lewis, J. J. Miller, and S. Winstein, *ibid.*, 1972, **37**, 1478; Y. Maki and M. Sako, *Tetrahedron Letters*, 1976, 851.

²⁰ P. Brownbridge and S. Warren, *J.C.S. Chem. Comm.*, 1975, 820.

TABLE 2
Composition of equilibrium mixtures in the [1,3] phenylthio shift in allyl sulphides



Compound (A)	R ¹	R ²	R ³	Conditions	% Composition		
					(A)	(E) - (B)	(Z) - (B)
(9; R = Ph)	Ph	H	Ph	<i>hν</i>	0	66	34
				Thermal	0	66	34
				Acid	0	100	0
(12)	<i>p</i> -Tol	H	<i>p</i> -Tol	<i>hν</i>	0	66	34
				Thermal	0	66	34
				Acid	0	100	0
(9; R = Me) ^a	Ph	H	Me	<i>hν</i>	5	60	35
				Thermal	5	60	35
				Acid	100	0	0
	Ph	Bu ¹	Me ^b	<i>hν</i>	100	0	0
				Thermal			
				Acid			
Ph	H	iso-C ₈ H ₁₁	<i>hν</i>	7	70	23	
			Acid	100	0	0	

^a Ref. 20. ^b P. Brownbridge and S. Warren, unpublished results.

reaction is carried out in the dark for a few minutes (see Experimental section) only the sulphide (9; R = Ar) is present. No [1,3] shift occurs in the aryl compounds (9; R = Ar) under these conditions in the absence of acid.

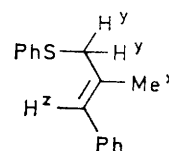
Both the photochemical and the thermal processes give the same mixture of *E*- and *Z*-isomers and the same equilibrium mixture of rearranged (10) and unrearranged (9) allyl sulphides (see Table 2), but the acid-catalysed reaction gives only a single isomer of the rearranged allyl sulphide (10; R = Ph), whose configuration was determined by nuclear Overhauser experiments.

The rearranged allyl sulphide (10; R = Ph) fortunately has an n.m.r. spectrum (see Table 3) with vinyl, methylene, and methyl signals in quite separate regions, making irradiation of each in turn a simple matter. The enhancement of the vinyl proton signal when the two methylene protons were irradiated was about twice as much as when the three methyl protons were irradiated, showing that this single isomer has the *E*-configuration. As expected, irradiation of the single vinyl proton had only a small effect on the other signals.

Mechanistic Work.—The very high efficiency of the

when the neat allyl sulphides (9) or their solutions in chloroform or acetonitrile are exposed to the same light

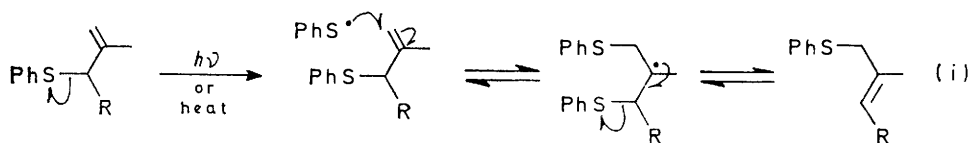
TABLE 3
Nuclear Overhauser effect experiments on 2-methyl-1-phenyl-(3-phenylthio)propene (10; R = Ph)^a



Protons irradiated	τ	Peak height enhancement (%) ^b		
		8.03 (x)	6.37 (y)	3.77 (z)
x	8.03		-17 ± 7	38
y	6.37	-19 ± 8		67
z	3.77	1	8	

^a Single isomer from acid-catalysed [1,3] phenylthio shift.
^b Measured by repeated integration; integrals accurate to ±10% of measured value except where given. Enhancements relative to effect of irradiation at τ 4.9.

source] suggested a photochemically initiated radical chain reaction [equation (i)] rather than a concerted

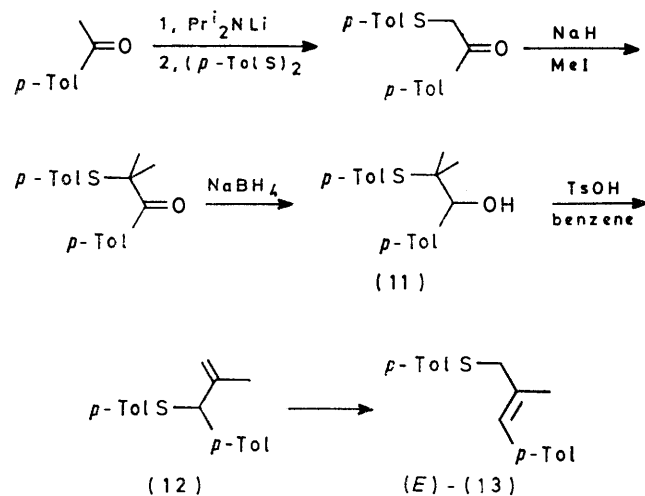


photochemical process (daylight filtered through two layers of glass is enough to cause complete equilibration at room temperature in solution) and the absence of solvent effects [the reaction occurs at about the same rate

process. This mechanism is well known for the [1,3] bromine shift in allyl bromides,²¹ it has been used to explain the exchange of RS groups during the addition of

²¹ F. R. Mayo and C. Walling, *Chem. Rev.*, 1940, **27**, 399.

thiols to allyl sulphides,²² and there are recorded cases of [1,3] arylthio shifts occurring by this mechanism.¹⁹



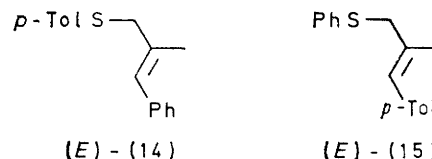
SCHEME 1

We have therefore carried out a series of experiments to test this mechanism. Since the aryl compound (9; R = Ph) showed the [1,3] shift under three different sets of conditions (thermal, photochemical, and acid-catalysed) we have synthesised the di-*p*-tolyl analogue (12) by the route shown in Scheme 1, and studied its rearrangement alone and in the presence of the phenyl compound (9; R = Ph).

sulphide (13) is formed under these conditions. The photochemical and thermal rearrangements (12) \rightarrow (13) occur at about the same rate as those of the phenyl compound (9; R = Ph) and again an equilibrium mixture of *E*- and *Z*-(13) is formed in the same proportions under the two conditions (Table 2).

We next carried out crossover experiments in which the two unrearranged allyl sulphides (9; R = Ph) and (12) were allowed to rearrange together under the three different conditions. The products could barely be distinguished in the n.m.r. from a mixture of the rearranged allyl sulphides (10; R = Ph) and (13), but could be analysed by mass spectroscopy since the rearranged allyl sulphides (10; R = Ph) and (13) each gave a molecular ion (M^+ 240 and 268, respectively) but neither gave a fragment of molecular weight 254, that of the molecular ion of either crossover product (14) or (15) (see Table 4).

The acid-catalysed rearrangement of the alcohols (8; R = Ph) and (11) to give the allyl sulphides (9; R = Ph) and (12) was used as a control experiment. This is presumably an intramolecular process, the sulphur atom



participating *via* an episulphonium ion (16), and indeed very little product (*m/e* 254 in column A, Table 4)

TABLE 4
Mass spectra of allyl sulphides from crossover experiments

Fragment	<i>m/e</i>	Intensity of ions as % of most abundant ion								
		Allyl sulphides				Crossover experiments †				
		(9; R = Ph) ^a	(12) ^a	(10; R = Ph) ^b	(13) ^{b,c}	A ^a	B ^b	C ^b	D ^b	E ^b
M^+	268		6		16	9	4	7	8	4
	254					0.6	6	12	16	6
	240	7		7		5	7	6	9	6
$M - ArS^+$	145		100		100	100	67	100	100	94
	131	100		100		46	100	83	91	100
ArS^+	123		4		8	4	7	18	8	28
	109			33		3	6	17	7	11
	129		11	10	2	11	15	25	17	33
Others	115	12	8	18		12	17	29	16	29
	105		10		1	10	9	20	14	19
	91	30	7	97	2	18	31	43	30	71

^a Injection temperature 60 °C. ^b Injection temperature 80 °C. ^c Metastable peaks: $M^+(268) \xrightarrow{m^* 78.3} M - ArS^+(145)$
 $m^* 114.8 \rightarrow (129) \xrightarrow{m^* 101.9} (115)$.

† Crossover experiments: A, acid-catalysed rearrangement of alcohols (8; R = Ph) and (11) to give (9; R = Ph) and (12); B, Acid-catalysed [1,3] ArS shift on (9; R = Ph) and (12), 16 h in benzene with TsOH under reflux; C, thermal [1,3] ArS shift on (9; R = Ph) and (12), neat, 103 °C, half-life 30 min; D, photochemical [1,3] ArS shift on (9; R = Ph) and (12), CDCl₃ solution, u.v. light at 254 nm, half-life 1.3 h; E, photochemical equilibration of (*E*)-(10; R = Ph) and (*E*)-(13) under same conditions as experiment D.

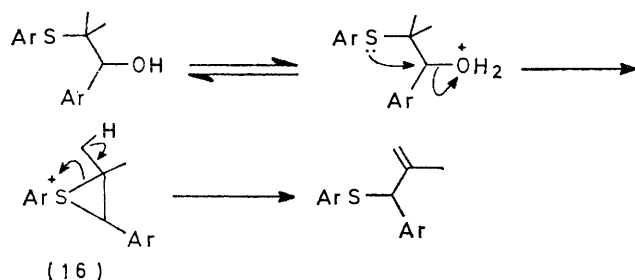
The di-*p*-tolyl alcohol (11) rearranges in acidic solution about three times faster than the corresponding phenyl compound (8; R = Ph), and the allyl sulphide product (12) also undergoes the acid-catalysed [1,3] arylthio shift more rapidly than does the phenyl compound (9; R = Ph). Again, only the *E*-isomer of the rearranged allyl

was formed when a mixture of alcohols (8; R = Ph) and (11) was treated with toluene-*p*-sulphonic acid in benzene under reflux for 3 min.

By contrast, when mixtures of the allyl sulphides (9;

²² D. N. Hall, A. A. Oswald, and K. Griesbaum, *J. Org. Chem.*, 1965, **30**, 3829.

R = Ph) and (12) underwent the [1,3] ArS shift under thermal (column C) or photochemical (column D, Table 4) conditions, an approximately 1 : 2 : 1 ratio of molecular ions at 268, 254, and 240 was observed, showing that



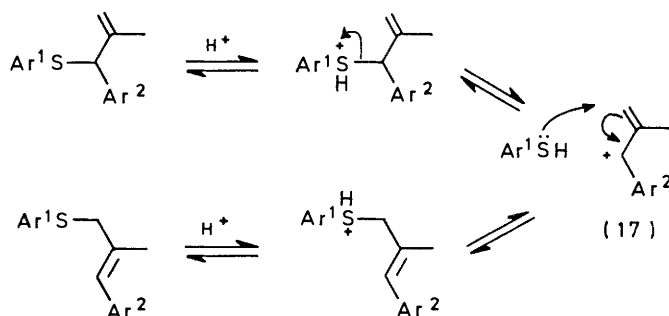
complete statistical equilibration had occurred. This suggests that both these reactions proceed by the radical chain process [equation (i)] in which the role of the heat or light is simply to initiate the chain by thermal or photochemical cleavage of the alkyl-S bond. This is the fragmentation observed as the major pathway in the mass spectra of all the allyl sulphides (base peaks $M - ArS$, see Table 4) and also occurred when we attempted to analyse our crossover products by g.l.c. Mass spectra of the fractions from g.l.c. showed that they were not the allyl sulphides but mixtures of diaryl disulphides and other compounds derived from cleavage of the S-alkyl bond such as 1-aryl-2-methylpropenes, 1-arylprenes, toluene, and ethylbenzene. We were not able to carry out the g.l.c. separation at a low enough temperature to prevent this decomposition.

The next step is the addition of the arylthiyl radical to the double bond of the allyl sulphide. This is known to be an exceptionally efficient process in comparison with other radical additions to olefins. For synthetic purposes, benzenethiol is added to the olefin: unless oxygen is carefully excluded, radical addition occurs to give good yields of the anti-Markovnikoff product.²³ To confirm the radical chain mechanism we added a catalytic amount of benzenethiol to the allyl sulphide (9; R = Ph).²³ The rearranged allyl sulphide (10; R = Ph) was rapidly formed in the same *E* : *Z* ratio as in the thermal or photochemical rearrangements; a control sample did not rearrange.

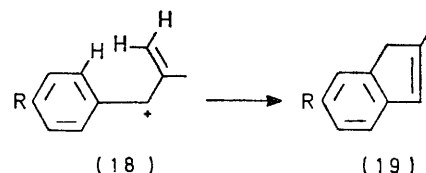
The [1,3] arylthio shift in these compounds under photochemical or thermal conditions thus occurs by the radical chain process observed for other allyl sulphides¹⁹ and by the same mechanism as the light- or radical-initiated 'allylic reversal' during the addition of thiyl radicals to allyl sulphides.^{22,*} Neither the concerted mechanism with a polarised transition state, nor the bimolecular pericyclic mechanism¹⁷ is consistent with initiation by light or radicals or the results of the crossover experiments.

* Our [1,3] shift is also reversible. A mixture of pure *E*-isomers of (10; R = Ph) and (12) gave, rather slowly, crossover products and *E*- and *Z*-isomers of (10; R = Ph) and (12) on exposure to light (column E, Table 4).

The crossover experiment on the acid-catalysed [1,3] arylthio shift (column B, Table 4) did not give complete equilibration, but gave an approximately 1 : 2 : 2 mixture of molecular ions at 268, 254, and 240. This confirms the dissociative mechanism²⁰ [equation (ii)] via the allyl cation (17) as the two allyl sulphides (9; R = Ph) and (12) rearrange at different rates in acid. Initially the mixture gives mostly the more stable *p*-tolyl-substituted cation (17; $Ar^2 = p\text{-Tol}$) and *p*-tolylthiol, and hence more (13) is formed. At the end of the reaction only (9; R = Ph) is left to rearrange, and only in the middle period can proper equilibration occur while substantial amounts of both allyl sulphides dissociate together. This rearrangement occurred more rapidly in acetonitrile than in the less polar benzene. This mechanism (dissociation to an allyl cation) is presumably responsible for the [1,3] shift observed by Baldwin¹⁶ in sulphonium salts.



The exclusive formation of the *E*-product in this acid-catalysed reaction requires the exclusive formation of the *E*-cation (17). This is likely, as the all planar cations will be particularly sensitive to steric crowding such as that in the *Z*-cation (18). In any case *Z*-cations of this kind are known to cyclise to indenes²⁴ [in this case (19)] and no products of this kind were observed.

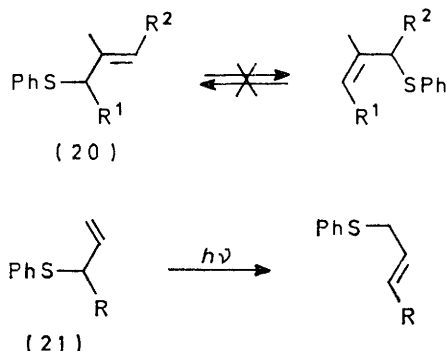


Position of Equilibrium in the [1,3] Arylthio Shift.—Whether radical or cationic intermediates are formed, the [1,3] isomerisation is an equilibrium process and the composition of the equilibrium mixture is largely determined by the substitution pattern of the double bond in each isomer (see Table 2). A trisubstituted double bond is preferred to a 1,1-disubstituted double bond, but only exclusively if conjugation is also established. We have been unable to equilibrate two trisubstituted double bonds in one case (20), but a monosubstituted double

²³ F. W. Stacey and J. F. Harris, *Org. Reactions*, 1963, 13, 164.

²⁴ N. C. Deno, C. U. Pittman, and J. O. Turner, *J. Amer. Chem. Soc.*, 1965, 87, 2153.

bond (21) can be completely converted into a 1,2-disubstituted double bond in bright sunlight.²⁵



These easily controlled [1,3] shifts make allyl sulphides attractive and versatile synthons for building allyl alcohols and γ -ketols.^{20,26}

EXPERIMENTAL

I.r. spectra were taken on a Perkin-Elmer 257, n.m.r. spectra on Hitachi-Perkin-Elmer R24A or Varian HA100D, mass spectra on an A.E.I. MS12 or MS30, and high resolution mass spectra on an A.E.I. MS902 instrument. T.l.c. was run on silica gel GF254 eluted with acetone (30%)–light petroleum (b.p. 60–80 °C). N.m.r. peaks marked with an asterisk are due to diastereotopic protons. Half-lives of reactions were estimated from n.m.r. integrals. 'Toluene-*p*-sulphonic acid' refers to the monohydrate B.D.H. micro-analytical reagent grade.

2-Methyl-3-phenyl-3-phenylthiopropene (9; R = Ph).—*2-Methyl-1-phenyl-2-phenylthiopropen-1-ol* (8; R = Ph)* (238 mg) was refluxed in dry benzene (40 ml) in a foil-wrapped flask and toluene-*p*-sulphonic acid (176 mg, 1 equiv.) was added. Refluxing was continued for 2 min, then the mixture was cooled in an ice-bath and poured into saturated sodium hydrogen carbonate solution. The benzene layer was separated and the aqueous layer extracted with dichloromethane (3 × 20 ml). The combined organic fractions were dried (Na₂SO₄) and evaporated to give the olefin (9; R = Ph) (217 mg, 98%) as an oil. N.m.r. showed it to contain less than 5% of (10; R = Ph). It had R_F 0.56, ν_{\max} (liq.) 1 642 (C=C) and 903 cm⁻¹ (C=CH₂), τ (CDCl₃) 2.5–3.0 (10 H, m, Ph), 4.90 (1 H, s, C=CH or SCH), 5.07 (1 H, q, J 1.5 Hz, MeC=CH), 5.18 (1 H, s, C=CH or SCH), and 8.24br (3 H, s, MeC=C), m/e 240 (M^+ , 7%), 131 (100), 115 (12), and 91 (30) (Found: M^+ , 240.0970. C₁₆H₁₆S requires M , 240.0972).

2-Methyl-1-phenyl-3-phenylthiopropene (10; R = Ph).—(a) (*E*)-*Isomer by acid-catalysed rearrangement*. The alcohol (8; R = Ph) (36 mg) and toluene-*p*-sulphonic acid (6 mg) were refluxed in dry benzene (20 ml) in a foil-wrapped flask. All the alcohol was consumed after about 5 min (t.l.c.). The initially formed olefin (9; R = Ph) isomerized to (10; R = Ph) with a half-life of about 3.7 h. After 18 h, the reaction was worked up as for (9; R = Ph), giving the olefin (*E*)-(10; R = Ph) (31 mg, 93%), R_F 0.56, ν_{\max} (CHCl₃) 1 640

cm⁻¹ (C=C), τ (CDCl₃) 2.4–3.0 (10 H, m, Ph), 3.77br (1 H, s, C=CH), 6.37 (2 H, s, CH₂), and 8.04 (3 H, d, J 1 Hz, MeC=CH), m/e 240 (M^+ , 7%), 131 (100), 109 (33), 91 (97), 65 (32), and 39 (37) (Found: M^+ , 240.0979. C₁₆H₁₆S requires M , 240.0972). Trifluoroacetic acid in benzene and toluene-*p*-sulphonic acid in acetonitrile have also been used for this rearrangement, but it did not occur in refluxing benzene, acetonitrile, or ethanol in the absence of acid.

(b) *By light-induced rearrangement of the olefin* (9; R = Ph). Samples of the olefin (9; R = Ph) neat and in deuteriochloroform were left in sunlight (inside the laboratory window) in Pyrex flasks. Both samples isomerized quantitatively to a 2 : 1 mixture of the *E*- and *Z*-isomers of (10; R = Ph) with a half-life of about 1 h. A control sample in a foil-wrapped flask did not rearrange, but a sample of (*E*)-(10; R = Ph) isomerized to the equilibrium (2 : 1) mixture of isomers with a half-life of about 6 h. The *Z*-olefin had R_F 0.56, τ (CDCl₃) 2.4–3.0 (10 H, m, Ph), 3.56br (1 H, s, C=CH), 6.27 (2 H, s, CH₂), and 7.99 (3 H, d, J 1.5 Hz, MeC=CH). This 2 : 1 mixture of isomers did not revert to the *E*-isomer on refluxing with toluene-*p*-sulphonic acid in benzene.

(c) *By thermally induced rearrangement of the olefin* (9; R = Ph). A neat sample of the olefin (9; R = Ph) was heated at 100 (±1) °C in a foil-wrapped thin-walled tube. It isomerized to (10; R = Ph) (2 : 1 isomer mixture) with a half-life of 35 min.

(d) *By phenylthiyl radical-catalysed rearrangement of the olefin* (9; R = Ph). The olefin (9; R = Ph) (70 mg) was dissolved in deuteriochloroform (0.8 ml) and the solution divided equally between two n.m.r. tubes. To one tube was added redistilled benzenethiol (5 mg), and both tubes were stored at 35 °C for 18 h. The tube without benzenethiol had an unchanged n.m.r. spectrum, but the olefin in the tube with benzenethiol had rearranged completely to the 2 : 1 isomer mixture of (10; R = Ph). The quantity of benzenethiol present was unchanged (within the limits of n.m.r. detection).

Determination of the Configuration of the Double Bond of the Olefin (10; R = Ph).—The nuclear Overhauser effect experiments were performed using a Hitachi-Perkin-Elmer R24A n.m.r. spectrometer. A sample of olefin (10; R = Ph) from the acid-catalysed rearrangement was dissolved in carbon tetrachloride (AnalaR; distilled under nitrogen) to give a 0.3M-solution, which was degassed with nitrogen for 2 h. The results obtained (using a second irradiating field of ca. 4 mG) are described in Table 3. The single isomer of (10; R = Ph) produced by acid-catalysed rearrangement of (9; R = Ph) was found to be the *E*-isomer. A confirmatory experiment was performed by making up a similar solution of the mixture of isomers of (10; R = Ph) produced by light-induced rearrangement of (9; R = Ph) and irradiating the methyl region (τ 8.0). The vinyl signal of the minor isomer (τ 3.58) was intensified about 23% more than that of the major isomer (τ 3.77). This indicates that the former has the methyl group *cis*, and is the *Z*-isomer.

1-(4-Tolyl)-2-(4-tolylthio)ethanone.—A solution of lithium di-isopropylamide was prepared by addition of butyllithium (30 ml of 1.35M-solution in hexane) to dry di-isopropylamine (10 ml) in dry tetrahydrofuran (50 ml) at 0 °C in a nitrogen atmosphere. The solution was cooled to -70 °C and 4'-methylacetophenone (5.40 g) in dry tetra-

* This compound was prepared in a similar way to (11), from α -phenylthioacetophenone.²⁶

²⁵ P. Brownbridge, I. Fleming, A. Pearce, and S. Warren, *J.C.S. Chem. Comm.*, in the press.

²⁶ P. Brownbridge and S. Warren, *J.C.S. Perkin I*, in the press.

hydrofuran (50 ml) added dropwise.²⁷ After 2 h stirring, the solution was transferred by syringe to a solution of di-4-tolyl disulphide (11.8 g) in dry tetrahydrofuran (50 ml), and the mixture stirred for 4 h. The mixture was poured into aqueous sodium hydroxide (5%) and extracted with chloroform (4 × 30 ml). The extracts were dried (Na₂SO₄) and evaporated to give an oil which solidified. The product was separated from starting materials by crystallization from di-isopropyl ether; yield 3.76 g (37%), m.p. 57–58°, R_F 0.46, ν_{\max} (CHCl₃) 1 674 cm⁻¹ (CO), τ (CDCl₃) 2.20 (2 H, d, J 8 Hz, ArH *ortho* to CO), 2.7–3.0 (6 H, m, Ar), 5.86 (2 H, s, CH₂CO), 7.63 (3 H, s, MeArCO), and 7.73 (3 H, s, MeArS), m/e 256 (M^+ , 100%), 123 (23), 119 (71), 91 (43), and 77 (23) (Found: C, 74.8; H, 6.4; S, 12.3. C₁₆H₁₆OS requires C, 75.0; H, 6.3; S, 12.5%).

2-Methyl-1-(4-tolyl)-2-(4-tolylthio)propan-1-one.—The foregoing ketone (3.10 g) was added in portions to petrol-washed sodium hydride (0.75 g) suspended in dry tetrahydrofuran (40 ml) by vigorous stirring at 0°C in a nitrogen atmosphere. After evolution of hydrogen had ceased, the mixture was refluxed for 20 min and methyl iodide (1.0 ml) added. Refluxing was continued for 1.5 h, then more methyl iodide (1.0 ml) was added and refluxing continued for a further 2.5 h. The mixture was cooled and quenched with aqueous ammonium chloride and sodium thiosulphate. The organic layer was separated and the aqueous layer extracted with chloroform (3 × 20 ml). The combined organic layers were dried (Na₂SO₄) and evaporated leaving a yellow oil, which was triturated with 95% ethanol at -15°C to give the product. Recrystallization from 95% ethanol gave the ketone (2.44 g, 71%), m.p. 75–76°, R_F 0.60, ν_{\max} (CHCl₃) 1 660 cm⁻¹ (CO), τ (CDCl₃) 1.84 (2 H, d, J 9 Hz, ArH *ortho* to CO), 2.7–3.0 (6 H, m, ArH), 7.59 (3 H, s, MeAr), 7.70 (3 H, s, MeAr), and 8.48 (6 H, s, CMe₂), m/e 284 (M^+ , 13%), 165 (100), 119 (36), 91 (53), and 43 (38) (Found: C, 76.1; H, 7.2; S, 11.1. C₁₈H₂₀OS requires C, 76.0; H, 7.1; S, 11.3%).

2-Methyl-1-(4-tolyl)-2-(4-tolylthio)propan-1-ol (11).—The foregoing dimethylated ketone (0.90 g) and sodium borohydride (0.04 g) were stirred for 3 h in water-ethanol-tetrahydrofuran (1 : 3 : 1). The mixture was poured into ammonium chloride solution and extracted with chloroform (4 × 20 ml). The combined extracts were dried (Na₂SO₄) and evaporated to give a viscous oil which was purified by t.l.c. and recrystallized from light petroleum (b.p. 40–50°C) giving the alcohol (0.73 g, 81%), m.p. 53–54°, R_F 0.50, ν_{\max} (CHCl₃) 3 460 cm⁻¹ (OH), τ (CDCl₃) 2.54 (2 H, d, J 7.5 Hz, ArH *ortho* to S), 2.76–3.00 (6 H, m, ArH), 5.64 (1 H, s, CH-OH), 6.42 (1 H, s, OH), 7.61 (3 H, s, MeAr), 7.68 (3 H, s, MeAr), and 8.80 * and 8.91 * (each 3 H, s, CMe₂), m/e 165 (100%), 123 (29), 91 (92), 77 (55), and 41 (47) (Found: C, 75.3; H, 7.8; S, 11.4. C₁₈H₂₂OS requires C, 75.5; H, 7.7; S, 11.2%).

2-Methyl-3-(4-tolyl)-3-(4-tolylthio)propene (12).—To a refluxing solution of the alcohol (11) (39 mg) in dry benzene (30 ml) in a foil-wrapped flask was added toluene-*p*-sulphonic acid (6 mg), and refluxing was continued for 5 min. The mixture was cooled in an ice-bath, poured into aqueous sodium hydrogen carbonate, and extracted with dichloromethane (3 × 10 ml). The extracts were dried (Na₂SO₄) and evaporated to give a white solid (35 mg, 98%), m.p. 53–57°, shown (n.m.r.) to be (12) containing less than 5% of (13). The olefin (12) was recrystallized by dissolving it in light petroleum (b.p. 40–50°C) at room temperature and cooling to -15°C. It had m.p. 59.8–61.0°, R_F 0.62, ν_{\max}

(CHCl₃) 1 637 (C=C) and 899 cm⁻¹ (C=CH₂), τ (CDCl₃) 2.7–3.0 (8 H, m, ArH), 4.94 (1 H, s, C=CH or SCH), 5.09 (1 H, q, J 1.5 Hz, HC=CMe), 5.25 (1 H, s, C=CH or SCH), 7.67 (3 H, s, MeAr), 7.70 (3 H, s, MeAr), and 8.23br (3 H, s, MeC=C), m/e 268 (M^+ , 6%), 146 (16), 145 (100), 129 (11), and 105 (10) (Found: C, 80.3; H, 7.6; S, 11.8. C₁₈H₂₀S requires C, 80.5; H, 7.5; S, 12.0%).

2-Methyl-1-(4-tolyl)-3-(4-tolylthio)propene (13).—(a) (*E*)-*Isomer by acid-catalysed rearrangement.* Dehydration of (11) and rearrangement of the initially formed (12) was performed as for (*E*)-(10; R = Ph), the rearrangement occurring about twice as fast as for the phenyl compound. The olefin (*E*)-(13) (89%) had R_F 0.62, ν_{\max} (liq.) 1 635 cm⁻¹ (C=C), τ (CDCl₃) 2.6–3.0 (8 H, m, ArH), 3.84br (1 H, s, C=CH), 6.42 (2 H, s, CH₂), 7.68 (6 H, s, MeAr), and 8.04 (3 H, d, J 1 Hz, MeC=CH), m/e 268 (M^+ , 16%), 145 (100), and 123 (8) (Found: C, 80.3; H, 7.7; S, 12.0. C₁₈H₂₀S requires C, 80.5; H, 7.5; S, 12.0%).

(b) *By light-induced rearrangement of the olefin (12).* An approximately 0.25M-solution of (12) in deuteriochloroform was irradiated in an n.m.r. tube 1 cm from a Hanovia Chromatolite u.v. lamp. The isomerization had a half-life of about 100 min, and gave quantitatively a 2 : 1 mixture of the *E*- and *Z*-isomers of (13). The *Z*-isomer had R_F 0.62, τ (CDCl₃) 2.6–3.0 (8 H, m, ArH), 3.62br (1 H, s, C=CH), 6.31 (2 H, s, CH₂), 7.68br (6 H, s, MeAr), and 8.01 (3 H, d, J 1.5 Hz, MeC=CH).

(c) *By thermally induced rearrangement of the olefin (12).* A sample of (12) heated at 103 (±1)°C in a foil-wrapped thin-walled tube isomerized quantitatively to the 2 : 1 mixture of isomers of (13) with a half-life of 30 min.

Crossover Experiments.—The mass spectra of these mixtures are described in Table 4.

(A) *Acid-catalysed dehydration of alcohols (8; R = Ph) and (11).* To a refluxing mixture of (8; R = Ph) (22 mg) and (11) (25 mg) in dry benzene (35 ml) in a foil-wrapped flask was added toluene-*p*-sulphonic acid (40 mg), and refluxing was continued for 3 min. The mixture was worked up as for (12), giving a mixture of (9; R = Ph) and (12) (43 mg, quantitative). N.m.r. spectroscopy showed a 1 : 1 mixture of the two olefins, with no (10; R = Ph) or (13) detectable. The *p*-tolyl alcohol was dehydrated about 3.5 times as fast as the phenyl compound.

(B) *Acid-catalysed rearrangement of the olefins (9; R = Ph) and (12).* To a refluxing mixture of (8; R = Ph) (26 mg) and (11) (28 mg) in dry benzene (45 ml) in a foil-wrapped flask was added toluene-*p*-sulphonic acid (9 mg), and refluxing was continued for 16 h. The mixture was worked up as for (12) giving an approximately 3 : 3 : 2 : 2 mixture of (*E*)-(10; R = Ph), (*E*)-(13), (*E*)-(14), and (*E*)-(15) (49 mg, 98%). N.m.r. showed the combined spectra of (*E*)-(10; R = Ph) and (*E*)-(13), except that the vinyl region showed three peaks at τ 3.77, 3.80, and 3.84 in the ratio 3 : 4 : 3.

(C) *Thermally induced rearrangement of the olefins (9; R = Ph) and (12).* The neat mixture of olefins (43 mg) was heated at 103 (±1)°C in a foil-wrapped thin-walled tube. The rearrangement had a half-life of 30 min for both olefins. After 3 h heating, the product was a 1 : 1 : 1 : 1 mixture of (10; R = Ph), (13), (14), and (15), each a 2 : 1 mixture of *E*- and *Z*-isomers. The n.m.r. spectrum consisted of the combined spectra of (10; R = Ph) and (13), but the vinyl region showed a broad peak at τ 3.6 (for the *Z*-compounds)

²⁷ B. M. Trost and T. N. Salzmann, *J. Amer. Chem. Soc.*, 1973, **95**, 6840.

and three peaks at τ 3.77, 3.80, and 3.84 in the ratio 1 : 2 : 1 for the *E*-compounds.

(D) *Light-induced rearrangement of the olefins* (9; R = Ph) and (12). A solution of (9; R = Ph) (0.2M) and (12) (0.2M) in deuteriochloroform was irradiated as for (12). The

2 : 2 : 1 : 1), indicating that complete equilibration was occurring, very slowly.

Gas-liquid Chromatography.—The gas chromatograph used was a Pye 104 instrument, with a 4 m \times 3.2 mm Apiezon L column, coupled to an A.E.I. MS12 mass spectro-

TABLE 5

G.l.c. data for crossover experiments

Sample:	(10; R = Ph)	(13)
Oven temp:	128 °C	123 °C
Carrier : gas	He, 4.5 ml min ⁻¹	He, 5 ml min ⁻¹
	<i>t_R</i> ^a	<i>t_R</i> ^a
	<i>m/e</i>	<i>m/e</i>
	5.0	5.3
	7.1	8.4
	14.5	28.1
	17.0	30.7
	20.1	47.1
^a Retention time in min. ^b <i>m</i> * 78.1 (106→91). ^c <i>m</i> * 103.8 (132→117). ^d <i>m</i> * 117.6 (146→131), 63.2 (131→91). ^e <i>m</i> * 113.0 (117→115), 103.8, 63.2.		

rearrangement of both olefins had a half-life of about 1.3 h. After 9 h, the n.m.r. spectrum was identical with that of the product from the thermal rearrangement (C).

(E) *Light-induced equilibration of the olefins* (E)-(10; R = Ph) and (E)-(13). A solution of the two *E*-olefins (each 0.25M) in deuteriochloroform was irradiated as for (12) above, for 3 days. N.m.r. spectroscopy showed a 2 : 1 mixture of *E*- and *Z*-isomers of (10; R = Ph), (13), (14), and (15) (*ca.*

meter. Samples were injected in chloroform solution (injection temperature 350 °C). G.l.c. of the crossover experiments gave mixtures of the peaks indicated in Table 5.

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