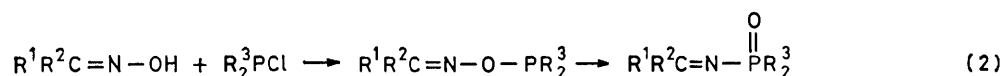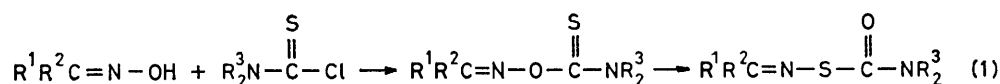# The Reaction Between Oximes and Sulphinyl Chlorides: a Ready, Low-temperature Radical Rearrangement Process

By **Charles Brown, Robert F. Hudson,*** and **Keith A. F. Record,** University Chemical Laboratory, Canterbury, Kent CT2 7NH

The reaction of ketoximes and amidoximes with sulphinyl chlorides at low temperatures produces the thermally unstable O-sulphinylated oximes (I). which have been characterised by ^{1}H and ^{13}C n.m.r. spectroscopy. At higher temperatures. the products are the thermally stable N-sulphonylimines (II). produced by thermal rearrangement of compounds (I). The rearrangement of (I) to (II) has been shown. by means of e.s.r.. ^{13}C CIDNP. and kinetic studies. to involve homolytic N—O bond cleavage to give iminyl and sulphonyl radicals followed by radical recombination with N—S bond formation.

MOST acid chlorides and anhydrides, including sulphonyl and thionyl chlorides, react with oximes to give an intermediate which undergoes the Beckmann rearrangement.

ethylamine in ether at $-30°$. Although the sulphinyl derivatives (I) of ketoximes and amidoximes can be isolated in the solid state at *ca.* $0°$, they have limited

$$R^1R^2C=N-OH \ + \ R_2^3N-\overset{\overset{S}{\|}}{C}-Cl \ \longrightarrow \ R^1R^2C=N-O-\overset{\overset{S}{\|}}{C}-NR_2^3 \ \longrightarrow \ R^1R^2C=N-S-\overset{\overset{O}{\|}}{C}-NR_2^3 \quad (1)$$

$$R^1R^2C=N-OH \ + \ R_2^3PCl \ \longrightarrow \ R^1R^2C=N-O-PR_2^3 \ \longrightarrow \ R^1R^2C=N-\overset{\overset{O}{\|}}{P}R_2^3 \quad (2)$$

The rate of the reaction depends on the leaving group ability of the displaced group, increasing generally with the acidity of the conjugate acid, *e.g.* $RSO_3 > R_2PO_2 > ClCH_2CO_2 > CH_3CO_2$. These reactions, which conform with the orbital symmetry rules, are promoted by electron-deficient nitrogen.

A second group of acid chlorides including thiocarbamoyl chlorides,[1] chlorophosphines,[2] chlorophosphites,[2] and sulphinyl chlorides [3,4] form similar intermediates which then undergo a more rapid rearrangement *of the acidic group*, involving homolytic N—O bond fission. These reactions, *e.g.* equations (1) and (2), are rarely accompanied by Beckmann rearrangement.
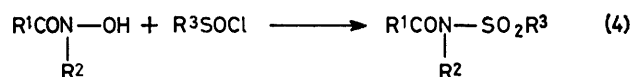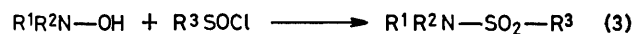
This type of reaction has also been observed for hydroxamic acid derivatives[5] using thiocarbamoyl chlorides, and for both hydroxylamines[6] [equation (3)] and hydroxamic acids[7] [equation (4)] using *sulphinyl chlorides*. Evidence for a radical pathway has been found for most of these reactions.[1-5,7]

This paper describes the reactions of ketoximes and amidoximes with sulphinyl chlorides and presents evidence for the radical nature of the second (rearrangement) stage of the reaction.

RESULTS AND DISCUSSION

Oximes are readily sulphinylated by sulphinyl chlorides in the presence of a molar equivalent of tri-

stability at room temperature, and these compounds were characterised by their n.m.r. spectra. When the

$$R^1R^2N-OH \ + \ R^3SOCl \ \longrightarrow \ R^1R^2N-SO_2-R^3 \quad (3)$$

$$\underset{\underset{R^2}{|}}{R^1CON}-OH \ + \ R^3SOCl \ \longrightarrow \ \underset{\underset{R^2}{|}}{R^1CON}-SO_2R^3 \quad (4)$$

sulphinylation reaction is carried out at room temperature in ether, the thermally stable N-sulphonylimine (II) is produced directly, in high yield.

Structures (I) and (II) were relatively easily distinguished by means of ^{1}H and ^{13}C n.m.r. spectroscopy (Table 1). The methylsulphonyl methyl ^{1}H resonance was typically *ca.* 0.5 p.p.m. to low field of the corresponding methanesulphinyl resonance. Similar downfield shifts have been observed[8] by Douglass *et al.* for methylsulphonyl protons. The ^{13}C shifts for the methyl-sulphinyl and -sulphonyl carbons are slightly different also, the latter being found at *lower* field than the former. The iminyl carbon resonances were particularly diagnostic, those of the N-sulphonylimines (II) being considerably downfield from those of their analogues (I).

In two cases (IIg and h) the N-sulphonylimine structure was confirmed by synthesis from the appropriate imine and sulphonyl chloride.

[1] R. F. Hudson, A. J. Lawson, and K. A. F. Record, *J.C.S. Perkin II*, 1974, 869; C. Brown, R. F. Hudson, and A. J. Lawson, *J. Amer. Chem. Soc.*, 1973, **95**, 6500.

[2] C. Brown, R. F. Hudson, A. Maron, and K. A. F. Record, *J.C.S. Chem. Comm.*, 1976, 663.

[3] R. F. Hudson and K. A. F. Record, *J.C.S. Chem. Comm.*, 1976, 831.

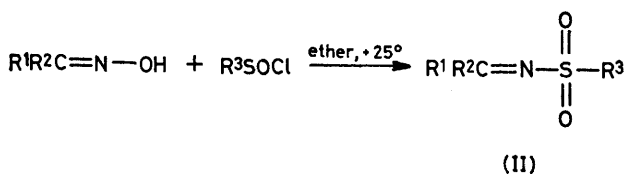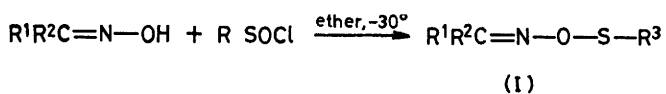[4] C. Brown, R. F. Hudson, and K. A. F. Record, *J.C.S. Chem. Comm.*, 1977, 540.

[5] W. B. Ankers, R. F. Hudson, and A. J. Lawson, *J.C.S. Perkin II*, 1974, 1826; W. B. Ankers, C. Brown, R. F. Hudson, and A. J. Lawson, *J.C.S. Chem. Comm.*, 1972, 935.

[6] H. F. Whalen and L. W. Jones, *J. Amer. Chem. Soc.*, 1925, **47**, 1353.

[7] W. J. Bouma and J. B. F. N. Engberts, *J. Org. Chem.*, 1976, **41**, 143.

[8] G. R. Pettit, I. B. Douglass, and R. A. Hill, *Canad. J. Chem.*, 1964, **42**, 2357.

In the case of the diphenylmethyl derivative (Ie), although initially the product of its thermolysis had the

$$R^1R^2C=N-OH + R\ SOCl \xrightarrow{\text{ether,}-30°} R^1R^2C=N-O-S-R^3$$

(I)

$$R^1R^2C=N-OH + R^3SOCl \xrightarrow{\text{ether,}\cdot 25°} R^1R^2C=N-\overset{\overset{\displaystyle O}{\|}}{\underset{\overset{\displaystyle \|}{O}}{S}}-R^3$$

(II)

a; R¹ = R² = R³ = Ph
b; R¹ = R² = Ph, R³ = Me
c; R¹ = Ph, R² = R³ = Me
d; R¹ = R² = Me, R³ = 4-MeC₆H₄
e; R¹ = Ph, R² = Ph₂CH, R³ = Me
f; R¹ = Ph, R² = Me₂N, R³ = Me
g; R¹ = R² = 4-MeC₆H₄, R³ = Me
h; R¹ = R² = 4-MeC₆H₄, R³ = Ph

structure (IIe) as shown by n.m.r. spectroscopy, this slowly tautomerised in CDCl₃ solution to the enamine (III).

on the participation of intramolecular processes, cannot be used, however, since N-sulphonylimines are configurationally unstable even at low temperatures.[9]

Thus, although the pure E-isomer of the acetophenone oxime derivative (Ic) produced a product with a single C-methyl ¹H resonance, and with only one ¹³C resonance for the C-methyl carbon and each of the carbons in the aromatic ring, this cannot be taken as evidence for a stereochemically pure product (IIc). The

(IIe)   (III)
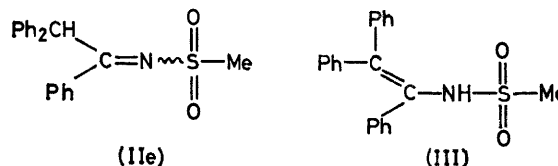
fluctional nature of N-sulphonylimines is clearly demonstrated by the n.m.r. spectra of the symmetrical species (IIb, g, and h). These show only one proton resonance for the E- and Z-aromatic methyls, and only one ¹³C resonance for the carbon atoms of the E- and Z-aromatic rings. In contrast, the O-sulphinyloxime precursors (Ib, g, and h), which would be expected to retain the geometry of the C=N bond, show separate resonances in

TABLE 1

¹³C and ¹H n.m.r. data [a] for compounds (I) and (II)

Compound	C=N	C-C=N	S-CH₃	S-CH₃ [b]	Aromatic H [b]	Others
(Ib)	163.4	131.1, 134.4	41.5	2.74	7.2—7.6	
(Ic)	161.7	14.0, 134.3	41.6	2.83	7.4, 7.7	2.36 (C-CH₃)
(Ie)	161.1	57.9, 137.7	41.4	2.57	7.2—7.4	5.52 (Ph₂CH)
(If)	166.6	130.4	41.0	2.57	7.2—7.5	2.82br (N-CH₃) 38.6br (N-CH₃)
(Ig)	163.6	129.4, 131.8 [c]	41.5	2.76	7.1—7.5	2.40, 2.45 (Ar-CH₃) 21.5 (Ar-CH₃)
(IIb)	179.5	136.4	43.1	3.18	7.4—7.8	
(IIc)	180.2	21.2, 137.4 ($^1J_{CH}$ 130 Hz)	43.2	3.22 ($^1J_{CH}$ 138 Hz)	7.5, 7.9	2.88 (C-CH₃)
(IId)	186.5	30.7		138.5 [d]		
(IIe)	185.3	61.2, 137.5	43.0	3.20	7.2—7.4	5.93 (Ph₂CH)
(IIf)	166.5	132.6	43.2	3.22	7.3—7.5	2.82, 2.87 (N-CH₃) 39.8, 38.0 (N-CH₃)
(IIg)	179.9	134.0	43.1	3.21	7.24, 7.52 (AA'BB', J 8 Hz)	2.45 (Ar-CH₃) 2.45 (Ar-CH₃) 142.9 (Ar-C-4) 21.7 (Ar-CH₃)
(IIh)	179.5	134.2	141.8 [d]		7.2, 7.5 (AA'BB', J 8 Hz) 7.5, 8.0 (SO₂Ar)	2.43 (Ar-CH₃) 142.6 (Ar-C-4) 21.7 (Ar-CH₃)

[a] 25 MHz (Fourier transform) ¹³C and 100 MHz (continuous wave) ¹H shifts both relative to internal Me₄Si. Only unambiguousry assigned ¹³C resonances are reported. [b] Correct integrated intensities were obtained for all ¹H resonances. [c] E- and Z-carbons anisochronous. [d] Arylsulphonyl C-1 (aromatic) carbon. [e] Spectra for (Ib—g) were recorded at —25°; for (IIb—g) at room temperature, in CDCl₃. Control experiments with (IIb) showed no significant effect of temperature on chemical shifts.

The sulphinylated ketoximes and amidoximes (I) rearrange on warming either in the solid state or in solution to give the corresponding N-sulphonylimines (II) in high yield (ca. 85%).

The rearrangement could proceed in the way shown in equation (5) either via the cyclic intermediate shown, or by a direct [1,2] sigmatropic shift. Stereochemical methods, which in principle could provide information

each case (Table 1; doubling of unassigned aromatic ¹³C resonances was also noted).

Previous experience of this type of reaction suggests that the rearrangement proceeds by a dissociative mechanism involving a radical pair * (Scheme). A number of experimental approaches were employed to test this proposal.

E.s.r. Studies.—Evidence for free radical formation is

* Ion pairs are evidently not formed, as the iminium ion would rapidly rearrange (Beckmann): iminyl radicals do not.

[9] F. A. Davis and E. W. Kluger, J. Amer. Chem. Soc., 1976, 98, 302 and references therein.

obtained from e.s.r. studies. When solutions of (I) prepared below room temperature are warmed to ca. 35° in the cavity of an e.s.r. spectrometer, strong signals due

(Table 2) correspond closely to those previously observed for iminyl[1,10] and sulphonyl radicals.[11] The signals persist during the course of the reaction.

(5)

(I)
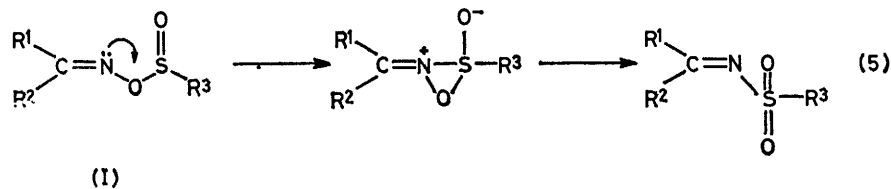
to both iminyl[10] and sulphonyl[11] radicals are detected (Figure 1). The e.s.r. spectra of the iminyl and sulphonyl

CIDNP Studies.—More direct evidence for the participation of these radicals in the formation of the

(II)

SCHEME
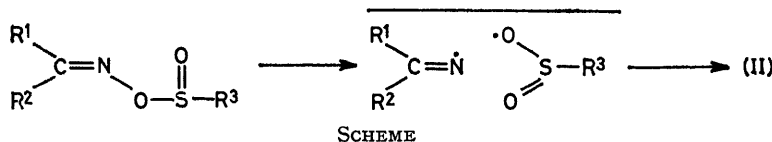
radicals overlap somewhat (Figure 1a), but clearcut characterisation of the sulphonyl species was achieved

products is obtained from CIDNP effects[12] detected in the ^{13}C n.m.r. spectra of the reaction products when the
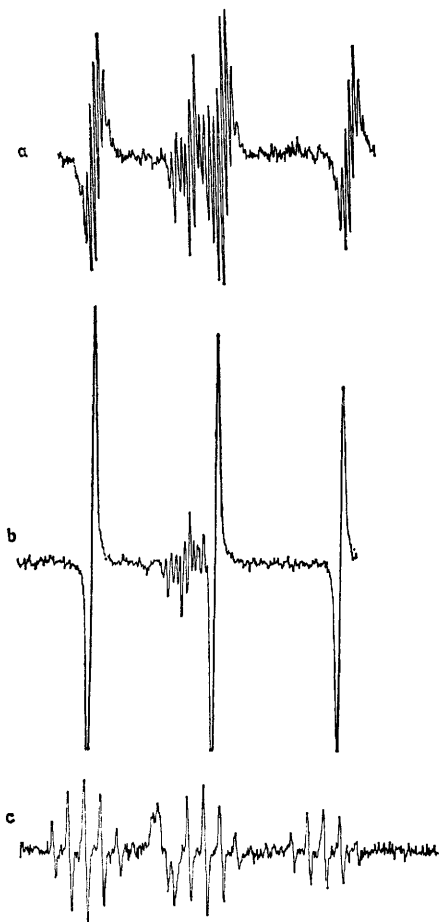
TABLE 2

E.s.r. spectral details of sulphinyl and iminyl radicals produced by pyrolysis of O-sulphinylated oximes (1) in tetrachloromethane at 35°

Radical	g[a]	A_i/mT[b]
$MeSO_2$	2.0049	
$PhSO_2$	2.0045	o-H 0.11, m-H 0.03, p-H 0.06
$4\text{-Me·}C_6H_4SO_2$	2.0046	o-H 0.12, m-H 0.03, p-CH_3 0.06
$Me_2C=\dot{N}$	2.0028	N 0.965, β-H 0.14
$PhMeC=\dot{N}$	2.0030	N 0.100
$Ph_2C=\dot{N}$	2.0033	N 0.100, o-H m-H 0.037
$(4\text{-MeC}_6H_4)_2C=\dot{N}$	2.0033	N 0.100, o-H m-H 0.037
$([^2H_5]Ph)_2C=\dot{N}$	2.0033	N 0.100

[a] Relative to diphenylpicrylhydrazyl. [b] Satisfactory fit with computer simulated spectra found in all cases, using data reported above.

above experiments are repeated in the probe of an n.m.r. spectrometer (Figure 2).

The results of the CIDNP experiments are collected in Table 3. Analysis of these results can be made using the radical pair model and the equations given by

$$\Gamma_{ne} = \mu\varepsilon\Delta g A_i \qquad (6)$$

$$\Gamma_{me} = \mu\varepsilon A_i A_j \sigma_{ij} J_{ij} \qquad (7)$$

Kaptein [(6) and (7) where the symbols have their usual significance].[13]

FIGURE 1 E.s.r. spectra of: a, $PhSO_2$ and $Ph_2C=\dot{N}$; b, $PhSO_2$ and $([^2H_5]Ph)_2C=\dot{N}$; and c, $MeSO_2$ and $Me_2C=\dot{N}$

using perdeuteriated derivatives (Figure 1b). The g values and hyperfine splitting constants * obtained

* No hyperfine structure was observed in the case of the methylsulphonyl radical, only a relatively broad signal, W_i ca. 0.1 mT, being observed, but this is not unexpected at room temperature[11] (Figure 1c).

[10] R. F. Hudson, A. J. Lawson, and K. A. F. Record, *J.C.S. Chem. Comm.*, 1974, 488.

[11] A. G. Davies, B. P. Roberts, and B. R. Sanderson, *J.C.S. Perkin II*, 1973, 626.

[12] For reviews, see 'Chemically Induced Magnetic Polarisation,' eds. A. R. Lepley and G. L. Closs, Wiley, New York, 1973; R. Kaptein, *Adv. Free Radical Chem.*, 1975, **5**, 319.

[13] R. Kaptein, *J. Amer. Chem. Soc.*, 1972, **94**, 6251.

In the case of net effects, Γ_{ne}, before we can determine ε, the mechanistically significant parameter, we need the signs of the term Δg and of A_i for the nuclei observed.*

minimised geometries have been employed in the case of the iminyl radicals and it has been established that for the (relatively large magnitude) hyperfine splittings
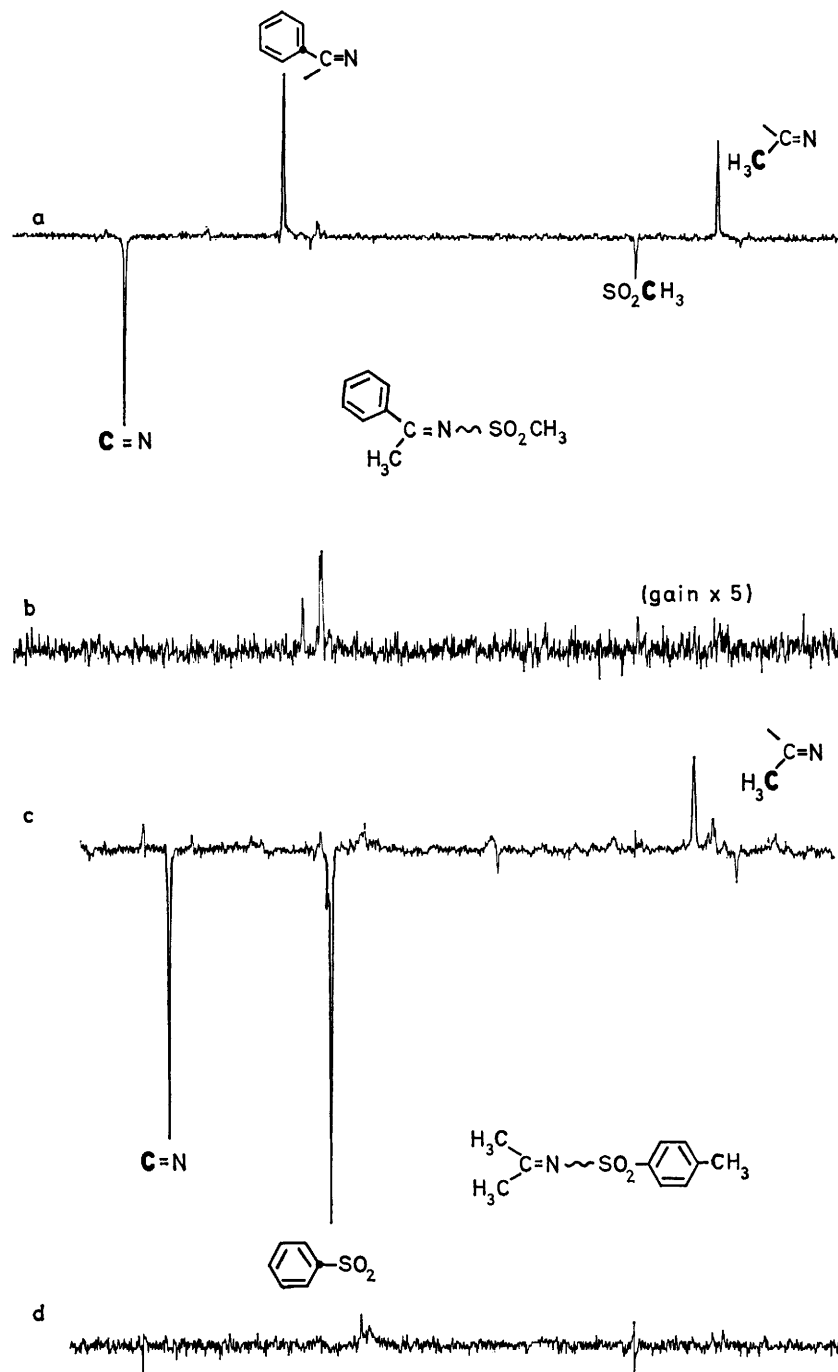

FIGURE 2   [13]C N.m.r. spectra of *ca.* 1.0M solutions of *O*-sulphinylated oximes in $CDCl_3$ prepared at 0° ·and inserted into preheated spectrometer probe: a, (Ic) after 35 s; b, (Ic) after 200 s; c, (Id) after 25 s, and d, (Id) after 150 s.   Times quoted are for start of pulse sequences   Spectra were recorded at 50° for (Ic) and at 60° for (Id)

The sign of Δg is available directly from the e.s.r. data, but that of A_i is not.   We have therefore used Pople's INDO procedure [14] to calculate A_i values.   Energy-

involved (typically >1.0 mT), even gross changes in geometry do not bring into doubt the *sign* of A_i.   The calculated A_i signs are negative for C=N, positive for

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* The sign of μ in the case of these *thermal* reactions is certainly negative (singlet state precursor).

[14] J. A. Pople and D. L. Beveridge, *J. Chem. Phys.*, 1968, **49**, 4725.

$C-C=N$ (C-1). It can be seen that for a geminate re-combination of the iminyl–sulphonyl radical pair, (ε positive), equation (6) predicts an emission signal

TABLE 3

CIDNP effects in the ^{13}C n.m.r. spectra of N-sulphonyl-imines (II) produced by thermolysis of O-sulphinylated oximes (I) in deuteriochloroform

Compound			Polarisations [a]		
R^1	R^2	R^3	$C=N$	$C-C=N$	SO_2-C
Ph	Ph	Ph	E(E)	A(A)	E
Ph	Ph	Me	E(E)	A(A)	E
Ph	Me	Me	E(E)	A(A); A(A)	E
Me	Me	4-MeC$_6$H$_4$	E(E)	A(A)	E
4-MeC$_6$H$_4$	4-MeC$_6$H$_4$	Me	E(E)	A(A)	E
Me$_2$N	Ph	Me	E(E)	A(A)	E
PhCH	Ph	Me	E(E)	A(A); A(A)	E

[a] Predicted polarisation on basis of INDO calculations of A_i in parentheses.

(E) and an enhanced absorption signal (A) for the iminyl and C-1 carbon atoms respectively in N-sulphonylimines (II). As can be seen from Table 3, this polarisation pattern is observed in all cases (e.g. Figure 2) and it can be concluded that the rearrangement (5) of (I) to (II) proceeds by geminate recombination of the iminyl–sulphonyl radical pair with formation of an N–S bond, at least in part.

It has recently been pointed [15] out, however, that the observation of strong CIDNP effects in most cases may be taken as good evidence for an important contribution to the overall reaction flux by a radical mechanism.

Using the polarisations (E in both cases) observed for the methylsulphonyl carbon in (IIb and c) and the C-sulphonyl carbon of (IId) we can assign a positive value to the α-carbon hyperfine splitting in both the methylsulphonyl and tolylsulphonyl radicals. This is in accord with Lucken's calculations which indicate [16] considerable localisation of the unpaired spin on a sulphur $3p$ orbital. Our e.s.r. measurements confirm the trend, noted by Davies,[11] towards small α-proton splittings in the methylsulphonyl radical at higher temperatures and so we neither expect nor find detectable net polarisation of the methylsulphonyl protons. Furthermore, the very small value for this hyperfine splitting predicts a negligible multiplet effect, Γ_{me} [equation (7)], for the methylsulphonyl carbon. As can be seen from Figure 3, a virtually pure emission signal is observed when the polarisation of this carbon atom is determined without proton noise-decoupling. A similar observation of pure emission effects was made for the methylsulphonyl (E) and C-methyl (A) ^{13}C resonances (quartets) in the undecoupled spectrum of (IIc).

We may conclude from these experiments that the re-arrangement of (I) to (II) is predominantly a radical process, with the observed polarisation arising from geminate recombination. In view of the high standing

[15] R. G. Lawler, N.A.T.O. A.S.I. on C.I.D.N.P., Sogesta, Urbino, Italy, 1977.

concentration of radical species, however, a contribution from induced decomposition of (I) by iminyl and/or sulphonyl radicals cannot be ruled out. Indeed, in the case of aldoxime derivatives *this* type of process may determine the sign of the observed polarisations.[4]

Kinetic Studies.—The CIDNP results show that at least part of the rearrangement occurs by a radical pathway, apparently largely geminate recombination dominated. In addition, however, there is the possi-bility of an intramolecular cyclic process of the type indicated in equation (5). Estimation of the importance of this type of process is always difficult, and as we point out (*vide supra*) stereochemical methods, in principle very powerful, may not be employed with the N-sulphonylimine system. We have therefore examined
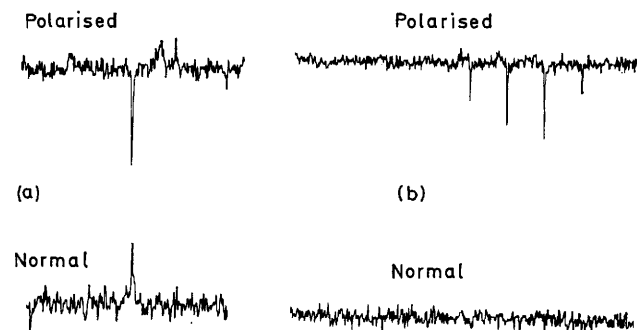

FIGURE 3 Polarised ^{13}C spectra of methylsulphonyl carbon in (IIb) (a) recorded with proton noise-decoupler on, and (b) with decoupler off. A relatively large flip-angle (ca. 45°) and only 0.7 s repetition time were employed in these experiments in view of the short T_1 of the methylsulphonyl carbon

the kinetics of the rearrangement of the ketoxime (Ib). In particular, support for a dissociative process can be drawn from measurement of activation entropies ΔS^* since negative values are normally obtained for con-certed processes. The rate of the reaction at several temperatures was followed by u.v.–visible spectrophoto-metry. Good first-order plots were obtained and from the data (Table 4) values of 22.4 ± 0.6 kcal mol^{-1} and

TABLE 4

Kinetic data for rearrangement of (Ib) in dichloromethane

$T/°C$	k_{obs}/s^{-1}	$\Delta H^*/$kcal mol^{-1}	$\Delta S^*/$cal mol^{-1} K^{-1}
14.2	5.96×10^{-4}		
22.4	1.47×10^{-3}		
27.8	2.95×10^{-3}	22.4 ± 0.6	6.5 ± 4
35.6	8.03×10^{-3}		
40.3	1.75×10^{-2}		

6.5 ± 4 cal m^{-1} K^{-1} were calculated for ΔH^* and ΔS^* respectively. These values are of the expected order for a dissociative process.

EXPERIMENTAL

Preparation of Starting Materials.—Methanesulphinyl chloride was prepared by the method of Douglass and

[16] M. Geoffroy and E. A. C. Lucken, *J. Chem. Phys.*, 1971, **55**, 2719.

Norton.[17] Benzenesulphinyl chloride and toluene-4-sulphinyl chloride were prepared by a similar route. Oximes were prepared by standard procedures,[18] with the exception of 1-hydroxyimino-1,2,2-triphenylethane. This was prepared by treatment of benzil with phenylmagnesium bromide, followed first by pinacol rearrangement to a mixture of aldehyde and ketone [19] and then by oximation [20] of the separated 2,2-diphenylacetophenone. This gave two isomers in *ca.* 1 : 1 ratio as deduced from ^{1}H n.m.r. peak areas due to the methine resonances at δ 5.31 and 6.30. Recrystallisation (ethanol) gave one isomer (δ 5.31) used to prepare (Ie). [^{2}H$_{10}$]Benzophenone oxime was prepared by the usual procedure [18] from [^{2}H$_{10}$]benzophenone, which in turn was synthesised [21] (from [^{2}H$_6$]benzene in place of benzene) using tetrachloromethane and aluminium trichloride.

Preparation of O-Sulphinylated Oximes.—The following procedure is typical. A solution of NN-dimethylbenzamidoxime (1.64 g) and dry triethylamine (1.01 g) in dry ether (100 ml) cooled to $-10°$ was treated with methylsulphinyl chloride (0.98 g). The triethylamine hydrochloride was filtered off and the solution concentrated by low temperature evaporation of the solvent under high vacuum. Light petroleum (b.p. 40—60°) (50 ml) was then added to the cold solution and the product, NN-dimethyl-O-methylsulphinylbenzamidoxime (If) (1.9 g, 84%), crystallised out. The product was characterised by low temperature (-20 to $-30°$) n.m.r. spectra (Table 1) and by conversion to the corresponding N-sulphonylimine. Compounds (Ia—e) were prepared in a similar fashion.

Preparation of N-Sulphonylimines.—*In the solid state.* Again the following procedure is typical. Benzophenone methylsulphinyloxime (1.0 g) was heated gently on a water-bath until it melted, when a vigorous reaction took place. On cooling the melt, a crystalline mass of N-diphenylmethylene-N-methylsulphonylamine (IIb) formed. Recrystallisation from benzene–light petroleum (b.p. 40—60°) gave the pure product (0.9 g, 90%), m.p. 146—147°.

In solution. When solutions of the sulphinylated oximes (I) in tetrachloromethane were warmed, the corresponding N-sulphonylimines were formed, and could be isolated in a pure state in $>80\%$ yield by recrystallisation. Compounds (IIa—h) were prepared by one or both of these methods and characterised by n.m.r. (Table 1) and elemental analysis (Table 5).

Unambiguous Synthesis of N-Sulphonylimines.—Methylsulphonyl chloride (1.96 g), triethylamine (2.0 g), and bis-(4-methylphenyl)methyleneamine (4.18 g; prepared by the method of Pickard and Tolbert [22]) were heated in benzene (50 ml) under reflux for 72 h. The mixture was cooled and the precipitated amine hydrochloride filtered off. Evaporation of the solvent gave a solid which was twice recrystallised from dry ethanol to give the N-bis-(4-methylphenyl)-methylene-N-methylsulphonylamine, m.p. 140—141°, in 54% yield. A similar procedure was used to make the N-phenylsulphonyl analogue (IIh) in 49% yield.

Preparation and Rearrangement of the Diphenylmethyl

Derivative (Ie).—The *ca.* 1 : 1 mixture of (*E*)- and (*Z*)-1-hydroxyimino-1,1,2-triphenylethane obtained by oximation of diphenylmethyl phenyl ketone was recrystallised from

TABLE 5

Analytical data for N-sulphonylimines (II)

Compound	Formula	M.p. (°C)	Required (%)			Found (%)		
			C	H	N	C	H	N
(IIa)	$C_{19}H_{15}NO_2S$	124—125	71.0	4.7	4.4	71.0	4.7	4.4
(IIb)	$C_{14}H_{13}NO_2S$	146—147	64.9	5.0	5.4	64.8	5.3	5.4
(IIc)	$C_9H_{11}NO_2S$	124—125	54.8	5.6	7.1	55.0	5.9	6.9
(IIe) [a]	$C_{21}H_{19}NO_2S$	193—194	72.2	5.4	4.0	72.4	5.4	4.1
(IIf)	$C_{10}H_{14}N_2O_2S$	127—128	53.1	6.2	12.4	53.4	6.1	12.3
(IIg)	$C_{16}H_{17}NO_2S$	140—141	66.9	5.9	4.9	66.7	5.7	5.0
(IIh)	$C_{21}H_{19}NO_2S$	131—132	72.2	5.5	4.0	72.4	5.4	4.0

[a] Analysed as tautomer (III).

ethanol to give a single isomer, m.p. 167—168°. This had only one methine resonance at δ 5.31, and probably has the E-stereochemistry.[23] The foregoing oxime (0.95 g) and triethylamine (0.33 g) were dissolved in dry ether (30 ml) and treated with freshly distilled methanesulphinyl chloride (0.33 g) at $-20°$. After removal of triethylamine hydrochloride, the solution was evaporated under vacuum at low temperature to give (Ie) (1.2 g) as an oil. When this oil was allowed to warm to room temperature, a solid, m.p. 193—194° (from ethanol), formed. Although this material analysed correctly for the N-sulphonylimine (IIe), the spectral data were not in accord with this structure (*cf.* Table 1). The ^{1}H n.m.r. (CDCl$_3$) had δ 2.53 (3 H, s), 5.97br (1 H, s, readily exchangeable with D$_2$O) together with complex multiplets centred at 7.0, 7.3, and 7.5 (15 H). Furthermore the absence of a C=N carbon resonance in the ^{13}C spectrum (highest shift resonance at 140.5 p.p.m.) at *ca.* 180 and of a methine resonance at *ca.* 56 p.p.m. ruled out the Ph$_2$CH–C=N part structure. Structure (III) is more in accord with the ^{1}H data and with the 15-line ^{13}C spectrum; 140.5, 140.2, 136.2, 134.1, 132.3 (low intensity singlets,* quaternary sp^2 carbons); 130.8, 130.7, 130.3 (strong doublets,* aromatic *ortho*-carbons); 128.7, 128.0, 127.6 (strong doublets,* aromatic *meta*-carbons); 128.2, 127.7, 126.5 (medium intensity doublets,* aromatic *para*-carbons); and 43.1 p.p.m. (quartet,* NHSO$_2$Me carbon). In addition the i.r. spectrum showed characteristic NHSO$_2$ bands [24] at 3 340, 3 300, 1 340, and 1 155 cm^{-1}.

When the reaction was monitored by ^{1}H and ^{13}C n.m.r. at temperatures just below zero, resonances due to (IIe) *could* be detected (Table 1), but these were finally replaced by resonances due to (III).

E.s.r. Experiments.—A JEOL PE IX e.s.r. spectrometer was employed. 0.3M-Solutions of the O-sulphinylated oximes were degassed thoroughly at *ca.* 0°, and placed in the cavity of the spectrometer at *ca.* 35°. Strong signals due to iminyl and to sulphinyl radicals were observed immediately. These persisted for *ca.* 10 min. The *g* values were measured using diphenylpicrylhydrazyl as reference (*g* 2.0036).

CIDNP Experiments.—The ^{13}C n.m.r. spectra were obtained with a JEOL PS-100 PFT instrument operating

* Off-resonance ^{13}C-{^{1}H} spectrum.

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at 25.15 MHz in the pulsed Fourier transform mode both with and without proton noise-decoupling. In a typical experiment a *ca.* 1.0M solution of the sulphinylated oxime prepared in $CDCl_3$ (^2H lock) at *ca.* 0° in a 10 mm n.m.r. tube was placed in the preheated probe (40—60°) of the spectrometer. About 30—50 s was generally required for spectrometer optimisation when (usually) 50 transients were accumulated (*ca.* 8 μs pulse, 30° flip-angle, 1 s repetition rate,* 4 or 5 kHz spectral width, 4 K data points). The accumulated F.I.D. was stored on a magnetic drum, and the experiment repeated. Transformation of these (polarised) spectra was then carried out, and the experiment repeated after *ca.* 20 min to obtain the analogous unpolarised spectrum. The delay between inserting the sample and recording the spectra varied slightly with sample and probe temperature, but generally maximum polarisations were observed *ca.* 1—2 min after sample insertion.

Kinetic Measurements.—Rate measurements were made with a Perkin-Elmer 124 u.v. spectrometer equipped with a thermostatted cell block. The appearance of *N*-sulphonyl-imine was followed at 280 nm for 4—5 half-lives. Dilute solutions (1 × 10^{-4}M) in dichloromethane were used (1 cm cell). No deviation from first-order kinetics were observed at any of the temperatures employed (Table 4) and ΔH^* and ΔS^* were obtained in the usual way from Arrhenius plots.

* Harder (*ca.* 45°) pulses and shorter repetition times (*ca.* 0.7 s) were employed in some cases, *e.g.* for protonated carbons.