Formation of Alkenes in the Pyrolysis and Photolysis of 1,2-Bis(phenylthio)ethanes

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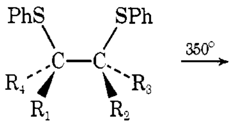
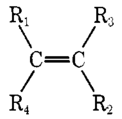
Abstract: Pyrolysis (350°) of 1,2-bis(phenylthio)ethanes (**1**) results in the elimination of two phenylthio groups and the formation of alkenes. The diastereomeric 2,3-bis(phenylthio)butanes (**1b** and **1c**) have been synthesized in order to study the stereochemistry of this elimination. The reaction is stereospecific, proceeding *via* a trans elimination. The data support a free radical mechanism.

We have observed that, upon pyrolysis, 1,2-bis(phenylthio)ethanes (**1**) lose their two adjacent thiophenoxy groups generating alkenes in moderate yield (eq 1). Thus, when 1,2-bis(phenylthio)ethane (**1a**)[1] is pyrolyzed at 350°, the products are ethylene, diphenyl disulfide, and thiophenol (Table I). The alkene is produced in a reaction which is formally the elimination of diphenyl disulfide. While the addition of disulfides to alkenes has been observed,[2] this is the first reported example of the corresponding elimination.



1a, $R_1 = R_2 = R_3 = R_4 = H$
b, $R_1 = R_2 = H$; $R_3 = R_4 = Me$
c, $R_1 = R_3 = H$; $R_2 = R_4 = Me$



+ PhSSPh + PhSH (1)

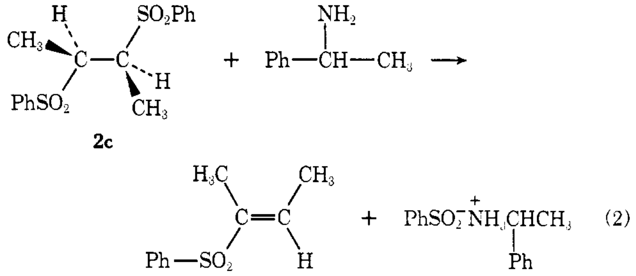
A similar elimination occurs when **1a** is photolyzed in a decalin solution under conditions such that ethylene is swept from the reactor in a nitrogen stream (Table I).

The stereochemistry of these reactions has been studied in order to elucidate the mechanism of the elimination. A stepwise process in which the breaking of a carbon–sulfur bond is anchimerically assisted by the second sulfur would result in a trans elimination. Alternatively, a concerted four-center elimination of diphenyl disulfide results in cis elimination. Orbital symmetry considerations preclude a simple four-center elimination in the ground state.[3] However, orbital symmetry restrictions on a concerted process may be lifted in a variety of ways. For example, participation of sulfur 2p electrons and/or vacant 3d orbitals could alter the symmetry of the system in such a way as to cause the concerted pathway to be no longer forbidden. In the photochemical reaction a simple cis elimination is allowed. In order to examine the stereochemistry of this elimination, both *meso*-2,3-bis(phenylthio)butane (**1b**) and the (±) isomer (**1c**) have been synthesized.

Preparation and Pyrolysis of 1b and 1c. A mixture of **1b** and **1c** is obtained from the reaction of sodium thiophenoxide with a mixture of *meso*- and (±)-2,3-dichlorobutane in dimethylformamide. The diastereomers are separated by column chromatography on silica gel.

Analysis of the nmr spectra of **1b** and **1c** permits a tentative assignment of structure to the diastereomers. Both **1b** and **1c** show complex $X_3AA'X'_3$ multiplets typical of 2,3-disubstituted butanes.[4] The equations given by Anet[4b] were used to prepare computer simulated spectra which were compared with experimental spectra giving $J_{AA'} = 2.5$ cps for one diastereomer and $J_{AA'} = 5.5$ cps for the other. The diastereomer with the larger $J_{AA'}$ was assigned the meso structure (**1b**) while that with the smaller coupling was assumed to be the racemic mixture (**1c**). It is assumed that the most stable conformation of each isomer is that with the phenylthio groups trans to one another. If this is true, the Karplus relationship permits assignment of structure.

To remove any ambiguity in structural assignment, **1c** was oxidized with hydrogen peroxide in glacial acetic acid to the disulfone (±)-2,3-bis(phenylsulfonyl)-butane (**2c**). The disulfone was partially resolved by a kinetic method.[5] The kinetic resolution involves the base-catalyzed elimination of phenylsulfinic acid from **2c** using the chiral base (*R*)-α-phenylethylamine (eq 2). When this elimination is carried to *ca.* 50% completion on **2c**, recovered **2c** shows optical activity ($[\alpha]^{25}\text{D}$ −109.5°). When the same experiment is repeated using (*S*)-α-phenylethylamine, recovered **2c** shows $[\alpha]^{25}\text{D}$ +36°. When the same elimination was repeated with the disulfone from oxidation of **1b** (*meso*-1,2-bis(phenylsulfonyl)butane (**2b**), recovered **2b** showed no optical activity.



The results of the pyrolysis of **1b** and **1c** in a sealed Pyrex bomb at 350°, given in Table I, show that both

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[1] E. V. Bell and G. M. Bennett, *J. Chem. Soc.*, 3190 (1928).

[2] F. W. Stacey and J. F. Harris, Jr., *Org. React.*, **13**, 150 (1963).

[3] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

[4] (a) A. A. Bothner-By and C. Naar-Colin, *J. Amer. Chem. Soc.*, **84**, 743 (1962); (b) F. A. L. Anet, *ibid.*, **84**, 747 (1962).

[5] P. B. Shevlin and J. L. Greene, Jr., *Chem. Commun.*, 874 (1972).

Table I. Products in Pyrolysis and Photolysis of 1,2-Bis(phenylthio)ethanes

Reactant	Conditions	% PhSSPh	% PhSH	% C_2H_4	% butenes	% composition of butenes *trans*-1	*cis*-2	1-
1a	*a*	40	12	13				
1a	*b*	51	21	40				
1b	*a*	19	34		24	43	35	22
1c	*a*	12	42		23	44	34	22
PhSSPh + *trans*-2-butene	*a*		29		48	45	31	24
1b	*c*				39	81	19	0
1c	*c*				38	32	68	0
1b	*d*				7	74	26	0
1c	*d*				5	30	70	0
1b	*b*	42	18		25	71	29	0
1c	*b*	44	24		31	62	38	0

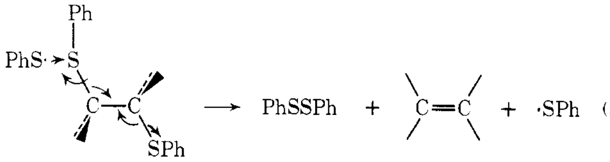
[a] Pyrolysis in a 60-ml Pyrex bomb at 350°. [b] Photolysis in N_2 stream. [c] Pyrolysis through a heated column at 360°. [d] Pyrolysis in a stream of N_2 at 350°.

diasteromers yield essentially the same mixture of butenes. This is not an unexpected result as thiophenoxy radicals, present at these temperatures, would be expected to effect isomerization of the butenes. Indeed, it was found that *trans*-2-butene is isomerized in the presence of diphenyl disulfide at 350° (Table I).

In order to minimize isomerization of the butenes the pyrolysis was carried out by passing the bis disulfides through a column at 360° under vacuum. It was assumed that, under these conditions, the butenes would be distilled from the column before appreciable isomerization could occur. The results of these reactions (Table I) show that **1b** gives mainly *trans*-2-butene while *cis*-2-butene predominates in the pyrolysis of **1c**. Thus, any mechanism proposed for this elimination must rationalize the predominance of trans elimination.

A similar stereochemical result is obtained when **1b** and **1c** are swept from a flask at 350° by a stream of nitrogen (Table I). When oxygen rather than nitrogen is used, the butene yield is reduced by 80%, indicating the free radical nature of this elimination.

Equation 3 shows a step in a hypothetical chain mechanism which would account for the stereochemistry of the elimination. A requisite for this mechanism is initiation by thiophenoxy radicals. Diphenyl disulfide, at elevated temperatures, should serve as a source of thiophenoxy radicals.[6] However, when **1b** and diphenyl disulfide are heated at 190° in decalin solution, only traces of the 2-butenes are observed. The presence of thiophenoxy radicals under these conditions is indicated by the formation of thiophenol. In a related experiment, AIBN-initiated production of thiophenoxy radicals in a thiophenol solution of **1b** gave no 2-butenes. Thus, a chain mechanism initiated by thiophenoxy radicals is ruled out. A displacement by thiophenoxide anion, in a process similar to that shown in eq 3, is precluded by the fact that no 2-butenes are formed when **1b** is heated with sodium thiophenoxide in thiophenol.



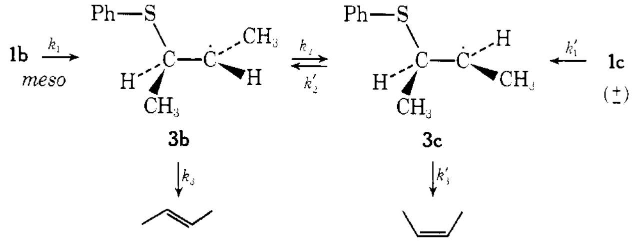
(3)

Photolysis of 1b and 1c. The results of photolysis of decalin solutions of **1b** and **1c** are shown in Table I. Both diastereomers yield a predominance of *trans*-2-butene when photolyzed under conditions such that the butenes are swept from the reactor by a nitrogen stream.

Discussion

The most plausible pathway for both the thermal and photochemical eliminations appears to be that shown in Scheme I. The stereospecificity of the pyrolysis demands that collapse of **3b** and **3c** to the butenes be more rapid than their interconversion ($k_3 > k_2$ and $k_3' > k_2'$). The observed reversal of stereochemistry in the photolysis of **1c** is most probably a result of the excess energy available in the photochemical process. If **3b** is more stable than **3c** ($k_2' > k_2$), it is expected to predominate if sufficient energy is available.

Scheme I



$$k_3 > k_2; k_3' > k_2'; k_2' > k_2$$

The ratios of rate constants proposed in Scheme I require that the stereospecificity of the pyrolytic elimination decrease as the temperature increases. This reduction in stereospecificity with increasing temperature is shown in Table II.

It is possible to obtain the values of k_2/k_3 and k_2'/k_3' from the observed ratios of *cis*- and *trans*-2-butene.

Table II. Butene Ratios as a Function of Temperature in the Pyrolysis of **1b** and **1c**

Reactant	*T*, °C	% *trans*-2-butene	% *cis*-2-butene
1b	301	89	11
1b	326	85	15
1b	360	81	19
1b	402	73	27
1c	326	26	74
1c	360	32	68

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[6] G. Leandri and A. Tundo, *Ann. Chim.* (*Rome*), **44**, 63 (1954); *Chem. Abstr.*, **49**, 4563*d* (1955).

The steady-state concentration of **3b** is

$$[\mathbf{3b}] = \frac{k_1[\mathbf{1b}] + k_2'[\mathbf{3c}]}{k_2 + k_3}$$

If A equals the ratio of *trans*-2-butene to *cis*-2-butene formed in the pyrolysis of pure **1c** ([**1b**] = 0), then

$$A = \frac{k_2'}{k_3'}\frac{k_3}{(k_2 + k_3)}$$

or

$$\frac{k_2}{k_3}A + A = \frac{k_2'}{k_3'} \tag{4}$$

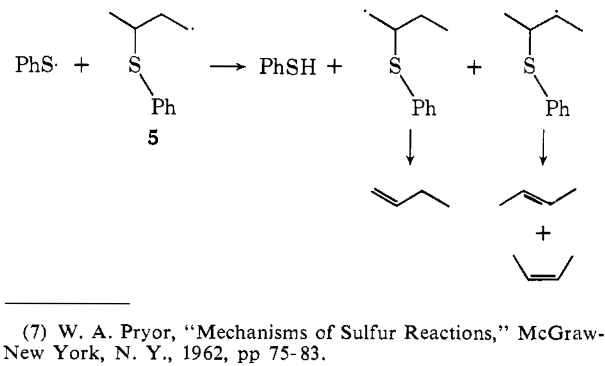
If B is the ratio of *cis*-2-butene to *trans*-2-butene when [**1c**] = 0, a similar steady-state expression for **3c** leads to

$$\frac{k_2'}{k_3'}B + B = \frac{k_2}{k_3} \tag{5}$$

Equations 4 and 5 may be solved simultaneously for k_2'/k_3' and k_2/k_3. At 360° $k_2/k_3 = 0.39$ and $k_2'/k_3' = 0.65$.

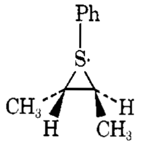
In Scheme I the intermediacy of β-phenylthio radicals (**3b** and **3c**) is proposed. Such radicals have been implicated as intermediates in the free radical addition of thiophenol to alkenes.[7] In free radical additions, the β-phenylthio radical abstracts a hydrogen from another molecule of thiophenol to continue the chain reaction. In the absence of readily abstractable hydrogens and at the elevated temperatures employed in this study, the β-phenylthio radical loses a phenylthio radical giving an alkene. This loss of phenylthio radical is the reverse of the first step in the free radical addition of thiophenol to 2-butene. It has been shown that recovered *trans*-2-butene is isomerized in the free radical addition of thiophenol.[8] This observation indicates that addition of phenylthio radical to 2-butene is reversible. Reversible additions of other thiyl radicals have also been noted.[9]

If β-phenylthio radicals are intermediates in this reaction, it should be possible to observe alkene formation from such radicals generated in a different manner. When 2-(phenylthio)butane (**5**) is treated with diphenyl disulfide in refluxing decalin, 1-butene and *cis*- and *trans*-2-butene are produced. The butenes most probably result from the decomposition of an intermediate β-phenylthio radical formed by hydrogen abstraction on **5** (eq 6). Thus, it appears likely that **3b** and **3c** will lose a phenylthio radical to give the butenes. This interesting free radical elimination is currently under study in this laboratory.

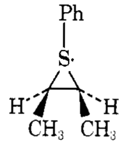


(6)

In the preceding discussion **3b** and **3c** have been written as open-chain radicals rather than bridged sulfur radicals (**4b** and **4c**). Bridged sulfur radicals have been postulated as intermediates in the free radical addition of methyl mercaptan to alkenes.[10] However, we do not believe that the evidence presented in our work requires the intermediacy of bridged radicals, although they are a distinct possibility. The data require only that the interconversion of **3b** and **3c** be slower than their decomposition to the butenes.

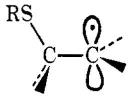


4b



4c

Studies of the free radical addition of thiophenol to 1-methylcyclohexene[11] and of *p*-thiocresol to norbornadiene[12] do not show evidence of sulfur bridging in the β-arylthio radical intermediates. Recent esr studies[13,14] of β-alkythio radicals (**6**, R = alkyl) have shown that the most stable conformation is a classical radical in which the carbon–sulfur bond is eclipsing the adjacent p orbital (**6**).



6

Thus, while there is compelling evidence that the ground state of β-phenylthio radicals does not involve sulfur bridging, such bridging may be important in the transition state leading to these radicals. A bridged species may be involved in the transition state for initial homolysis of the carbon–sulfur bond in **1**. This bridging should be particularly important if the homolysis is assisted by the second sulfur. If such anchimeric assistance is operative, it is possible that some or all of the butenes arise from decomposition of **4b** and **4c** before opening to the more stable **3b** and **3c** can occur.

Anchimeric assistance by sulfur has been proposed in the abstraction of hydrogens β to sulfur[15] and in the homolysis of aromatic peresters.[16] Experiments designed to test the intermediacy of bridged radicals in this work are in progress.

Experimental Section

General. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Melting points are corrected and were determined in a Mel-Temp apparatus (Laboratory Devices, Cambridge, Mass.). Infrared spectra were taken on a Perkin-Elmer 621 spectrometer. Nmr spectra were obtained with the Varian HA-60 spectrometer; chemical shifts are reported in ppm downfield from internal tetramethylsilane. Optical rotations were observed in a J. and J. Fric (Prague) polarimeter. Gaseous product

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[7] W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill, New York, N. Y., 1962, pp 75-83.

[8] R. H. Pallen and C. Sivertz, *Can. J. Chem.*, **35**, 723 (1957).

[9] C. Walling and W. Helmreich, *J. Amer. Chem. Soc.*, **81**, 1144 (1959).

[10] P. D. Readio and P. S. Skell, *J. Org. Chem.*, **31**, 759 (1966); P. S. Skell and R. G. Allen, *J. Amer. Chem. Soc.*, **82**, 1511 (1960).

[11] F. G. Bordwell and W. A. Hewett, *ibid.*, **79**, 3493 (1957).

[12] S. J. Cristol, G. D. Brindell, and J. A. Reeder, *ibid.*, **80**, 635 (1958).

[13] P. J. Krusic and J. K. Kochi, *ibid.*, **93**, 846 (1971).

[14] T. Kawamura, M. Ushio, T. Fujimoto, and T. Yonezawa, *ibid.*, **93**, 908 (1971).

[15] W. A. Pryor and K. Smith, *ibid.*, **92**, 2731 (1970).

[16] T. H. Fisher and J. C. Martin, *ibid.*, **88**, 3382 (1966).

distributions were determined by gas chromatography using a 20 ft × 0.25 in. 20% dimethylsulfolane on Firebrick column at 25°. All other products were determined by gc using a 20 ft × 0.25 in. 20% SE-30 on a 60–80 Chromosorb W column.

meso- **and (±)-2,3-Bis(phenylthio)butane (1b and 1c).** Thiophenol (82.5 g, 0.75 mol), dimethylformamide (300 ml), and sodium hydroxide (30.0 g of 98.6% NaOH; 0.74 mol) were stirred together under nitrogen until the solution became homogeneous. The solution was cooled to room temperature and treated with 2,3-dichlorobutane (43.0 g, 0.34 mol of a *meso, dl* mixture). Stirring was continued at room temperature under nitrogen for 48 hr before the precipitated NaCl was collected on a filter and the clear filtrate transferred to a separatory funnel containing water (700 ml). The filtrate was extracted with ether (400, 300, 200 ml). The ether extracts were combined and washed successively with 400-ml portions of 2% NaOH, 2% HCl, and water. The extract was dried (Drierite) and ether removed on a rotary evaporator to leave 60.0 g (65%) of crude product which was distilled through a 10-in. Vigreux column to yield 52 g (56%) of a product boiling at 157–163° (0.2 mm). Thin layer chromatography revealed this product to be a mixture of two substances: spot I, 25%; spot II, 75%.

The distilled product was chromatographed on a silica gel column eluted with *n*-heptane to give two pure forms of 2,3-bis(phenylthio)-butane.

Fraction I (subsequently shown to be the (±) form of 2,3-bis-(phenylthio)butane: nmr (CCl_4) 1.30 (d, 6, J_{AX} = 6.95 Hz), 3.32 (m, 2, J_{AX} = 6.95, $J_{AA'}$ = 2.5, $J_{AX'}$ = 0.05 Hz), 7.10 (s, 10).

Anal. Calcd for $C_{16}H_{18}S_2$: C, 70.03; H, 6.61; S, 23.37. Found: C, 70.37; H, 6.71; S, 23.09.

Fraction II (subsequently shown to be the meso form of 2,3-bis(phenylthio)butane): nmr (CCl_4) 1.35 (d, 6, J_{AX} = 6.70 Hz), 3.26 (m, 2, J_{AX} = 6.7, $J_{AA'}$ = 5.5, $J_{AX'}$ = −0.10 Hz), 7.17 (m, 10).

Anal. Calcd for $C_{16}H_{18}S_2$: C, 70.03; H, 6.61; S, 23.37. Found: C, 70.16; H, 6.69; S, 23.21.

meso- **and (±)-2,3-Bis(phenylsulfonyl)butane (2b and 2c).** 2,3-Bis(phenylthio)butane (8.3 g; 0.03 mol of unresolved meso and (±) mixture) was dissolved in glacial acetic acid (50 ml). Hydrogen peroxide (14 g; 0.12 mol of 30% H_2O_2) was added and the resulting mixture was heated over boiling water with stirring for 1.5 hr. The cooled solution was poured with vigorous stirring into ice–water (600 ml). The white precipitate was collected, washed free of acid with water, and air-dried to a constant weight of 7.8 g (76%), mp 119–146°. Thin layer chromatography revealed the crude product to be a mixture of two substances which were separated on a silica gel column eluted with dichloromethane to give two pure substances.

Fraction I ((±)-2,3-bis(phenylsulfonyl)butane) (**2c**): mp 152–154°; nmr ($CDCl_3$) 1.43 (d, 6, *J* = 7.0 Hz), 3.88 (q, 2, *J* = 7.0 Hz), 7.6 (m, 10).

Anal. Calcd for $C_{16}H_{18}O_4S_2$: C, 56.78; H, 5.36; S, 18.95. Found: C, 56.96; H, 5.41; S, 18.76.

Fraction II (*meso*-2,3-bis(phenylsulfonyl)butane) (**2b**): mp 151–153°; nmr ($CDCl_3$) 1.55 (d, 6, *J* = 7.0 Hz), 3.66 (m, 2), 7.8 (m, 10).

Anal. Calcd for $C_{16}H_{18}O_4S_2$: C, 56.78; H, 5.36; S, 18.95. Found: C, 56.63; H, 5.48; S, 18.85.

Oxidation of a small sample of pure **1c** by the above procedure gave material which was identical with **2c**.

Partial Kinetic Resolution of 2c. A solution of **2c** (1.015 g, 3 mmol) and (*R*)-α-phenylethylamine (0.363 g, 3 mmol) was refluxed in xylene (10 ml) while being protected from atmospheric CO_2 and H_2O until tlc revealed that *ca.* 50% of **2c** had reacted (5 hr). The xylene was removed *in vacuo* and the residue recrystallized from aqueous ethanol to give 0.239 g of recovered **2c**, mp 151–154°. Measurement of the optical rotation of the recovered **2c** gave $[\alpha]^{25}D$ −109.5° (2.5% in CH_2Cl_2).

Repetition of the above experiment using (*S*)-α-phenylethylamine gave recovered **2c** with $[\alpha]^{25}D$ +36.0° (2.5% in CH_2Cl_2).

When the above experiment was repeated with **2b** and (*R*)-α-phenylethylamine, the recovered **2b** showed no optical activity.

Pyrolysis of 1 in a Closed Vessel. The bis disulfide (50 mg) placed in a 60-ml Pyrex bulb was degassed and sealed under vacuum. The bulb was then immersed in a molten KNO_3–$NaNO_2$ bath at 350°. The pyrolysis was carried out for 12 hr during which time the temperature of the bath was kept at 350 ± 2°. The Pyrex bulbs were opened on a vacuum line and the products analyzed by gas chromatography. Product distributions are given in Table I.

Pyrolysis of 1b and 1c in a Heated Column. The bis disulfide (50 mg) was vaporized at 150° under vacuum into a Pyrex column (650 × 5 mm) which was heated (300–400°) with nichrome wire. The temperature was measured by means of an iron–constantan thermocouple placed at the center of the column. The products were collected in traps at −78 and −195° and analyzed by gas chromatography. The ratios of butenes are given in Table II.

Pyrolysis of 1b and 1c in a Nitrogen Stream. The bis disulfide (50 mg) was heated at 350° under a stream of N_2 (30 ml/min). The volatile products were swept into a trap at −195° and analyzed by gas chromatography.

Photolysis of 1. Solutions of the bis disulfide (50 mg) in decalin (5 ml) were placed in a Vycor tube and photolyzed with a Hanovia 654A36 medium-pressure Hg lamp for 1 hr. During photolysis the solution was swept with a stream of N_2 (30 ml/min). The volatile products were trapped at −195° and analyzed by gas chromatography.