Sulphines. Part V.[1] Configurational Assignment and Interconversion Barriers for *syn*- and *anti*-Isomers of Aromatic Sulphines

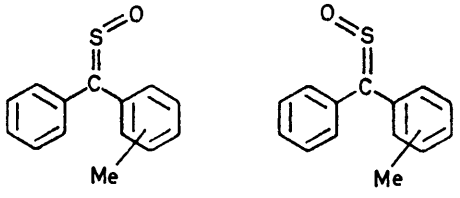
By **Bianca F. Bonini, Lodovico Lunazzi,* Gaetano Maccagnani,* and Germana Mazzanti,** Laboratorio C.N.R. dei Composti del Carbonio contenenti eteroatomi, Istituto di Chimica Organica dell'Università, Viale Risorgimento, 4, 40136-Bologna, Italy

Unambiguous configurational assignment of *syn* and *anti*-isomers of methyl-substituted aromatic sulphines has been achieved by means of: (a) intermolecular hydrogen bonding with weak acids; (b) intramolecular association in 2-hydroxy-(2'-methyl)thiobenzophenone *S*-oxide; (c) aromatic solvent induced shift measurements; and (d) carbon-13 n.m.r. spectra. The thermodynamic and kinetic parameters for the thermal interconversion of the isomers have also been determined. These values are discussed in terms of possible isomerisation mechanisms.

SULPHINES (thione *S*-oxides) are readily available from thiones by oxidation with peroxy-acids.[2] They exist as *syn*- and *anti*-isomers,[3] and the bent nature of the thiocarbonyl oxide group is well established ($\widehat{CSO} = 109{\cdot}4°$).[4]

Additional evidence for the existence of geometrical isomers of sulphines, and their configurational assignment, has been obtained from dithiocarboxylic ester oxides [5] and from diaryl sulphines.[6]

Zwanenburg and his co-workers [5,7] based their assignment on the assumption that the SO group causes a downfield shift of the neighbouring aromatic protons, by analogy with the behaviour of nitrones [8] where the downfield shift is assumed to derive from the anisotropic effect of the NO group. These conclusions are an extrapolation of the downfield shift of the *ortho*-protons in aromatic carbonyl derivatives, interpreted [9,10] as being due to the anisotropy of the CO group. However, a re-interpretation [11] showed that, depending on the molecular geometry, an upfield instead of a downfield shift may occur: [12] this has been experimentally verified in at least one case.[13] Since the positions of the NO and SO groups in aromatic nitrones and sulphines, with respect to the *ortho*-hydrogens, are different from that of CO in aromatic ketones, the reliability of such an analogy for



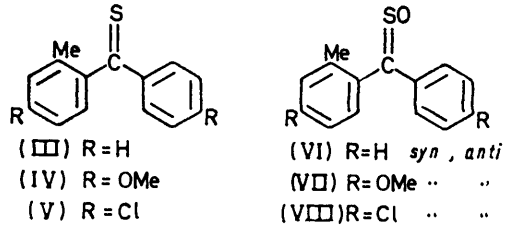
(I) *syn* (II) *anti*

assigning the structures of isomeric sulphines may be questionable, even though the results obtained in such a way were internally consistent.[7] Moreover, because of the complex spectral patterns of the aromatic protons, the method is not well suited for the configurational assignment of sulphines having substituents in positions other than *para*.

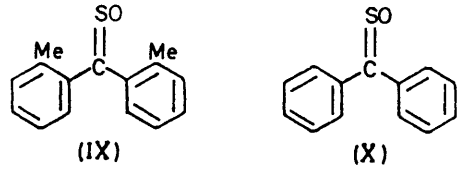
This paper describes an unambiguous assignment of the *syn*- (I) and *anti*- (II) sulphines and the determination of the energy barrier required for the isomerisation around a C=S double bond.

RESULTS AND DISCUSSION

In order to isolate both isomers of some aromatic sulphines we prepared, by peroxy-acid oxidation [2] of the corresponding thioketones (III)—(V), the *ortho*-methyl derivatives (VI)—(VIII). These compounds were thought to be suitable since the n.m.r. spectrum of the



(III) R=H (VI) R=H *syn*, *anti*
(IV) R=OMe (VII) R=OMe " "
(V) R=Cl (VIII) R=Cl " "



(IX) (X)

analogous symmetric derivative, (2,2'-dimethyl)thiobenzophenone *S*-oxide (IX), showed a chemical shift difference large enough (0·45 p.p.m.) to allow a clear distinction between the two methyl groups.

All the isomers were isolated through column chromato-

[1] Part IV, B. Bonini, G. Maccagnani, A. Wagenaar, L. Thijs, and B. Zwanenburg, *J.C.S. Perkin I*, 1972, 2490.
[2] J. Strating, L. Thijs, and B. Zwanenburg, *Tetrahedron Letters*, 1966, 65; B. Zwanenburg, L. Thijs, and J. Strating, *Rec. Trav. Chim.*, 1967, **86**, 577.
[3] J. F. King and T. Durst, *J. Amer. Chem. Soc.*, 1963, **65**, 2676.
[4] R. B. Bates and G. A. Wolfe, *J. Amer. Chem. Soc.*, 1968, **90**, 6854.
[5] B. Zwanenburg, L. Thijs, and J. Strating, *Rec. Trav. Chim.*, 1971, **90**, 614.
[6] S. Ghersetti, L. Lunazzi, G. Maccagnani, and A. Mangini, *Chem. Comm.*, 1969, 834; B. Bonini, L. Lunazzi, G. Maccagnani, and G. Mazzanti, *Quart. Reports Sulphur Chem.*, 1970, **5**, 210.
[7] B. Zwanenburg, L. Thijs, and A. Tangerman, *Tetrahedron*, 1971, **27**, 1731.
[8] K. Koyano and H. Suzuki, *Tetrahedron Letters*, 1968, 1859.
[9] L. M. Jackman and S. Sternhell, 'Applications of N.M.R. spectroscopy in Organic Chemistry,' Pergamon, Oxford, 1969, p. 88.
[10] J. A. Pople, *J. Chem. Phys.*, 1962, **37**, 60.
[11] J. W. ApSimon, W. G. Craig, P. V. De Marco, P. W. Mathieson, A. K. G. Nasser, I. Saunders, and W. B. Whalley, *Chem. Comm.*, 1966, 754; J. W. ApSimon, P. V. De Marco, D. W. Mathieson, W. G. Craig, A. Karim, L. Saunders, and W. B. Whalley, *Tetrahedron*, 1970, **26**, 119.
[12] G. J. Karbatsos, G. C. Sonnichsen, N. Hsi, and D. J. Fenoglio, *J. Amer. Chem. Soc.*, 1967, **89**, 5067.
[13] K. I. Dahlqvist and A. B. Hörnfeldt, *Tetrahedron Letters*, 1971, 3837.

graphy. The difference between the methyl shifts of each pair of isomers was not as large as in the symmetric derivative (IX), which probably experiences greater steric hindrance. However, it was possible to observe for each pair of isomers, that one had the methyl resonance closer to that of the corresponding thioketone (Table 1). The isomers having the higher field methyl signals (which are similar to the values in the corresponding thioketones) were tentatively assigned the Me-*anti* configuration, while those with the lower field methyl signals were given the Me-*syn* configuration. In the case of (VI), the isomer with m.p. 60° is therefore

TABLE 1

Methyl chemical shifts for thioketones and sulphines

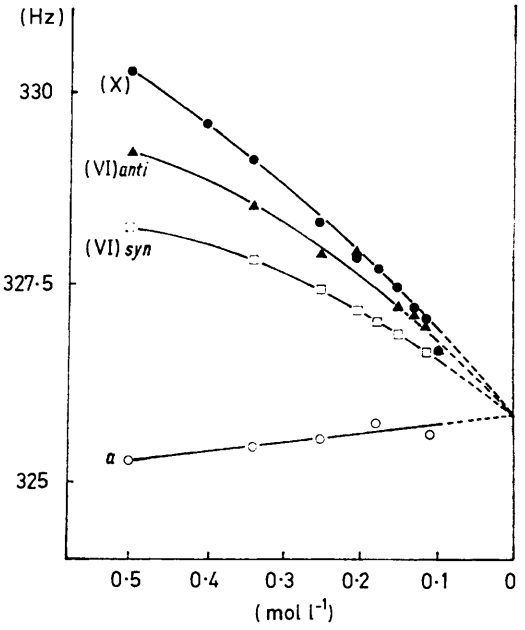
Thioketones	M.p. or b.p. (mmHg)	δ_{Me} (p.p.m.)	Sulphines	M.p.	δ_{Me} (p.p.m.)
(III)	44—45°	2·08	(VI) *anti*	59—60°	2·14
			(VI) *syn*	81—82°	2·24
(IV)	77—78°	2·05	(VII) *anti*	65—66°	2·06
			(VII) *syn*	86—87°	2·18
(V)	130—132° (2)	2·05	(VIII) *anti*	77—78°	2·13
			(VIII) *syn*	103—104°	2·21

assigned as *anti* and that which melts at 82° as the *syn*-isomer (Table 1).

To check the correctness of the assignments, other investigations were performed on the geometrical isomers of (VI).

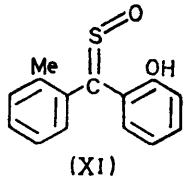
(i) Since the hydrogen bond between a weak acid and a weak base is known to be affected by the steric hindrance of the base itself [14] we measured the SH chemical shift in the binary system thiophenol–sulphine (ratio 1 : 1) at various concentrations in carbon tetrachloride. If thiophenol alone is dissolved in CCl_4, the lower its concentration the greater is the absolute value of its chemical shift (measured in Hz from tetramethylsilane at 100 MHz), since association with the solvent becomes more important than self-association. On the other hand, when sulphine is also present, the lower the concentration of the binary system thiophenol–sulphine, the lower is the SH chemical shift since, as the sulphine is a stronger base than CCl_4, the association with the oxygen of the CSO group is always more efficient than that with the solvent. Obviously the extrapolation to infinite dilution gives the same value for the SH shift (325·75 Hz at 100 MHz) irrespective of the system examined (Figure). A more important point however is that the association depends on the sulphine employed and, whatever the concentration of the binary system, association is greater for the unsubstituted diphenyl sulphine (X) than for the isomers (VI), m.p. 60° and 82°. The results for the unsubstituted sulphine, shown in the Figure, suggest that the greater the steric hindrance experienced by the SO group, the lower is the association shift of the thiophenol. Accordingly the isomer with m.p. 60°, which induces a larger association shift on the thiophenol, is expected to have the *anti* configuration and the isomer with m.p. 82° the *syn* configuration. This conclusion agrees with that based upon the analogies of the methyl chemical shifts.

(ii) In a sulphine such as 2-hydroxy-(2′-methyl)thiobenzophenone *S*-oxide (XI) the existence of an intramolecular hydrogen bond between the C=SO and OH groups should allow an unambiguous assignment of the chemical shift of a methyl group *anti* to the CSO group.



Chemical shifts (in Hz downfield from Me_4Si) of the SH proton of thiophenol in a 1 : 1 molar ratio with sulphines (X), (VI) *anti*, and (VI) *syn* respectively as function of the concentration of the binary mixture in CCl_4. Curve (*a*) represents the shifts of thiophenol in the same solvent.

In this case we were able to detect and isolate only one of the two possible isomers, to which structure (XI) was assigned on the grounds that intramolecular hydrogen bonding would stabilise the Me-*anti* configuration with

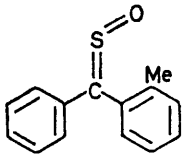


(XI)

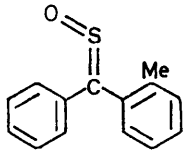
respect to the *syn* enough to make the probability of obtaining the other isomer almost negligible. The existence of structure (XI) was proved by the detection in the n.m.r. and i.r. spectra of a strong intramolecular hydrogen bond. The OH chemical shift (in CCl_4) was found to be 8·55 p.p.m. [*cf.* 6·30 and 6·32 for intermolecularly hydrogen bonded phenol (1 : 1 ratio) with the sulphines (VI), m.p.s 82° and 60° respectively]. Such a downfield shift is typical of an intramolecular hydrogen bonded OH and this confirms that the CH_3 has to be *anti* to the SO group. The i.r. spectra are also indicative of an intramolecular association since ν_{OH} is *ca.* 3000 cm^{-1} in C_2Cl_4 irrespective of the concentration of the sulphine (XI).

[14] L. Lunazzi and F. Taddei, *Spectrochim. Acta*, 1969, **24***A*, 1479.

(iii) The third approach used aromatic solvent induced shift (ASIS) measurements.[15] In the methyl groups of the two isomers of (VI) an upfield shift was observed in benzene solution with respect to the values in CCl_4; with the higher melting derivative the amount is 0·11 p.p.m. while with the lower melting compound it is 0·33 p.p.m. Since it has been established that benzene associates with the positive end of a dipole [15] (in this case the sulphur atom of the SO group), the more affected methyl group should be that of the *anti*-derivative (VI). The benzene will collide preferentially with sulphur from the left hand side in *syn*-(VI) and from the right hand side in *anti*-(VI),[16] and in the latter case the methyl group will experience much larger ASIS effect.



(VI) *syn*

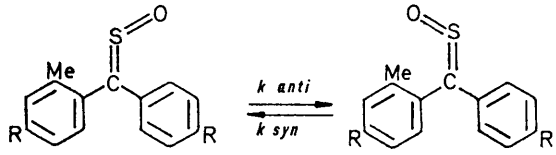


(VI) *anti*

(iv) The fourth approach to the assignment used ^{13}C n.m.r. spectra. The shift of the methyl carbon itself does not give any structural information since the difference of the $\delta_{^{13}C}$ values lies within the range of experimental errors. On the other hand the chemical shifts of ^{13}C are mainly dependent on changes of the immediate electronic environment of carbon; [17] therefore through-space effects, such as those experienced by the *ortho*-methyl groups in these compounds, are less effective than in proton resonance. Moreover, the methyl carbon is more distant from the CS or CSO group than the methyl protons and this also contributes to make $\delta_{^{13}CH_3}$ almost insensitive to the structural arrangement.

The chemical shift of carbonyl carbon atoms in aromatic ketones is strongly affected by the presence of an *ortho*-substituent.[18] This can be rationalised on the grounds that conjugation with the aromatic rings shifts the $\delta_{^{13}CO}$ values upfield with respect to aliphatic or alicyclic carbonyls.[19] Accordingly substituents in an *ortho*-position displace the shifts of carbonyl carbons downfield with respect to unsubstituted derivatives, because they disrupt the coplanarity of the CO group with the benzene ring, thus reducing the possibility of conjugation.[18] This is also observed in thioketones and we think it can be possibly extended to the CSO group. Therefore in the case of (VI) the isomer which experiences a greater steric hindrance (the Me-*syn*) is expected to have $\delta_{C(SO)}$ at lower field than the less hindered Me-*anti* isomer if the reasonable assumption is made that the conformation of the unsubstituted phenyl ring is not affected by the configuration of the CSO group. On this basis, the sulphine with m.p. 82° ($\delta_{C(SO)}$ 193·8 p.p.m. downfield from Me_4Si) is the *syn*- and the sulphine with m.p. 60° ($\delta_{C(SO)}$ 185·8 p.p.m.) the *anti*-isomer, in agreement with the assignment based on the criteria above.

Having established the configuration of the pairs of geometrical isomers of (VI)—(VIII), we studied the *syn–anti*-isomerisation rate. These sulphines can be thermally isomerised without appreciable decomposition.



The isomerisation rate has been studied at temperatures between 110 and 180°, the kinetics being followed by n.m.r. All the reactions under investigation reached thermodynamic equilibrium, and the equilibrium constant was almost independent of temperature in the range examined. Reproducible values of the thermodynamic as well as kinetic parameters could be obtained either studying the *anti–syn*- or the *syn–anti*-isomerisation.

The results fit a first-order rate equation for reversible processes; [20] the rate constants appear to be invariant over a fifty-fold variation of initial concentration of sulphine (Table 2). Intermolecular pathways can thus be excluded. On the other hand the rate constants are strongly affected by the presence of atmospheric oxygen; its influence, however, is undetectable at pressures below 10^{-2} mmHg. For this reason the kinetic measurements were made in sealed n.m.r. tubes under high vacuum (10^{-5} mmHg), after having carefully degassed the solutions.

TABLE 2

Influence of sulphine concentration on isomerisation rate [sulphine (VI) in benzene at 156 °C]

Concentration (mol l^{-1})	$k_{syn} \times 10^5$ (s^{-1})
0·01	14 ± 2
0·05	12 ± 2
0·1	11 ± 2
0·5	15 ± 2

The kinetic and thermodynamic parameters and the data on the solvent effect for the thermal isomerisation of sulphines (VI)—(VIII) are reported in Table 3.

At equilibrium the less crowded *anti* forms predominate over the *syn* especially in the case of the *para*-methoxy-substituted sulphine (VII).*

The rather high values of the activation parameters $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ indicate high configurational stability of sulphines, provided that the presence of oxygen is

* It should be noted that the direct oxidation of the parent thioketones gives a *syn*/*anti* ratio close to one [21] thus indicating that kinetic control prevails in the peroxy-acid oxidation.

[15] P. Laszlo in ' Progress in N.M.R. Spectroscopy,' eds. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, vol. 3, Pergamon, Oxford, 1967.

[16] A. Tangerman and B. Zwanenburg, *Tetrahedron Letters*, 1973, 79.

[17] B. V. Cheney and D. M. Grant, *J. Amer. Chem. Soc.*, 1967, **89**, 5319.

[18] K. S. Dhami and J. B. Stothers, *Canad. J. Chem.*, 1965, **43**, 479; K. S. Dhami, *ibid.*, p. 499.

[19] C. E. Maciel, *J. Chem. Phys.*, 1965, **42**, 2746; D. H. Marr and J. H. Stothers, *Canad. J. Chem.*, 1967, **45**, 226.

[20] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanism,' 2nd edn., Wiley, New York, 1961, p. 186.

[21] Unpublished results from this laboratory.

avoided. If a comparison is possible it should be noted, however, that these values are considerably lower than those for the racemisation of sulphoxides.[22]

In sulphines, as in imines,[23] there are two possible methods for the *syn–anti*-isomerisation: rotation around the C=S bond axis, and inversion at the sulphur atom.

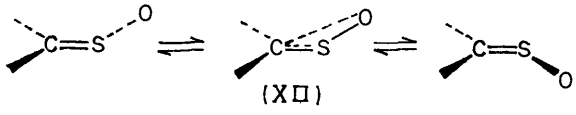
CNDO (complete neglect of differential overlap) calculations on a model sulphine predict [24] activation energies for the isomerisation which agree with our experimental findings; unfortunately the difference in the computed energies when a rotation (24 kcal) or an inversion (26 kcal) mechanism is assumed does not allow a clear discrimination between the two processes on theoretical grounds, although the rotation mechanism seems favoured.

The data in our hands do not allow a definite conclusion concerning the interconversion mechanism of sulphines to be reached but some hypotheses can be put forward.

The computed [24] pathways for both inversion and rotation of model sulphines predicted a small reduction in polarity for both mechanisms in going from the reactants to the transition states. This finding is in agreement with the low sensitivity of our processes to change of solvent and substituent. Also on this basis it is difficult to discriminate between the two mechanisms. Nevertheless a mechanism of isomerisation through inversion at the sulphur atom seems most improbable to us since one would expect for such a process a negligible value of the activation entropy.[22,23] Furthermore the catalytic effect of the oxygen can be better explained with the occurrence of a bond breaking mechanism.

A mechanism of rotation around the C=S bond seems more satisfactory. However, the usual picture of this mechanism involving charge separation cannot be easily accepted, owing to the lack of appreciable influence of solvent polarity on the activation parameters and the negligible effect of substituents in the *para*-position (Table 3).

The high negative entropy of activation which corresponds to a low frequency factor (Table 3), and is unusual for a geometric isomerisation,[23] could be better explained through the intervention, during the rotation around the carbon–sulphur bond, of a highly rigid transition state like (XII).



(XII)

This hypothesis is in agreement with recent findings [25] about the mechanism of oxidation of sulphines to ketones and with the proposed mechanism [26] of photodesulphurisation of sulphines.

An alternative mechanism could involve a diradical species. This would explain the sensitivity of the reaction to the presence of oxygen and be consistent with the absence of solvent and substituent effects.*

TABLE 3

Kinetic and thermodynamic parameters and solvent effect on the thermal isomerisation of sulphines (VI)—(VIII)

Sulphine	Solvent	Temperature (°C)	$K_{anti/syn}$	$k_{syn} \times 10^5$ * (s^{-1})	$\Delta G^{\ddagger}$ (kcal mol^{-1})	E_a (kcal mol^{-1})	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (e.u.)	log A (A = frequency factor)
(VI)	C_6H_6	110	3·3	0·43	32·0	23·0 ± 0·7	22·2 ± 0·7	−26·0 ± 1·7	7·7 ± 0·4
		126	3·3	1·1	32·6				
		156	3·3	11·0	33·2				
		180	3·3	41·0	33·9				
(VI)	CD_3CN	126	2·5	1·5	32·4	21·5 ± 1·6	20·8 ± 1·6	−29·0 ± 4·0	6·9 ± 0·8
		156	2·4	7·1	33·6				
		180	2·0	39·5	34·0				
(VI)	$PhNO_2$	156	1·5	5·5	33·7				
(VII)	C_6H_6	126	5·3	4·1	31·6	21·0 ± 2·5	20·0 ± 3·0	−29·0 ± 6·0	7·0 ± 1·4
		156	5·5	14·4	32·9				
		180	4·9	99·4	33·1				
(VIII)	C_6H_6	126	2·6	2·17	32·1	24·5 ± 0·2	23·7 ± 0·2	−21·2 ± 0·4	8·8 ± 0·1
		156	2·6	18·1	32·8				
		180	2·3	86·6	33·2				

* The error on the kinetic constants has been estimated about 5% of the reported values.

EXPERIMENTAL

4-Methoxy-2-toluoyl Chloride.—This was prepared by the usual method from 4-methoxy-2-toluic acid [27] and thionyl chloride, m.p. 50° (from petroleum) (Found: C, 57·8; H, 4·95. $C_9H_9ClO_2$ requires C, 58·55; H, 4·9%).

Ketones.—2-Methylbenzophenone,[28] b.p. 168° at 12 mmHg; 2,2′-dimethylbenzophenone,[29] m.p. 64—67°; 2-hydroxy-2′-methylbenzophenone,[30] m.p. 65—67°.

* It has been suggested [22] that a high negative entropy of activation could indicate a triplet state transition, but at this stage we have not sufficient data to discuss this hypothesis.

[22] D. R. Rayner, A. J. Gordon, and K. Mislow, *J. Amer. Chem. Soc.*, 1968, **90**, 4854.

[23] H. Kessler, *Angew. Chem. Internat. Edn.*, 1970, **9**, 219.

[24] D. N. Harpp and J. P. Snyder, *J.C.S. Chem. Comm.*, 1972, 1305.

[25] A. Battaglia, A. Dondoni, G. Maccagnani, and G. Mazzanti, Abstracts, Symposium on Organic Sulphur Chemistry, Lund, Sweden, June 1972; to be published.

[26] R. H. Schlessinger and A. G. Schultz, *Tetrahedron Letters*, 1969, 4513.

[27] O. A. Zeidz and B. M. Dubinin, *J. Gen. Chem.* (*U.S.S.R.*), 1932, **2**, 472.

[28] H. Goldschmidt and H. Stocker, *Ber.*, 1891, **24**, 2797.

[29] J. W. Cook, *J. Chem. Soc.*, 1930, 1091.

[30] N. C. Lothrop and P. A. Goodwin, *J. Amer. Chem. Soc.*, 1943, **65**, 365.

4,4'-Dimethoxy-2-methylbenzophenone. A solution of 4-methoxy-2-toluoyl chloride (3·4 g) in CS_2 (30 ml) was added at room temperature to a mixture of anisole (2·2 ml), anhydrous aluminium chloride (2·7 g), and CS_2 (22 ml). After 3 h heating on a steam-bath, the product was decomposed with ice and hydrochloric acid, the CS_2 was distilled off, and the residue was extracted with ether and washed with water. The residue from evaporation afforded *4,4'-dimethoxy-2-methylbenzophenone* (2·6 g), m.p. 78—80° (from EtOH) (Found: C, 74·7; H, 6·2. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·3%).

4,4'-Dichloro-2-methylbenzophenone. A solution of 4-chloro-2-toluoyl chloride [31] (4·3 g) in CS_2 (10 ml), was added at room temperature to a mixture of chlorobenzene (3·2 g), anhydrous aluminium chloride (3·2 g), and CS_2 (10 ml). The mixture was heated under reflux for 24 h and then decomposed with ice and hydrochloric acid. After removal of the CS_2, the residue was extracted with ether and distilled. The *ketone* (2·1 g) was collected at 142—144° at 0·5 mmHg (Found: C, 63·0; H, 3·7. $C_{14}H_{10}Cl_2O$ requires C, 63·4; H, 3·8%).

Thioketones.—Thioketones were prepared from the corresponding ketones following the procedure of Gofton and Braude [32] (method A) or that of Lozac'h and Guillouzo [33] (method B). *(2-Methyl)thiobenzophenone* (III) (A), m.p. 44—45° (from petroleum) (Found: C, 79·1; H, 5·8; S, 14·8. $C_{14}H_{12}S$ requires C, 79·2; H, 5·7; S, 15·1%). 2,2'-Dimethylthiobenzophenone [34] (A), m.p. 45—48° (from petroleum), δ (CCl_4) 2·10 p.p.m. (Me).

2-Hydroxy-(2'-methyl)thiobenzophenone (A), m.p. 31—32° (from petroleum) (Found: C, 73·6; H, 5·45; S, 13·9. $C_{14}H_{12}OS$ requires C, 73·65; H, 5·3; S, 14·05%), δ (CCl_4) 2·11 (Me), 13·28 p.p.m. (OH).

4,4'-Dimethoxy-(2-methyl)thiobenzophenone (IV) (B), m.p. 77—78° (from benzene–petroleum) (Found: C, 70·5; H, 5·8; S, 11·5. $C_{16}H_{16}O_2S$ requires C, 70·55; H, 5·9; S, 11·75).

4,4'-Dichloro-(2-methyl)thiobenzophenone (V) (B), b.p. 130—134° at 2 mmHg (Found: C, 59·8; H, 3·55; S, 12·1. $C_{14}H_{10}Cl_2S$ requires C, 59·8; H, 3·6; S, 11·4%).

Sulphines.—Sulphines were prepared by oxidation of the corresponding thioketones with monoperphthalic acid following the procedure of Zwanenburg, Thijs, and Strating.[2] The i.r. spectra of each product showed a band in the region 1100 cm^{-1} which has been attributed to the S=O stretching.[35]

(2-Methyl)thiobenzophenone S-oxide (VI). The crude oxidation product was chromatographed on silica. Elution with benzene gave first unchanged starting material (III), then the anti-*sulphine*, m.p. 59—60° (from n-pentane) (Found: C, 73·6; H, 5·3; S, 13·9. $C_{14}H_{12}OS$ requires C, 73·65; H, 5·3; S, 14·05%), and finally the syn-*sulphine*, m.p. 81—82° (from benzene–petroleum) (Found: C, 73·4; H, 5·4; S, 14·0%).

(2,2'-Dimethyl)thiobenzophenone S-oxide (IX). The crude oxidation product was chromatographed on silica. Elution with benzene gave starting material and subsequently, with benzene–ether (1 : 1), the *sulphine* (IX), m.p. 66—67° (from petroleum) (Found: C, 74·3; H, 5·8; S, 13·2. $C_{15}H_{14}OS$ requires C, 74·35; H, 5·8; S, 13·25%), δ (CCl_4) 1·94 and 2·39 p.p.m. (Me).

2'-Hydroxy-(2-methyl)thiobenzophenone S-oxide (XI). The crude oxidation product was chromatographed on silica. Elution with benzene gave first starting material and then the *sulphine* (XI), m.p. 91—92° (from petroleum) (Found: C, 68·9; H, 5·0; S, 12·9. $C_{14}H_{12}O_2S$ requires C, 68·85; H, 4·95; S, 13·1%), δ (CCl_4) 2·00 (Me) and 8·55 p.p.m. (OH).

4,4'-Dimethoxy-(2-methyl)thiobenzophenone S-oxide (VII). The crude oxidation product was chromatographed on silica. Elution with benzene–ethyl acetate (10 : 1) gave first starting material (IV), then the anti-*sulphine*, m.p. 65—66° (from ether–petroleum) (Found: C, 66·8; H, 5·65; S, 11·1. $C_{16}H_{16}O_3S$ requires C, 66·65; H, 5·6; S, 11·1%), and finally the syn-*sulphine*, m.p. 86—87° (from ether–petroleum) (Found: C, 66·3; H, 5·75; S, 10·9%).

4,4'-Dichloro-(2-methyl)thiobenzophenone S-oxide (VIII). The crude oxidation product was chromatographed on silica. Elution with benzene–petroleum (1 : 1) gave starting material (V), then the anti-*sulphine*, m.p. 77—78° (from ether–petroleum) (Found: C, 56·5; H, 3·2; S, 10·6. $C_{14}H_{10}Cl_2OS$ requires C, 56·6; H, 3·4; S, 10·8%). Elution with benzene–ethyl acetate (10 : 1) gave the syn-*sulphine*, m.p. 103—104° (from ether–petroleum) (Found: C, 56·7; H, 3·15; S, 10·8%).

Spectral and Kinetic Measurements.—Proton magnetic resonance spectra were recorded on JEOL PS 100 and JNM-C-60 HL spectrometers operating at 100 and 60 MHz respectively in the field–frequency mode with internal lock.

Carbon-13 magnetic resonance spectra (25·15282 MHz) were recorded in $CDCl_3$ solutions on a JEOL PS 100 machine in the continuous wave mode by accumulating the signals with a J.A.R. computer.

Some of the ^{13}C spectra were also recorded by Fourier transform techniques through the courtesy of Dr. Bannon of the JEOL Company (England).

Carbon and proton chemical shifts are expressed in Hz or p.p.m. with positive sign when at higher frequency (lower field) with respect to tetramethylsilane as internal standard.

The samples for the kinetic measurements were prepared directly in clean n.m.r. tubes, dissolving the sulphines in benzene, [$^2H_3$]acetonitrile, or nitrobenzene purified and dried many times according to the usual methods. They were then degassed and sealed under vacuum at 10^{-5} mmHg (samples prepared without degassing gave unreproducible results). Sample concentrations ranged within 10^{-2}—5×10^{-1} mol l^{-1}. The equilibration at different temperatures was carried out using solvents with suitable boiling points: toluene (b.p. 110°), ethylene glycol monomethyl ether (b.p. 126°), ethylene glycol monomethyl ether acetate (b.p. 156°), and *o*-dichlorobenzene (b.p. 180°). At certain intervals the reaction was stopped by cooling the samples and the relative amounts of *syn*- and *anti*-isomers were determined by integrating the methyl signals of the n.m.r. spectra. The possibility that cooling down and heating up the sample tubes could introduce any error was ruled out by performing the kinetic measurements on different tubes.

An average of 10 values for each kinetic run was taken, the process being followed up to 70% of the interconversion; to ensure the reproducibility of the results each run was repeated at least 4 times. During the isomerisation processes samples were kept in the dark.

The rate constants were calculated by using the first order equation for reversible processes.[20]

[31] F. Mayer, H. Albert, and K. Schon, *Ber.*, 1932, **65**, 1295.
[32] B. F. Gofton and E. A. Braude, *Org. Synth.*, 1955, **35**, 97.
[33] N. Lozac'h and G. Guillouzo, *Bull. Soc. chim. France*, 1957, 1221.
[34] O. Korver, J. U. Veenland, and Th. J. De Boer, *Rec. Trav. Chim.*, 1965, **84**, 289.
[35] B. F. Bonini, S. Ghersetti, G. Maccagnani, and G. Mazzanti, *Boll. Sci. Fac. Chim. ind. Bologna*, 1969, **27**, 419.

The activation energies were obtained from standard least squares treatment of the Arrhenius equation. The thermodynamic data for the activated complex result from application of the Eyring equation with a path degeneracy factor of one; the $\Delta G^{\ddagger}$ values were computed for each temperature and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ resulted as intercept and slope of the relationship $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$.

All the calculations were carried out on a CDC 6600 computer and the quoted errors represent the standard deviations.

We thank Dr. J. P. Snyder and Professor B. Zwanenburg for many helpful discussions.

[3/769 *Received*, 11*th April*, 1973]