Reaction between Aldehyde Oximes and Methanesulphinyl Chloride

Malcolm R. Banks,* Charles Brown, Robert F. Hudson, and Keith A. F. Record
University Chemical Laboratory, University of Kent at Canterbury, Canterbury, Kent CT2 7NJ

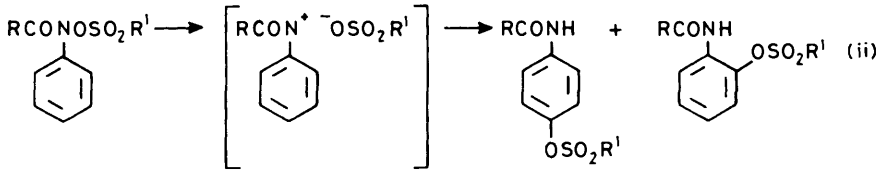
The reactions of several (*E*)- and (*Z*)-benzaldehyde oximes with methanesulphinyl chloride at −70 °C give benzaldehyde *O*-methylsulphinyloxime intermediates. These rearrange above 0 °C to give the corresponding sulphonylimines in good yield, accompanied by minor products including nitriles and products derived from the decomposition of methanesulphinic acid. N.m.r. spectra (^{1}H and ^{13}C) show strong polarizations in the sulphonylimines, indicating a radical-cage mechanism. Further evidence for the involvement of radicals comes from the observation of strong e.s.r. signals. Kinetic measurements of the activation parameters support the conclusions that homolytic dissociation of the N–O bond is the major pathway in this rearrangement.

The reaction between oximes and sulphonyl halides gives an intermediate which readily undergoes the Beckmann rearrangement. This particular rearrangement has been studied in great detail by Kuhara,[1] Chapman,[2] Kenyon,[3] and others, establishing that an intramolecular *anti* displacement occurs, in a heterolytic mechanism.

On the other hand, we have shown that sulphinyl chlorides react with oximes to give thermally unstable *O*-sulphinyloximes, which decompose above 0 °C by a homolytic process to give the corresponding thermally stable *N*-sulphonylimines[4] [reaction (i)].

$$R_2C{=}NOH + R^1SOCl \xrightarrow{-30\ °C} R_2C{=}NOSOR^1 \xrightarrow{25\ °C} R_2C{=}NSO_2R^1 \quad (i)$$

Recently, in a similar investigation, Heesing[5] has shown that whereas sulphonyl chlorides react with *N*-phenylhydroxamic acids by a heterolytic S_N1 mechanism [reaction (ii)], sulphinyl chlorides react by a radical-pair mechanism, to give a variety of products[6] [reaction (iii)]. However, attempts to isolate the *O*-sulphinyl intermediates, even at −70 °C, were futile.



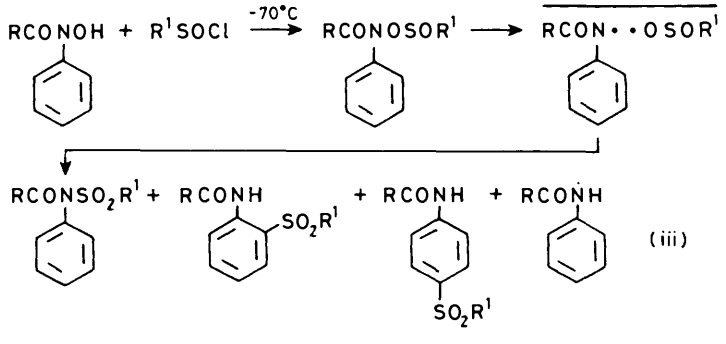
These and other investigations have led to our generalization that hydroxylamine derivatives react with acid chlorides in the higher oxidation states to give intermediates which rearrange by heterolytic mechanisms, whereas the products formed from acid chlorides in a lower oxidation state rearrange by a homolytic mechanism. Lower oxidation state acid chlorides studied include sulphinyl chlorides,[4,7–10] thiocarbamoyl chlorides,[11] chlorophosphines, and chlorophosphites.[12]

In the present work we have studied the thermal decomposition of benzaldehyde *O*-methylsulphinyloximes formed by the action of (*E*)- and (*Z*)-benzaldehyde oximes on methanesulphinyl chloride.

Results and Discussion

Aldehyde oximes react with methanesulphinyl chloride at low temperature (−70 °C) in the presence of triethylamine to give an unstable product (**1**), which can be isolated at 0 °C, and characterized as the *O*-sulphinyl derivative. On warming to room temperature this spontaneously rearranges to the sulphonylimine (**2**) in good yield.

The product isomers were characterized by ^{13}C and ^{1}H n.m.r. spectroscopy (Table 1) and in the case of the sulphonylimines (**2**) by elemental analysis (Table 6). These were prepared in some cases (**2a** and **c**) by treatment of a suitable oxime with sulphinyl chloride at room temperature in the presence of triethylamine.



In all cases (**1a**—**e**) the ^{13}C absorption of the imino carbon atom was *ca.* 16 p.p.m. to higher field than that of the corresponding sulphonylimine (**2a**—**e**) carbon atom; C-1 of the aromatic group showed a similar shift, although only *ca.* 3—4 p.p.m. The ^{13}C shifts for the methyl-sulphinyl and -sulphonyl

$$R^1R^2C{=}NOH + MeSOCl \xrightarrow{-70\,^\circ C} R^1R^2C{=}NOSOMe$$

(1) (~95%)

$$R^1R^2C{=}NOSOMe \xrightarrow{+20\,^\circ C} R^1R^2C{=}NSO_2Me + R^2C{\equiv}N + [CH_3SO_2R^1]$$

(1) (2) (~61–77%) (3) (~10–23%)

	R^1	R^2
a;	H	Ph
b;	D	Ph
c;	H	4-MeC_6H_4
d;	D	4-MeC_6H_4
e;	H	4-$NO_2C_6H_4$

Table 1. N.m.r. data (^{13}C and ^1H) for compounds (1)—(3)

	δ_C[a,c]						δ_H[b]			
Compd.	C=N	*C*-C=N	SOMe	SO_2Me	C≡N	*C*-C≡N	HC=NSO	$HC=NSO_2$	SOMe	SO_2Me
(*Z*)-(**1a**)	154.2	128.6	40.8				8.34		2.84	
(*Z*)-(**1b**)	154.2[e]	128.5	40.7						2.83	
(*E*)-(**1b**)		127.8	42.0						2.92	
(*Z*)-(**1c**)	154.2	128.1	40.8				8.30		2.85	
(*Z*)-(**1d**)	154.2[e]	128.1	40.8						2.84	
(*Z*)-(**1e**)	152.1	129.3	40.8				8.32		2.83	
(**2a**)	171.7	132.1		40.2				9.04		3.16
(**2b**)	171.5[e]	132.8		40.3						3.19
(**2c**)[d]	171.4	129.5		40.3				9.00		3.18
(**2d**)	171.4[e]	129.7		40.3						3.19
(**2e**)	169.2	133.5		40.2				9.16		3.25
(**3**)					112.5	118.7				

[a] 50.3 MHz (Fourier transform); ^{13}C shifts relative to internal Me_4Si. [b] 100 MHz (continuous wave); ^1H shifts relative to internal Me_4Si. [c] Compounds (**1a**—**e**) at −10 °C in $CDCl_3$; (**2a**—**e**) and (**3**) at 25 °C in $CDCl_3$. [d] Control experiment with (**2c**) showed no significant effect of temperature on chemical shifts. [e] Appears as a triplet.

Table 2. Composition of reaction mixtures produced by thermolysis of various *O*-methylsulphinyloximes (**1a**—**e**)

	A[a]			B[b]	C[c]
Compd.	%(2)[d]	%(3)	(2):(3)	(2):(3)	(2):(3)
(*Z*)-(**1a**)	61	23	73 27		
(*Z*)-(**1b**)	74	10	88 12		
(*E*)-(**1b**)	77	12	87 13		
(*Z*)-(**1c**)	69	20	77 23	66 34	
(*Z*)-(**1d**)	72	11	86 14	81 18	84 16
(*Z*)-(**1e**)	69[e]	20	78 22		

[a] Method A. Reaction mixtures from (**1a**—**d**) were separated by distillation to remove the relatively volatile nitrile, followed by crystallization of the pot residue. [b] Method B. Product distribution in cyclohexane at 22 °C was estimated by quantitative u.v. measurement (see Experimental section). [c] Method C. Product distribution in $CDCl_3$ at 34 °C was estimated by ^1H n.m.r. spectroscopy. [d] Percentage yields quoted are those of isolated compounds. [e] Reaction mixture was separated by medium-pressure liquid chromatography [solvent cyclohexane–ether (2:1); support silica (Merck, 230—400 mesh)] and the product estimated after hydrolysis to 4-nitrobenzaldehyde.

carbon atoms are slightly different also, the latter signal being at higher field than the former (*ca.* 0.5 p.p.m.). In the ketone oxime series[4] a small downfield shift is observed in the analogous compounds.

The methylsulphonyl ^1H resonance was typically *ca.* 0.4 p.p.m. to low field of the corresponding methylsulphinyl resonance, and a similar low-field shift of *ca.* 0.8 p.p.m. was observed for the proton bonded to the imino carbon atom. Similar downfield shifts have been observed by Hudson[4,7,8] and Douglass[13] for the methylsulphonyl protons.

The rearrangement is accompanied by the formation of a nitrile in an elimination process. The products were separated by distillation of the mixture to give the nitrile, followed by recrystallization of the pot residue to yield the sulphonylimine.

From the data in Table 2 it can be seen that the 4-unsubstituted (*Z*)-oxime (**1a**) gives rise to 61% of sulphonylimine (**1a**) and 23% of benzonitrile (**3a**) (*i.e.* 72:27). Replacement of the imino hydrogen atom by deuterium changes this ratio to 88:12. Thus the isotope effect for the removal of the imino hydrogen atom in this elimination process is 2.5. The 4-tolualdehyde (*Z*)-oximes (**1c** and **d**) show the same trend. Experiments with the (*Z*)-oximes (**1a**—**c**) and the *E*-isomer (**1b**) gave a similar product distribution of sulphonylimine (**2**) and benzonitrile (**3**) (Table 2).

Direct evidence for the participation of free radical intermediates in the 1,2-rearrangement comes from the observation of strong e.s.r. and CIDNP signals when the reaction was carried out in the probe of the appropriate spectrometer.

E.s.r. Studies.—When the reaction was carried out in the probe of an e.s.r. spectrometer at 35 °C with tetrachloromethane as the solvent, strong signals due to iminyl[11,14] and sulphonyl radicals[15] were observed, and characterized by the parameters recorded in Table 3. The large value of the hyperfine splitting constants (*a*) for the iminyl hydrogen atom (a_H 78 G) shows the presence of a high spin density on the proton, which suggested that strong polarizations might be observed under CIDNP conditions. The signals persisted during the course of the reaction.

Table 3. E.s.r. spectral details[a,b] of iminyl and sulphinyl radicals produced by the thermolysis of *O*-sulphinyl oximes in CCl_4 at 35 °C

	R^1R^2C=NOSOMe						
	R^1	R^2	$g(R^1R^2C{=}N^{\cdot})$	a_N	a_H	a_D	*o*-H, *m*-H	$g(MeSO_2^{\cdot})$
(**1b**)	D	Ph	2.0028	10.0		12.5		2.0049
(**1c**)	H	4-MeC_6H_4	2.0028	10.0	78			2.0049
	Ph	Ph[c]	2.0033	10.0			3.7	2.0049

[a] *g* Values relative to diphenylpicrylhydrazyl. [b] Hyperfine splitting constants (*a*) measured in Gauss (G). [c] Data from ref. 4.

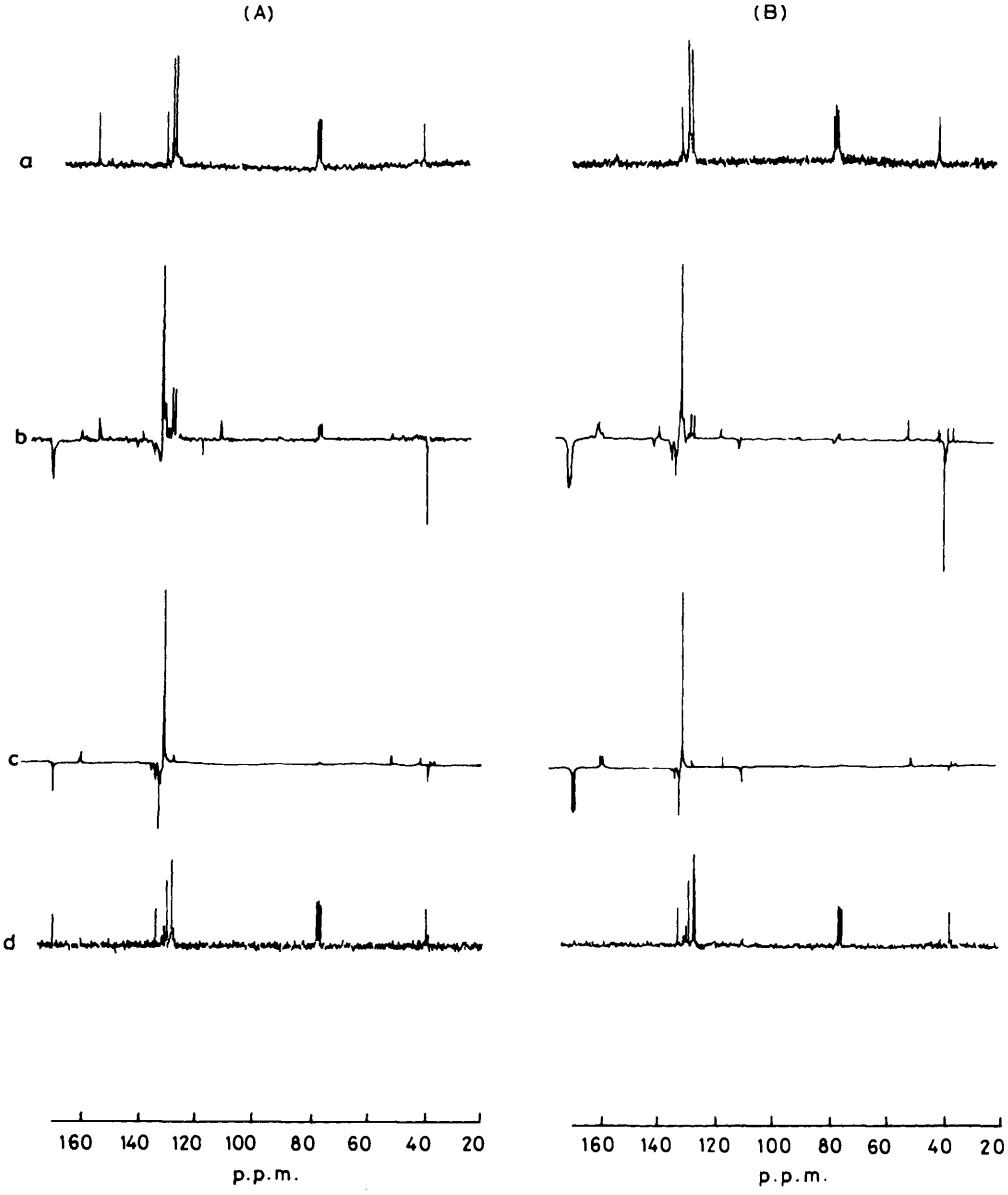


Figure 1. (A) a: ^{13}C N.m.r. spectrum of benzaldehyde (*Z*)-*O*-methylsulphinyloxime (**1a**) in $CDCl_3$ (10% w/v) at −10 °C. b: Polarized ^{13}C n.m.r. spectrum of the products of the thermolysis of (**1a**) *ca.* 29 s after insertion into the probe at 60 °C. c: Polarized spectrum after *ca.* 45 s. d: Analogous spectrum after 4 min. (B) Analogous ^{13}C n.m.r. spectra for [^2H]benzaldehyde (*Z*)-*O*-methylsulphinyloxime (**1b**)

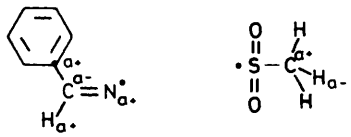
CIDNP Studies.[16]—Further evidence for the involvement of radical species in the 1,2-rearrangement was obtained from nuclear polarizations in certain nuclei of the product when the reaction was carried out in the probe of an n.m.r. spectrometer at 60 °C in $CDCl_3$. In particular, enhanced *absorption* was observed in the ^{13}C n.m.r. spectrum (after *ca.* 30 s) of the aromatic C-1 (δ 132.1) of compound (**2a**), and *emissions* were observed from the nucleus of the imino carbon atom (δ 171.7) and the sulphonyl methyl group (δ 40.2) [Figure 1(A)]. In addition, strong absorption of the imino hydrogen atom (δ 9.04)

was seen in the ^1H n.m.r. spectrum of this compound (**2a**) under CIDNP conditions. As seen from Figure 1(B), similar polarizations were observed for the deuterio compound (**1b**). These results can be analysed in terms of the Radical Pair Model, using the sign equation (1) for net polarization (Γ_{ne})

$$\Gamma_{ne} = \mu\varepsilon\Delta g A_i \quad (1)$$

given by Kaptein,[17] where μ is negative for a singlet precursor, Δg is the difference between the g values of the two radicals involved in the radical pair formed by homolysis, and A_i is the sign of the hyperfine splitting constant. The mechanistically significant parameter ε is positive for an in-cage combination and negative for out-of-cage reaction of the radicals. The observed net polarization, Γ_{ne}, takes a positive sign for enhanced absorption and a negative one for emission.

From experimental values given in Table 3, $g(MeSO_2^{\bullet}) > g(R^1R^2C{=}N^{\bullet})$. Experimental values of A_i are usually not available; in our work these have been obtained from Pople's INDO procedure,[18] using energy-minimized geometries. It has been established that for the relatively large hyperfine splittings involved, even gross changes in geometry do not bring into doubt the *sign* of A_i. The calculated signs are negative for imino carbon and positive for C-1 of the aromatic substituent (Scheme 1). A positive value for the carbon atom of the methyl-



Scheme 1.

sulphonyl radical was obtained from CIDNP experiments with the corresponding ketone oximes.[4,7,8] Our e.s.r. measurements[4] and those of Davies[15] show very small α-proton splittings in the methylsulphonyl radical; the absence of significant polarizations of this nucleus in the ^1H n.m.r. spectrum is not surprising.

It can be seen from Table 4 that for a geminate recombination of the iminyl–sulphonyl radical pair (ε positive), Kaptein's equation would predict an emission (−) and an enhanced absorption (+) for the iminyl carbon atom (δ *ca.* 171) and C-1 (δ *ca.* 130), respectively, in the sulphonylimines (**2**), in addition to an emission due to the methylsulphonyl carbon atom (*ca.* 40.2). These predictions were borne out experimentally (Figure 1 and Table 4). The conclusion drawn is that the sulphonylimine (**2**) is formed, at least in part, in a radical cage. Kinetic measurements (see later) suggest that this is the major pathway.

Relatively weak polarizations are observed for the minor products, in particular the nitrile (**3**). As can be seen in Figure 1(B), enhanced absorbtion occurs at δ 118.7, corresponding to the C-1 nucleus of the aromatic ring, and emission at δ 112.5 corresponding to the nitrile carbon atom for the nitrile (**3**) from the deuterio derivative. These observations are in accord with those predicted by Kaptein's equation for an in-cage process (Scheme 2). According to this Scheme methanesulphinic acid is formed in an elimination process. Methanesulphinic acid is known to undergo a disproportionation reaction, which was shown by Kice and others[19] to involve a homolytic cleavage (Scheme 3).

Verification for this mode of decomposition has been given in previous papers.[9,10] This process may be responsible for some of the minor polarizations observed around δ 40—50 in the ^{13}C n.m.r. CIDNP experiments (Figure 1); however, the position is complex. The ^{13}C n.m.r. spectrum of the analogous protio-compound (**2a**) shows C-1 (δ 118.7) and C=N (δ 112.5)

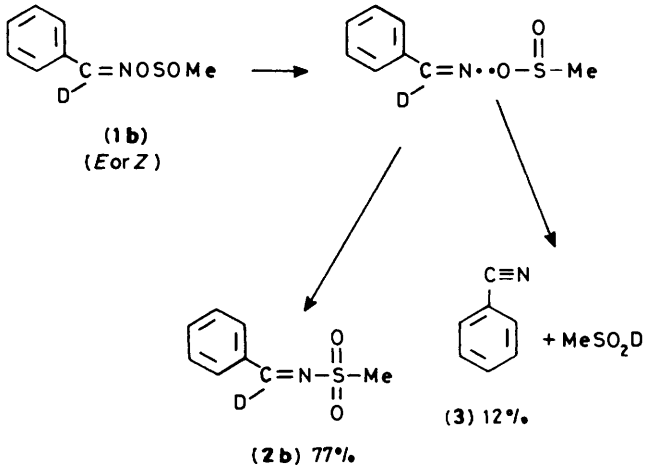
Table 4A. Predicted net polarizations (Γ_{ne}) from Kaptein's equation for the sulphonylimines (**2**) and the nitriles (**3**)

Imines (**2**)	Γ_{ne}	μ	ε	Δg	A_i
C=N	(−)	(−)	(+)	(−)	(−)
C–C=N	(+)	(−)	(+)	(−)	(+)
H–C=N	(+)	(−)	(+)	(−)	(+)
SO_2CH_3	(−)	(−)	(+)	(+)	(+)
Nitrates (**3**)					
C≡N(D)	(−)	(−)	(+)	(−)	(−)
C–C≡N(D)	(+)	(−)	(+)	(−)	(+)
C≡N(H)	(+)	(−)	(−)	(−)	(−)
C–C≡N(H)	(−)	(−)	(−)	(−)	(+)

Table 4B. CIDNP effects (E = emission; A = absorption) in the ^{13}C and ^1H n.m.r. spectra of sulphonylimines (**2**) and nitrile (**3**) from the thermolysis of (*E*)- and (*Z*)-oximes (**1**)

	$^{13}C^a$					$^1H^b$	
	Sulphonylimine			Nitrile		Sulphonylimine	
Compd.	C=N	C–C=N	SO_2Me	C≡N	C–C≡N	HC=N	SO_2Me
(*Z*)-(**2a**)	E	A	E			A	N.o[d]
(*Z*)-(**2b**)	E[c]	A	E			A	N.o
(*E*)-(**2b**)	E[c]	A	E			A	N.o
(*Z*)-(**2c**)	E	A	E			A	N.o
(**3**)-(H)				A	E		
(**3**)-(D)				E	A		

[a] At 60 °C. [b] At 35 °C. [c] Observed as a triplet. [d] Not observed.

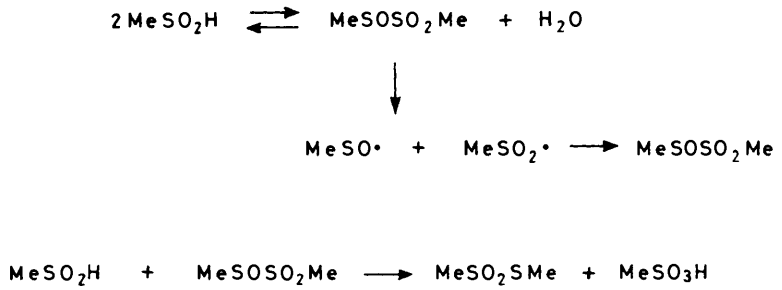


Scheme 2.

polarizations in the opposite sense [Figure 1(A)]. The decomposition of (**1a**) leads to a greater proportion of nitrile (**3**) than the decomposition of the deuterio compound (**1b**) (Table 2). Application of Kaptein's equation leads to the conclusion that in this case the nitrile from the protio derivative is formed predominantly from escaped iminyl radicals, which lose the β-hydrogen atom on encounter with a scavenger other than the sulphinyl radical.

It is possible that this scavenging process involves deuteriochloroform present as a solvent, but this suggestion is speculative. Further work is planned to explain this interesting anomaly.

Kinetic Studies.—These CIDNP results show that at least part of the reaction leading to rearranged product occurs by an in-cage process. There is always the possibility that part of the



Scheme 3.

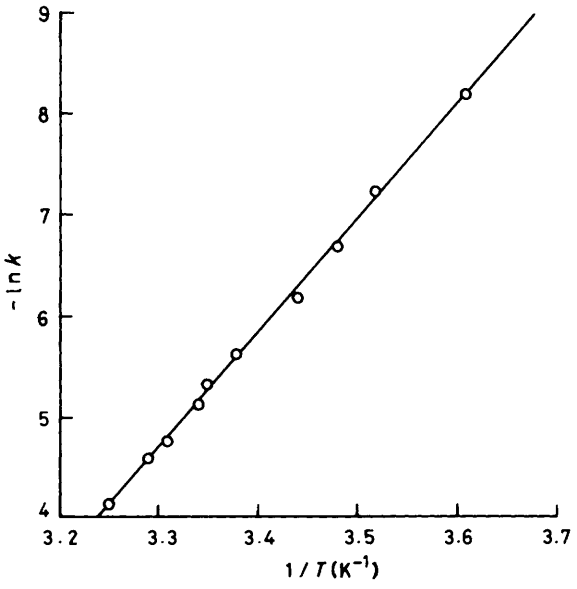


Figure 2. Arrhenius plot of data presented in Table 5(a) for 4-tolualdehyde (*Z*)-*O*-methylsulphinyloxime (**1c**)

Table 5. Kinetic data for the rearrangements of (a) the oxime (**1c**) and (b) the oxime (**1d**) in dichloromethane

(a)	*T*/°C	10^3 *k*/s^{-1}	ΔH^*/kcal mol^{-1}	ΔS^*/cal mol^{-1} K^{-1}
(**1c**)	3.5	0.275		
	10.5	0.728		
	14.5	1.26		
	17.5	2.08		
	22.5	3.62	21.6 ± 0.2	5.7 ± 0.7
	25.0	4.88		
	26.0	5.88		
	29.0	8.57		
	30.5	10.2		
	34.5	15.9		
(b)				
(**1d**)	21.5	2.98		
	26.0	5.05	21.3 ± 0.5	4.0 ± 1.4
	30.5	9.15		
	35.5	16.3		

reaction may proceed by an intramolecular cyclic process, although this is formally symmetry-forbidden. In these reactions, the stereochemistry cannot be followed since the product is configurationally unstable, although the initial intermediate (**1**) can be obtained in both *Z*- and *E*-forms.

As these stereochemical isomers gave similar yields of nitrile (Table 2) it may be assumed that the reaction proceeds exclusively by an in-cage process, since a synchronous symmetry-allowed six-electron process would be favoured by the *E*-isomer.

Cyclic and dissociative mechanisms can in principle be differentiated by determining the activation entropy: negative values are characteristic of cyclic transition states.[20] The rearrangements were followed by u.v. spectroscopy in dichloromethane. Good first-order plots were obtained in all cases, from which first-order rate constants for various temperatures were calculated (Table 5). From these values the enthalpy of activation for (**1c**) was found to be 21.6 + 0.2 kcal mol^{-1} (Figure 2) and that for (**1d**) to be 21.3 ± 0.5 kcal mol^{-1}; *cf.* 22.4 ± 0.6 kcal mol^{-1} for the corresponding oxime derived from benzophenone.[4] In all cases, positive entropies of activation were obtained; for example 5.7 ± 0.7 cal mol^{-1} K^{-1} for (**1c**), and 4.0 ± 1.4 cal mol^{-1} K^{-1} for (**1d**). These values are in agreement with the proposed dissociative mechanism for the formation of both sulphonylimine (**2**) and nitrile (**3**).

Experimental

Preparation of Starting Materials.—Methanesulphinyl chloride was prepared by the modified method of Douglass and Norton.[9,21] Protio-aldehydes employed in this study were obtained from the Aldrich Chemical Company, and deuterio-aldehydes were prepared by the method of Burgstahler.[22] Aldehyde oximes were prepared by standard methods[23] to yield the *Z*-isomers.

(*E*)-Benzaldehyde oxime (**1b**) was prepared from the *Z*-isomer by treatment with hydrogen chloride in anhydrous diethyl ether.[23]

Benzaldehyde O-Methylsulphinyloximes (**1**).—This procedure is typical. An equimolar solution of (*Z*)-benzaldehyde oxime (2.00 g) and dry triethylamine (1.67 g) in dry dichloromethane (10 ml), cooled to −70 °C, was treated dropwise with a solution (5 ml) of methanesulphinyl chloride (1.63 g) in CH_2Cl_2. The mixture was filtered and evaporated (0 °C) under high vacuum and the O-*methylsulphinyloxime* (**1a**) was obtained as a white crystalline solid (2.9 g, 95%). The product was kept well below room temperature to avoid explosion; $\delta_H(CDCl_3)$ 2.84 (s, 3 H, SOMe), 7.40 (m, 5 H, aromatic), and 8.34 (s, 1 H, H–C=N); $\delta_C(CDCl_3)$ 40.80 (SOMe), 126.64, 127.72, and 128.61 (*C*–C=N), 130.29, and 154.18 (C=N). Table 1 gives ^{13}C and ^1H n.m.r. data for the *O*-sulphinyloximes (**1a**–**e**).

Product Analysis of Thermal Rearrangement of the Oxime (**1a**).—Compound (**1a**) (2.0 g) was dissolved in dry dichloromethane (20 ml) and stirred overnight at room temperature. The colourless mixture was evaporated *in vacuo* and the resultant oily solid (2.0 g) was distilled (Kugelrohr). One fraction was obtained (b.p. 65—70 °C at 10 mmHg) which was shown to be benzonitrile (0.4 g, 23%) by comparison (^1H and ^{13}C n.m.r., and i.r. spectroscopy) with an authentic specimen.

Table 6. Analytical data for *N*-sulphonylimines (**2**)

Compound	Formula	M.p. (°C)	Required (%)			Found (%)		
			C	H	N	C	H	N
(**2a**)	$C_8H_9NO_2S$	94—95	52.5	4.9	7.7	52.5	5.0	7.7
(**2b**)	$C_8H_8DNO_2S$	91—93	51.9	4.9	7.6	51.9	4.9	7.7
(**2c**)	$C_9H_{11}NO_2S$	80—82	54.8	5.6	7.1	55.0	5.7	7.0
(**2d**)	$C_9H_{10}DNO_2S$	81—82	54.2	5.6	7.0	54.0	5.3	7.0
(**2e**)	$C_8H_8N_2O_4S$		42.1	3.5	12.3	42.1	3.5	12.2

The pot-residue was taken up in diethyl ether and the solution was treated with charcoal, filtered, and kept at −20 °C overnight. N-*Methylsulphonylbenzylideneamine* (**1a**) (1.85 g, 61%) was obtained as colourless needles, m.p. 94—96 °C; $\delta_H(CDCl_3)$ 3.16 (s, 3 H, SO_2Me), 7.85 (m, 5 H, aromatic), and 9.04 (s, 1 H, H–C=N); $\delta_C(CDCl_3)$ 39.35 (SO_2Me), 127.28, 130.16, and 132.10 (*C*–C=N), and 170.57 (C=N). Table 2 shows the product distributions from the rearrangements of compounds (**1a**—**e**), determined by three methods: product isolation, quantitative u.v. spectroscopy, and ^1H n.m.r. spectroscopy.

N-*Methylsulphonyl*-4-*methylbenzylideneamine* (**2c**).—A solution of (*Z*)-4-tolualdehyde oxime (1.35 g) and dry triethylamine (1.01 g) in dry ether (100 ml) was treated with methanesulphinyl chloride (0.99 g) at room temperature. After the removal of triethylamine hydrochloride by filtration, the filtrate was evaporated to dryness *in vacuo* to give an oily residue (2.0 g). The oil (0.6 g) was chromatographed on silica and eluted with 70:30 diethyl ether–light petroleum (b.p. 40—60 °C) to give toluonitrile (0.2 g), m.p. 29 °C. Elution with diethyl ether gave the N-*methylsulphonylimine* (**2c**) (0.26 g), m.p. 81—82 °C; $\delta_H(CDCl_3)$ 2.46 (s, 3 H, $CH_3C_6H_4$), 3.18 (s, 3 H, SO_2Me), 7.34 (d, 2 H) and 7.86 (d, 2 H) ($CH_3C_6H_4$), and 9.00 (s, 1 H, H–C=N); $\delta_C(CDCl_3)$ 22.01 and 40.30 (SO_2Me), 129.5 (*C*–C=N), 130.03, 131.40, 146.61, and 171.4 (C=N). The N-*methylsulphonylimine* (**2a**) was prepared similarly; elemental analyses are given in Table 6.

Rearrangement of (E)-*Benzaldehyde* O-*Methylsulphinyloxime* (**1b**).—The oxime (**1b**) (2.8 g) was dissolved in $CDCl_3$ (15 ml) and cooled to −30 °C. The ^{13}C n.m.r. spectrum was recorded. When the sample had warmed to the n.m.r. probe temperature (34 °C) CIDNP signals were seen, identical to those seen during the decomposition of the *Z*-isomer. The spectrum recorded after 10 min showed absorption due mainly to the sulphonylimine (**2b**) and benzonitrile (**3**). The product analysis was carried out as already described. The reaction mixture yielded benzonitrile (**3**) (12%) and the sulphonylimine (**2b**) (77%).

E.s.r. Experiment.—A degassed 0.3M-solution of the *O*-methylsulphinyloxime (**1a**) in tetrachloromethane was placed in the probe of a JEOL-PE IX e.s.r. spectrometer at room temperature. E.s.r. signals due to iminyl and sulphonyl radicals were observed immediately and recorded (Table 3).

CIDNP Experiment.—Solutions of (**1a,b,** and **c**) (10% w/v in $CDCl_3$) were prepared at −60 °C and filtered into precooled 10 mm n.m.r. tubes. Each tube was placed immediately into the probe (at 60 °C) of a Brucker WM 200 SWB spectrometer operating at 50.3 MHz. The ^{13}C n.m.r. spectra were recorded using the pulsed Fourier transform mode. About 10 s elapsed when 20 transients were accumulated (*ca.* 5 μs pulse, 22.5° flip angle, 0.655 s repetition rate, 12.5 kHz spectral width, 16 K data points). The accumulated free induction decay was stored and the experiment repeated. The analogous unpolarized spectrum was obtained after 4 min.

Kinetic Procedure.—The appearance of the sulphonylimine was followed spectrophotometrically at 280 nm for 4—5 half-lives. The absorbances of dilute solutions (1×10^{-4}M) of the sulphinyloxime in dichloromethane were measured by using 1 cm pathlength cells in the thermostatically controlled cell block of a Perkin-Elmer 124 u.v. spectrometer. No deviations from first-order kinetics were observed over a series of temperatures. Arrhenius activation parameters were obtained from rate measurements taken at several temperatures in the range +3.5 to +35 °C (Table 5).

The yields of nitrile and sulphonylimine obtained during a kinetic run were calculated using the Beer–Lambert Law. The absorbances of the reaction mixture were measured at 280 and 238 nm [ε_{238} for 4-toluonitrile 145 237, $\varepsilon_{280} = 0$; ε_{238} for the *N*-methylsulphonylimine (**2c**) 2 343.2, $\varepsilon_{280} = 16\,125.6$].

In a typical kinetic run at 22 °C, a 1.108×10^{-4}M-solution of (**1c**), after rearrangement, gave absorbances of 1.22 (280 nm) and 0.73 (238 nm). From the measured extinction coefficients and the Beer–Lambert Law, these absorbances correspond to a solution 7.56×10^{-5}M in sulphonylimine (**2c**) (66%) and 3.76×10^{-5}M in 4-toluonitrile (34%) (see Table 2).

Acknowledgements

We thank Dr. D. O. Smith for assistance with the n.m.r. measurements, and British Petroleum p.l.c. for financial assistance during this work.

References

1 M. Kuhara and Y. Todo, *Mem. Coll. Sci. Eng. Kyoto*, **2**, 387 (*Chem. Abstr.*, 1911, **5**, 1278); M. Kuhara and H. Watanabe, *Mem. Coll. Sci. Eng. Kyoto, Imp. Univ.*, 1916, **I(9)**, 349 (*Chem. Abstr.*, 1917, **11**, 579).
2 A. W. Chapman and F. A. Fidler, *J. Chem. Soc.*, 1936, 448.
3 J. Kenyon and D. P. Young, *J. Chem. Soc.*, 1941, 263.
4 C. Brown, R. F. Hudson, and K. A. F. Record, *J. Chem. Soc., Perkin Trans. 2*, 1978, 822.
5 D. Gutschke and A. Hessing, *Chem. Ber.*, 1973, **106**, 2379.
6 A. Heesing, W. K. Homan, and W. Mullers, *Chem. Ber.*, 1980, **113**, 152.
7 R. F. Hudson and K. A. F. Record, *J. Chem. Soc., Chem. Commun.*, 1976, 831.
8 C. Brown, R. F. Hudson, and K. A. F. Record, *J. Chem. Soc., Chem. Commun.*, 1977, 540.
9 M. R. Banks and R. F. Hudson, *J. Chem. Soc., Chem. Commun.*, 1985, 799; M. R. Banks and R. F. Hudson, *J. Chem. Soc., Perkin Trans. 2*, 1986, 151.
10 M. R. Banks and R. F. Hudson, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1211.
11 R. F. Hudson, A. J. Lawson, and K. A. F. Record, *J. Chem. Soc., Perkin Trans. 2*, 1974, 869; C. Brown, R. F. Hudson, and A. J. Lawson, *J. Am. Chem. Soc.*, 1973, **95**, 6500.
12 C. Brown, R. F. Hudson, A. Maron, and K. A. F. Record, *J. Chem. Soc., Chem. Commun.*, 1976, 663.
13 G. R. Pettit, I. B. Douglass, and R. A. Hill, *Can. J. Chem.*, 1964, **42**, 2357.
14 R. F. Hudson, A. J. Lawson, and K. A. F. Record, *J. Chem. Soc., Chem. Commun.*, 1974, 488.
15 A. G. Davies, B. P. Roberts, and B. R. Sanderson, *J. Chem. Soc., Perkin Trans. 2*, 1973, 626.

16 For general reviews see 'Spin Polarization and Magnetic Effects in Radical Reactions,' ed. Y. N. Molin, Elsevier, Amsterdam, 1984; 'Chemically Induced Magnetic Polarization,' eds. A. R. Lepley and G. L. Closs, Wiley, New York, 1973; R. Kaptein, *Adv. Free Radical Chem.*, 1975, **5**, 319.
17 R. Kaptein, *J. Am. Chem. Soc.*, 1972, **94**, 6251.
18 J. A. Pople and D. L. Beveridge, *J. Chem. Phys.*, 1968, **49**, 4725.
19 J. L. Kice, *Adv. Phys. Org. Chem.*, 1980, 102,
20 G. B. Gill and M. R. Willis, in 'Pericyclic Reactions,' Chapman and Hall, 1974, p. 68; T. H. Lowry and K. S. Richardson, in 'Mechanism and Theory in Organic Chemistry,' Harper and Row, New York,
21 I. B. Douglass and R. V. Norton, *J. Org. Chem.*, 1968, **33**, 2104.
22 A. W. Burgstahler, D. E. Walker, J. P. Kuebrich, and R. L. Schowen, *J. Org. Chem.*, 1972, **37**, 1272.
23 'Vogel's Textbook of Practical Organic Chemistry,' 4th edn., Longman, London, 1978, p. 810.

Received 5*th December* 1985; *Paper* 5/2134