The Photochemistry of Sulphoxides. A CIDNP Study of Carbon–Sulphur Bond Cleavage Paths [1]

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A comparative photo-CIDNP study of triplet benzophenone sensitized C–S photocleavage of sulphoxides reveals significant structural dependence of the cage recombination and escape processes. In the photoreactive *ortho*-substituted phenyl methyl sulphoxides the triplet spin-correlated methyl–arylsulphinyl radical pair, ^{3}RP1, $^{3}\overline{\mathrm{CH}_3^{\bullet} + \mathrm{ArSO}^{\bullet}}$, is formed by triplet benzophenone sensitization or in some molecules, by direct excitation and intersystem crossing. Polarized methane and ethane are formed by the escape path of ^{3}RP1, while the methyl- and aryl-H polarized starting molecule is obtained by the recombination path. The methyl-H polarized thioanisole product is obtained by deoxygenation of ArSO$^{\bullet}$ escaped from ^{3}RP1 and subsequent reaction of ArS$^{\bullet}$ with a polarized methyl radical. In the absence of an active *ortho*-substituent, phenyl methyl sulphoxides give by direct excitation singlet state methyl–sulphinyl bond cleavage and form polarized methane as a minor escape product. The benzophenone triplet sensitized path takes place as a very inefficient process. The photocleavage reactivity of the methyl vinyl sulphoxides (3) and (4) is similar to that of the *ortho*-substituted methyl phenyl sulphoxides (1). In the methyl β-substituted ethyl sulphoxide (5a) photocleavage takes place only at the ethyl–sulphinyl bond. Polarized (5a) is obtained by the recombination path, while the escape path leads by the rare SO extrusion process to a ^{1}H methyl polarized n-propyl product (5b). Fluorenyl cinnamyl sulphoxide (6) undergoes two parallel bond cleavage processes, at the fluorenyl–sulphinyl and at the cinnamyl–sulphinyl bonds. The in-cage recombination in both radical pairs gives rise to (6*) polarized on both fluorenyl and cinnamyl moieties. The present work indicates that the recently described complex photorearrangement of the closely related cyclic sulphoxides (7a—d) is not a free radical reaction but rather a concerted electrocyclic process. The bond cleavage processes of (6) were not observed in these systems. 4-Methylpentadienyl phenyl sulphoxide (9a) and its sigmatropic rearrangement isomer (9b) undergo photocleavage at the pentadienyl–sulphinyl bond. In the two isomers the alternating sign polarization pattern due to the recombination path was evidenced at 90 MHz and more clearly so in the recently obtained 270 MHz photo-CIDNP spectra. Good correlation can be established between the photocleavage reactivity and ground state bond dissociation energies for C–S bonds of sulphoxides, while the escape path reactivity can be correlated with the C–H bond dissociation energies of the hydrocarbon product.

In the present series we shall explore the free radical aspects of the photochemistry of organosulphur molecules by means of the CIDNP † technique. This experimental technique studies free radical reactions at their spin correlated radical pair (RP) interaction stage. Being essentially an n.m.r. method it provides product-specific information on the chemical structure of the RP components A$^{\bullet}$ and B$^{\bullet}$, on the total spin state of the RP and on that of its precursor, and on the chemical path by which the polarized product is formed. Of particular importance is the immediate and straightforward identification of chemically degenerate paths, *e.g.*, $\mathrm{C} \xrightarrow{h\nu} \overline{\mathrm{A}^{\bullet} + \mathrm{B}^{\bullet}} \longrightarrow \mathrm{C}^{*}$, made possible by this method. In an initial application of the CIDNP method to the study of photochemical processes of organosulphur compounds we studied the sensitized photodecarboxylation of phenylthioacetic acid by ^{1}H CIDNP,[3] a system which was recently re-examined by ^{13}C CIDNP.[4] The photo-CIDNP investigation of sulphoxides has revealed a wide range of photocleavage reactivity both by reaction from directly excited triplet and singlet states and by sensitization with triplet ketones.[5,6] While methylphenyl sulphoxide is relatively unreactive in this process,[5] a remarkable photoreactivity enhancement is brought about through neighbouring group effects [5] which will be examined in the present work. We have recently found that other structural factors also exert a decisive role in determining the photoreactivity of sulphoxides, and some of these will be presented here. Thus we shall describe and compare the photoreactivity effects specific to the vinyl group, the alkyl chain, the allylbenzyl system, and pentadienyl system.[7] Another subject treated in the present paper is the photodeoxygenation process. In this field the CIDNP method has provided some direct insight into the mechanism of the photodeoxygenation process of sulphoxides,[6] which was shown to take place in the aryl-(or alkyl-)sulphinyl radical. This conclusion has prompted us to examine the triplet sensitized photoprocesses of the corresponding aryl alkyl sulphides, in particular the processes of hydrogen atom abstraction and of electron transfer which will be described elsewhere.[6] That work has revealed that the nuclear polarization of sulphides formed by photodecarboxylation or photodeoxygenation is due to the primary bond cleavage step and not acquired in a subsequent process.[6]

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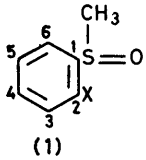
† Chemically induced dynamic nuclear polarization. The standard symbols of the Radical Pair (RP) theory [2] for the net effect (NE) on nucleus *i* in a chemical product derived from radical A$^{\bullet}$ in RP A$^{\bullet}$ + B$^{\bullet}$ will be used: Γ, sign of nuclear polarization effect; μ, sign parameter for electron spin of RP (+triplet, −singlet); ε, path parameter for RP chemical product (+recombination, −escape); Δ*g*, sign of *g*-factor difference of the RP components A$^{\bullet}$ and B$^{\bullet}$; A_i, sign of electron spin–nuclear spin hyperfine coupling interaction of nucleus *i*. The spin correlation of the RP is denoted by a horizontal bar. The RP model expression for the Γ_{NE} is (1). Γ is positive for enhanced absorption (A)

$$\Gamma_{\mathrm{NE}} = \mu\epsilon\Delta g A_i \qquad (1)$$

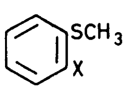
and negative for (enhanced) emission (E). Nuclear polarization is denoted by an asterisk (*).

RESULTS AND DISCUSSION

I *Aryl Methyl Sulphoxides*.—The photoreactive *ortho*-substituted phenyl methyl sulphoxides (1) present a uniform pattern of photochemical reactivity, irrespective of their mode of excitation (see below). Those listed in Table 1 (1a—h) react both by direct excitation and by triplet sensitization while those listed in Table 2 (1i—l) react only by sensitization with triplet benzophenone. The photochemical process results in the formation of methane and ethane (δ 0.18 and 0.78 respectively, in C_6D_6 solution) showing strong negative net effects, and in the formation of the corresponding thioanisole derivative (2), again with negative ^1H n.m.r. polarization in the methyl group. These effects are evident in the 90 MHz ^1H photo-CIDNP spectra of Figures 1—4. In addition to the formation of these polarized products the photoreaction also produces nuclear polarization in the nuclei of the starting compound. The sulphinyl methyl protons show enhanced absorption (see, *e.g.* Figures 1—3) while the proton *ortho* to the methylsulphinyl group, 6-H, shows an emission effect (see *e.g.* Figures 2 and 3). By prolonged irradiation the most reactive systems [*e.g.* (1a, b, f, h, and i)] form significant amounts of methane. Conversions of *ca.* 30% were indicated by n.m.r. for (1i)–benzophenone.



(1)



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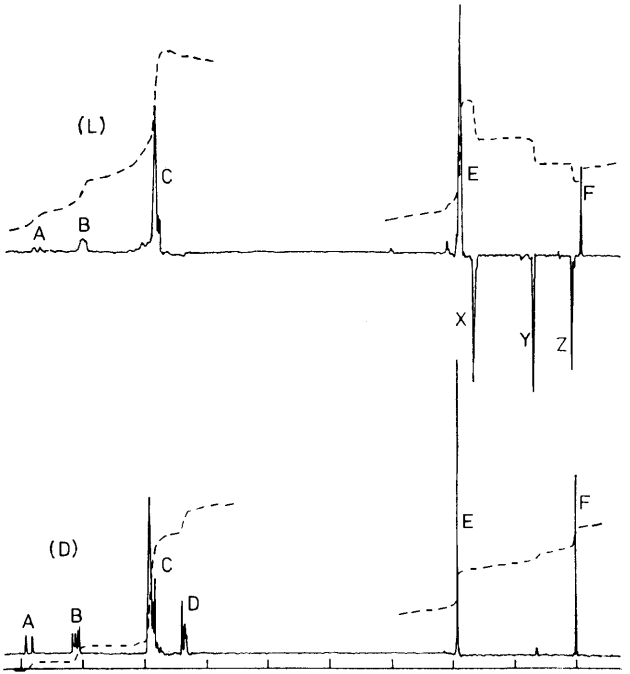


FIGURE 1 90 MHz ^1H Photo-CIDNP effects in 0.1M-2-$C_6H_5CONHC_6H_4SOCH_3$, in [$^2H_6$]benzene. (D), Dark spectrum; (L), light spectrum, obtained from 10 cycles of light (2 s), radio-frequency pulse, f.i.d. acquisition (see Experimental section). Assignment: A, 6-H; B, benzoyl-H, *ortho*; C, aromatic H and C_6HD_5 impurity; D, aromatic H; E, CH_3SO; F, Me_4Si. Products: Z, CH_4; Y, C_2H_6; X, CH_3S. Integration spectra (broken lines) are superimposed

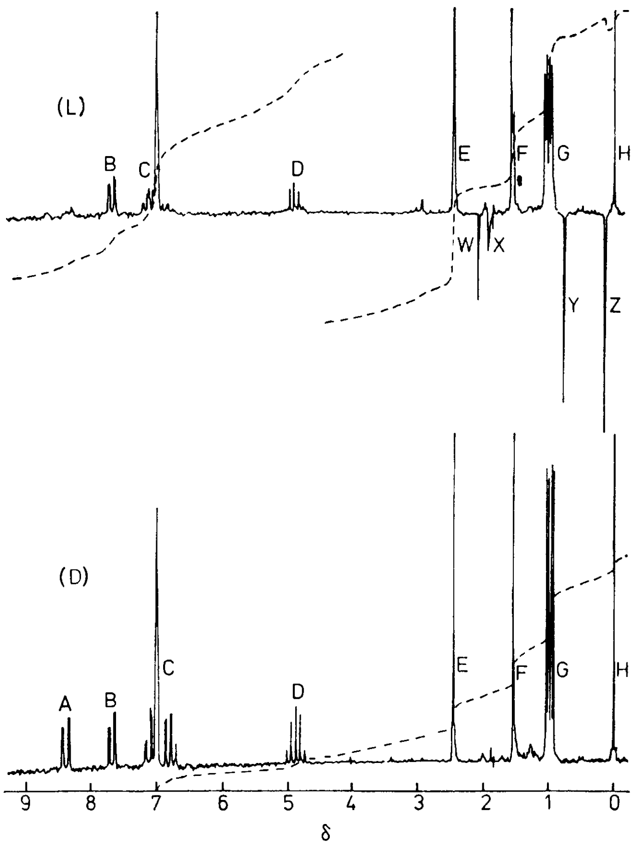


FIGURE 2 ^1H Photo-CIDNP effects in 0.1M-2-$Pr^iOCOC_6H_4SOCH_3$ in [$^2H_6$]benzene. See caption to Figure 1. (D), Dark spectrum; (L), light spectrum. Assignment: A, 6-H; B, 3-H; C, aromatic H and C_6HD_5 impurity; D, methine H; E, CH_3SO; F, impurity; G, methyl H; H, Me_4Si. Products: Z, CH_4; Y, C_2H_6; X, CH_3S; W, undetermined

The formation of methane and ethane and the polarization in both products and parent molecules clearly point out to a cleavage process of the methyl–arylsulphinyl C–S bond as the primary photochemical process in *ortho*-substituted aryl methyl sulphoxides R^1SOCH_3 where $R^1 = 2\text{-}XC_6H_4$.

$$R^1SOCH_3 \longrightarrow \underbrace{CH_3^{\bullet} + R^1SO^{\bullet}}_{\text{RP1}} \tag{2}$$

The analysis of the signs of the polarization in all the products nuclei (see Scheme 1) as well in those of the parent molecules according to the radical pair model of CIDNP [2] supports this conclusion and also provides detailed information on the different stages of the photochemical process.

The radical pair RP1 (we shall be concerned here with the electron spin correlated pairs $CH_3^{\bullet} + 2\text{-}XC_6H_4SO^{\bullet}$) in

TABLE 1

^{1}H 90 MHz Photo-CIDNP effects in *ortho*-substituted methyl phenyl sulphoxides (1) reacting by both direct excitation and by sensitization (triplet benzophenone, [$^2H_6$]benzene solution)

		Parent molecule			Products [a]			
Compound	X	MeSO–	6-H	Other aromatic protons	CH_4	C_2H_6	Me(S)	Other protons
(1a)	$4\text{-MeC}_6\text{H}_4\text{O}\underset{\overset{\|}{\text{O}}}{\text{C}}$	2.38(A) [b]	8.42d(E) [c] $J \sim 8$		E	E	1.87(E)	1.73, 2.09(E)
		2.8(A) [d]			E		2.18(E)	
(1b)	$(\text{Et})_2\text{N}\underset{\overset{\|}{\text{O}}}{\text{C}}$	2.58	(8.14) [e]		E		2.07(E)	
(1c)	$\text{Ph(Me)N}\underset{\overset{\|}{\text{O}}}{\text{C}}$	2.67(A)	8.0d(E)		E	E	2.07(E)	
(1d)	HOCH_2	2.21(A)	(7.73)		A [g] E [f]		1.89(E)	9.18(A) CHO 10.04(A) COOH [f]
(1e)	$\text{H}\underset{\overset{\|}{\text{O}}}{\text{C}}$	2.31(A)	8.26d(E)		E	E	2.07(E)	1.87(A)
(1f)	$\text{Ph}\underset{\overset{\|}{\text{O}}}{\text{C}}\text{NH}$	1.98(A)	9.78d(E) $J \sim 9$	6.3d(E) 3-H, $J \sim 5$	E	E	1.73(E)	2.91, 3.1(A)
(1g)	$\text{Ph}\underset{\overset{\|}{\text{O}}}{\text{C}}\text{OCH}_2$	2.14(A)	(7.91)		E	E	1.84(E)	3.6(E), 7.56(A) [h]
(1h)	$\text{Pr}^i\text{O}\underset{\overset{\|}{\text{O}}}{\text{C}}\text{–}$	2.4(A)	8.3d(E) $J \sim 9$	6.8t(E) 4-H	E	E	1.93(E)	2.07(E), 2.9(A)

[a] C_2H_6 = ethane protons; Me(S) = methyl protons of sulphide. [b] δ Values downfield from tetramethylsilane; J in Hz. [c] d = doublet, t = triplet, m = multiplet. [d] In $CDCl_3$. [e] Parentheses indicate absence of polarization. [f] By triplet benzophenone sensitization. [g] By direct excitation. [h] *ortho*-Protons of benzophenone.

A = Enhanced absorption, E = emission.

TABLE 2

^{1}H 90 MHz Photo-CIDNP effects in *ortho*-substituted methyl phenyl sulphoxides (1) reacting by sensitization (triplet benzophenone, [$^2H_6$]benzene solution) [a]

		Parent molecule			Products			
Compound	X	MeSO	6-H	Other aromatic protons	CH_4	C_2H_6	Me(S)	Other protons
(1i)	Ph	1.82(A)	8.3d(E) $J \sim 9$		E	E	1.7(E)	2.04(E), 2.18(A) 2.47(A), 3.13t(A) 3.47(E)
(1j)	$\text{Ph}\underset{\overset{\|}{\text{O}}}{\text{C}}\text{–O–}$	2.2(A)	(7.93)		E	E	2.07(E)	6.28—6.38 (E) 7.78—7.98(E)
(1k)	$2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{S}\underset{\overset{\|}{\text{O}}}{\text{C}}$	2.32(A) [b]	8.34d(E) $J \sim 8$	7.82d(E) $J \sim 8$	E	E	1.87(E)	1.96(E), 2.24(A)
(1l)	$\text{MeS}\underset{\overset{\|}{\text{O}}}{\text{C}}$	2.44(A)	8.31d(E) $J \sim 9$	6.79(E); 7.14(E)	E	E	1.71(E)	

[a] See footnotes to Table 1. [b] In the presence of 0.5M-benzophenone.

cases of both direct excitation and benzophenone sensitization is formed in a triplet spin state (μ +), as the results of sensitization by benzophenone (a well established triplet sensitizer[8]) are entirely analogous to those of the direct excitation. However the path preceding the formation of ^{3}RP1 $\overset{3}{\overline{(CH_3\cdot + 2\text{-}XC_6H_4SO\cdot)}}$ is different for the two modes of excitation, direct excitation leading into triplet state sulphoxide molecules $^3(2\text{-}XC_6H_4SOCH_3)$ by an intersystem crossing process.

In most of the benzophenone sensitized systems examined (1a—l) no significant nuclear polarization could be observed in the nuclei of the sensitizer, and in particular in the easily studied *ortho*-protons of benzophenone at δ *ca.* 7.6 (in C_6D_6). This observation is important as it indicates that benzophenone does not participate in the primary spin correlated radical pair RP1 but only provides the proper energy and electronic spin state. The limited polarization seen in benzophenone *ortho*-protons in a few systems (*e.g.* in the case of $4\text{-}CH_3C_6H_4SOCH_3$) seems to be due to a small contribution by another process.

Both the electron spin–nuclear spin hyperfine coupling constants and the electronic g factor for the two free radical components $CH_3^{\cdot}$ and $RC_6H_4SO^{\cdot}$ of radical pair RP1 are well known.[9,10] For $XC_6H_4SO^{\cdot}$ (X = H or

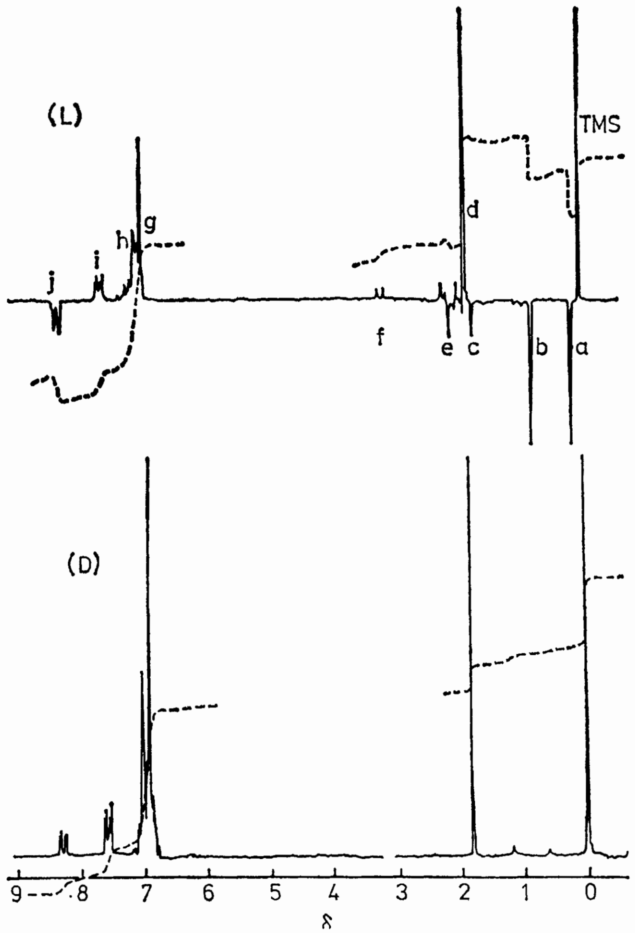


FIGURE 3 ^1H Photo-CIDNP effects in 0.1M-2-$C_6H_5C_6H_4SOCH_3$ in [$^2H_6$]benzene in the presence of 0.07M-benzophenone. See caption to Figure 1. (D), Dark spectrum; (L), light spectrum. Assignment: j, 6-H; i, benzophenone 2-H; h, C_6HD_5 and other aromatic H; d, CH_3SO. Products: a, CH_4; b, C_2H_6; c, CH_3S; e and f, undetermined

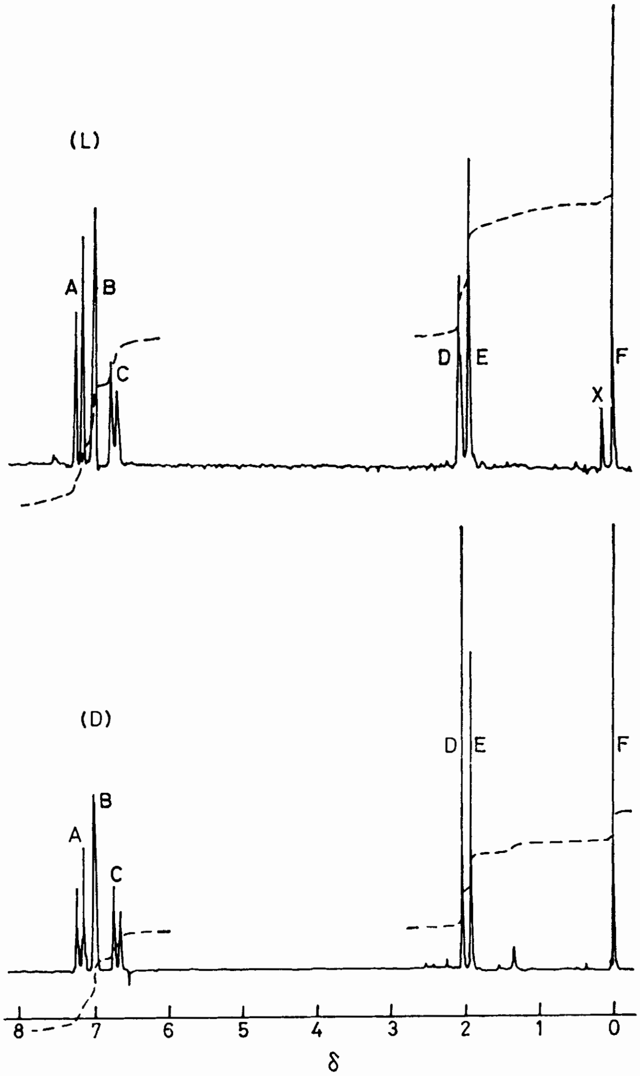
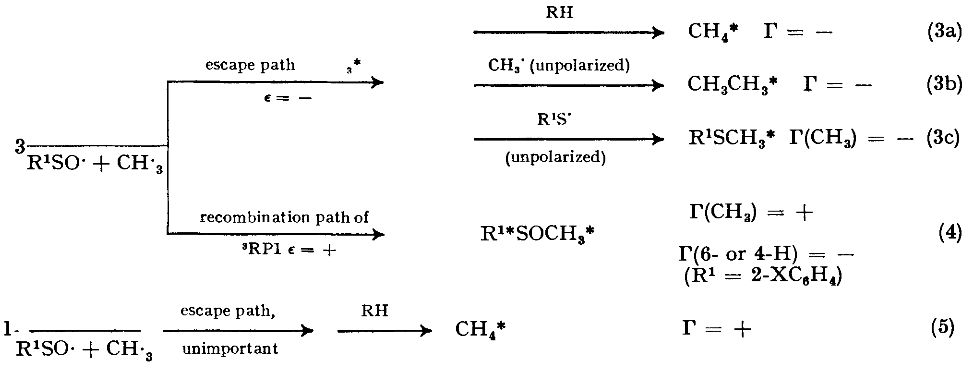


FIGURE 4 ^1H Photo-CIDNP effects in 0.1M-4-$CH_3C_6H_4SOCH_3$ in C_6D_6. (D), Dark spectrum; (L), light spectrum. See caption to Figure 1. Assignment: A, 2,6-H; B, C_6HD_5 impurity; C, 3,5-H; D, CH_3SO; E, 4-CH_3; F, Me_4Si. Product: X, CH_4

CH_3 in 2-, 3-, or 4-position or Cl in the 4-position) g is 2.0084—2.0092, A (*ortho*) is negative,[11] −2.3 to −3.2 G, and A (para) is −2.4 to −2.6 G. For CH_3, g is 2.003 and A −23.0 G.[10,11] It is thus possible to establish with certainty that for all the protons of $XC_6H_4SO^{\bullet}$ $\Delta g(XC_6H_4SO^{\bullet})$ is positive and $A_{\rm i}$ for the aromatic protons is negative. For the protons of the methyl radical in RP1 both $\Delta g(CH_3^{\bullet})$ and $A_{\rm i}$ are negative. The polarized methane, ethane, and methyl protons of the sulphide product are all formed through an ' escape ' path of RP1 (see Scheme 1). The polarized methane is formed by the abstraction of substrate hydrogen atoms by the polarized methyl radicals, the ethane by recombination of escaped polarized methyl radicals with other, already nuclear-spin relaxed methyl radicals, while the polarized aryl methyl sulphide is obtained by the reaction of nuclear-spin relaxed 2-$XC_6H_5S^{\bullet}$ radicals (see below) with polarized methyl radicals. For these three products $\Gamma = \mu\varepsilon\Delta g A_{\rm i} = + - - -$ is negative, as observed. In the presence of more efficient hydrogen atom donors (than the substrate or the solvent used, [$^2H_6$]benzene) the amount of polarized ethane decreases. Thus no ethane is formed in $CDCl_3$ solution or in the presence of the efficient hydrogen atom donors thiophenol or 4-methyl-2,6-di-t-butylphenol (*cf.* refs. 12*c* and *d*), and for the same reason no polarized 2-$XC_6H_4SCH_3$ is obtained in this solvent. The results of the direct excitation of (1a) in $CDCl_3$ solution are also of particular interest in another context: no ^2H splitting in the methane signal is seen which implies that there is a large deuterium isotope effect in the hydrogen atom abstraction by the methyl radical which favours the formation of CH_4 over that of CH_3D.

The recombination path of ^{3}RP1 is clearly evident from the polarization of the parent molecule methyl protons and 6-H (and other) ring protons observed in several of the molecules of Tables 1 and 2. The combined photochemical path leading to nuclear polarization in the 2-$XC_6H_4SOCH_3$ molecules is a virtual chemical path which



SCHEME 1

leads to the dissipation of electronic excitation energy and should be also considered as a possible path in some sulphoxides undergoing photoracemization. The signs of the polarization of the methyl and ring protons due to this path, *i.e.* $\Gamma = -$ for *o*- and *p*-aromatic protons, $\Gamma = +$ for methyl protons, are again in complete agreement with the conclusions of the RP model: for the methyl protons $\Gamma = \mu\varepsilon\Delta gA_i = ++ \; -- = +$, and for the ring 4- or 6-H, $\Gamma = +++ \; - = -$.

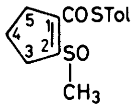
The Role of ortho-*Groups*.—Methyl phenyl sulphoxide, 4-substituted derivatives $4\text{-}XC_6H_4SOCH_3$ (X = CH_3 or Br), and several 2-substituted molecules $2\text{-}XC_6H_4SOCH_3$ (*e.g.* X = CH_3, Cl, NH_2, RO, CH_3CO, and a few others) are relatively inert to the photocleavage process. In these cases the triplet benzophenone sensitized path leads to a weak negative peak of polarized methane. The direct excitation path of these molecules is very inefficient, much as is the sensitized process, and in several instances leads to a weak negatively polarized methane ^1H signal which most probably originates from a triplet state molecule. In this sense the result obtained on direct excitation of $4\text{-}CH_3C_6H_4SOCH_3$ (Figure 4) are of particular interest. Here the CH_4 protons are positively polarized, most probably because the radical pair RP1 is formed in an initial singlet spin state from an excited singlet state sulphoxide molecule [see process (5) in Scheme 1].

The intensity of the enhanced absorption A of CH_4 in this case is increased in the presence of the hydrogen donors 4-methyl-2,6-di-t-butylphenol and thiophenol as would be expected for an escape product. The escape path is possible at all in such a case of singlet-born pair because of the stability (inertness) of the $XC_6H_4SO^{\cdot}$ radical.

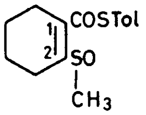
The strong enhancement of reactivity by many of the *ortho*-substituents as shown by the nuclear polarization effects in the products constitutes a clearcut case of a neighbouring group effect on the photochemical reactivity of sulphoxides. Several examples of such neighbouring group effects (but on ground state properties) have been described for suitably *ortho*-substituted alkyl phenyl sulphoxides.[13] In the present study, small *ortho*-groups with differing electron-releasing properties, such as methyl, amino, and chloro did not show any reactivity enhancement. Thus ' through bond ' transmitted electronic effects do not seem to influence strongly the dealkylation reactivity. However a ' through space ' interaction of a nearby polar group which could form a five- (or six-)membered ring structure by interaction with the sulphinyl group seems to be important. Several of these ring structures can be considered for many of the substituents of Tables 1 and 2.

II *Alk*-1-*enyl Sulphoxides*.—Two R^1SOCH_3 compounds of this type, a cyclopent-1-enyl sulphoxide (3) and the cyclohex-1-enyl sulphoxide (4) were found to give polarized photocleavage products by the triplet benzophenone sensitized path, as in the *ortho*-substituted methyl phenyl sulphoxides. The photo-CIDNP spectrum of (3), triplet sensitized by benzophenone ([$^2H_6$]benzene solution) is shown in Figure 5(L). Strong emission (E) is seen in the methane and ethane products as well as in the methyl protons of the sulphide R^1SCH_3 (3').

These three molecules are escape products of the polarized methyl radical from the triplet born radical pair ^{3}RP1. The polarization signs are as given in Scheme 1, paths 3 and 4.



(3)



(4)

(Tol = $4\text{-}CH_3C_6H_4$)

The recombination path of ^{3}RP1 is responsible for the enhanced absorption of the sulphinyl methyl of (3) (signal D in Figure 5L). This outcome is predicted by the RP model and establishes the cleavage path of (3), as recombination of the RP $\overset{3}{\overline{R^{1\cdot} + CH_3SO^{\cdot}}}$ would give a product with strong polarization at the C-3 and -5 cyclopentene protons. The chemical species responsible for signal W in Figure 5(L) has not yet been definitely determined. One possibility would be the coupling product $R^1SCH_2CH_2SR^1$. This could be a secondary product formed in the hydrogen atom abstraction by triplet benzophenone.[6] However the other typical product of the secondary photoreaction of sulphides,

$R^1SCH_2{}^*C(OH)(C_6H_5)_2$[6] is not observed. This result also leads to the conclusion that the $R^1SCH_3{}^*$ is formed in the primary photocleavage step.[6]

Compound (4), differing only in one additional ring methylene group is less reactive than (3). Benzophenone-triplet sensitization results in the formation of methane (E effect) but not of other polarized products.

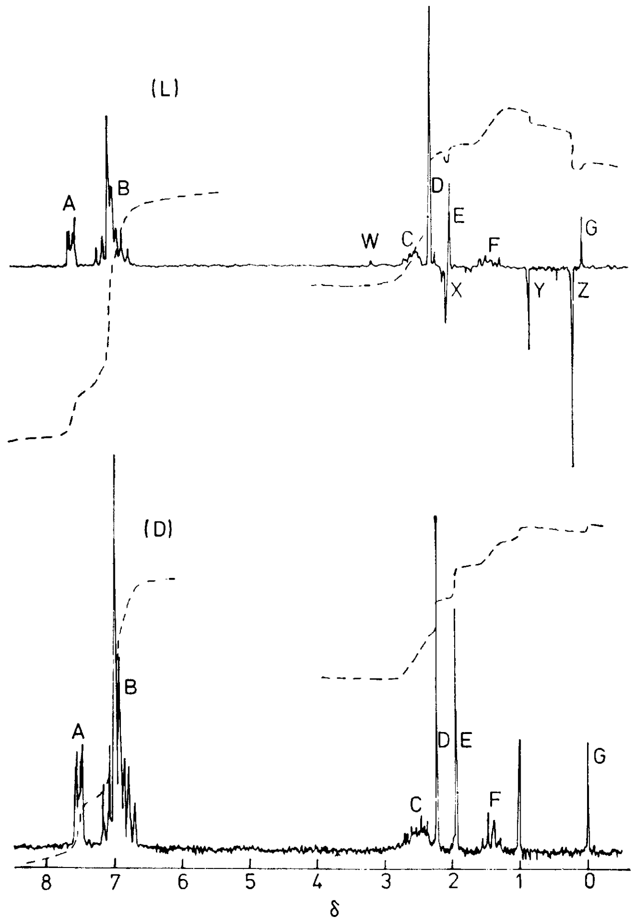


FIGURE 5 (L), 90 MHz Photo-CIDNP effects in 0.1M-(3) in [$^2H_6$]-benzene in the presence of 0.05M-benzophenone. See caption to Figure 1. (D), Dark spectrum. Assignment: A (δ 7.46—7.55), benzophenone *ortho*-H; B (δ 6.69—7.18), other aromatic protons, solvent; C (δ 2.37—2.70), methylene 3- and 5-H; D (δ 2.23), CH_3SO; E (δ 1.94), CH_3, tolyl; F (δ 1.28—1.54), methylene 4-H; G, Me_4Si. Products: Z (δ 0.18), CH_4; Y (δ 0.78), C_2H_6; X (δ 2.03), CH_3S; W (δ 3.10), not yet determined, probably SCH_2CH_2S

III *Alkyl Sulphoxides*.—The methyl–S bond cleavage is the preferred process only in compounds in which the methylsulphinyl group is attached to a C=C double bond or to an aromatic system. Figure 6(L) shows the effects in an alkyl methyl sulphoxide (5a), in which such structural elements are absent. The extent of polarized methane formation is minimal. The sulphinyl methyl protons of the substrate molecule (5a) are not affected, but the methylene protons on C-3 show an A effect while the methylene protons on C-2 have an E effect. This pattern is that predicted for a recombination product of the triplet-born RP2, in which the bond cleavage took place at the R^2–$SOCH_3$ bond.

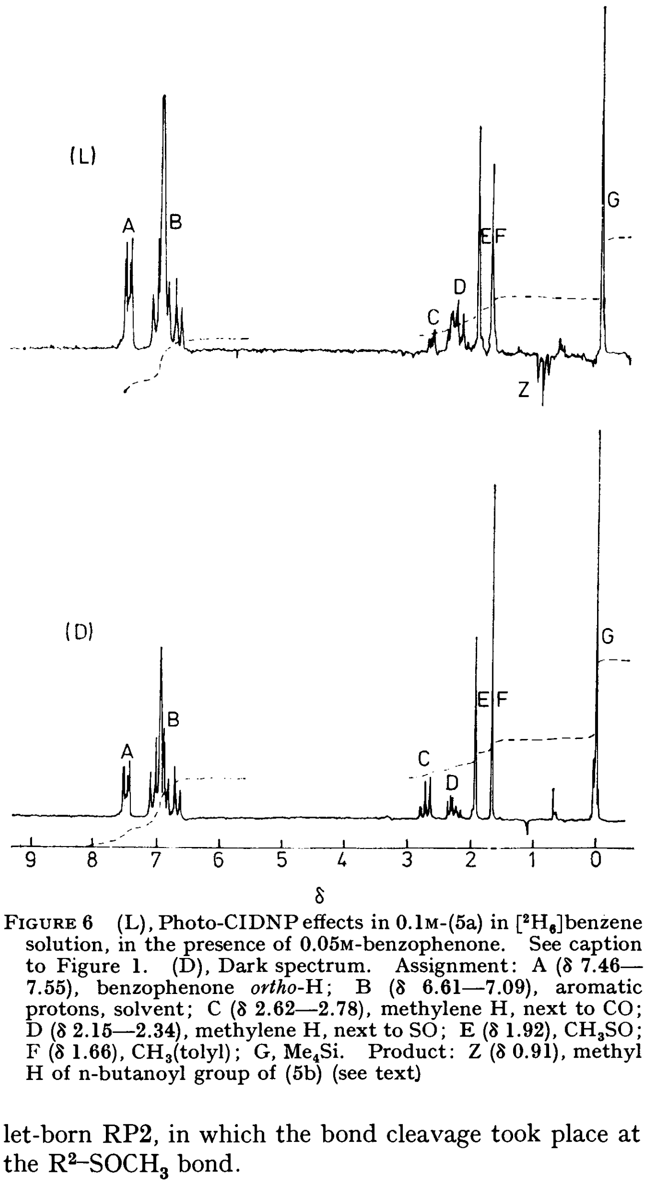
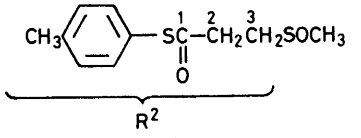
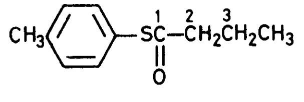


FIGURE 6 (L), Photo-CIDNP effects in 0.1M-(5a) in [$^2H_6$]benzene solution, in the presence of 0.05M-benzophenone. See caption to Figure 1. (D), Dark spectrum. Assignment: A (δ 7.46—7.55), benzophenone *ortho*-H; B (δ 6.61—7.09), aromatic protons, solvent; C (δ 2.62—2.78), methylene H, next to CO; D (δ 2.15—2.34), methylene H, next to SO; E (δ 1.92), CH_3SO; F (δ 1.66), CH_3(tolyl); G, Me_4Si. Product: Z (δ 0.91), methyl H of n-butanoyl group of (5b) (see text)

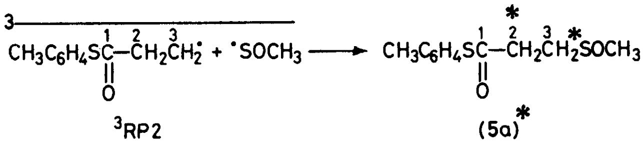
For the C-3 methylene protons in (5a)*, μ +, ε +, Δ*g* —, *A* —[9,11] leading to Γ = +. For the C-2 methylene



(5a)



(5b)



$$\overline{{}^{3}\,CH_3C_6H_4S\underset{\underset{O}{\|}}{\overset{1}{C}}-\overset{2}{C}H_2\overset{3}{C}H_2^{\bullet} + {}^{\bullet}SOCH_3} \longrightarrow CH_3C_6H_4S\underset{\underset{O}{\|}}{\overset{1}{C}}-\overset{*}{\overset{2}{C}}H_2\overset{3\,*}{C}H_2SOCH_3$$

^{3}RP2

(5a)*

protons, A is positive[9,11] so that $\Gamma = -$. The negatively polarized product protons (δ 0.9, triplet E) are assigned to the end-chain methyl group of *S*-4-methylphenyl thiobutyrate (5b). This chemical shift in [$^2H_6$]benzene as solvent is typical for such protons on an n-propyl group. These protons show a net E effect with possibly traces of multiplet effect[2] and the J value of 8 Hz (t) further supports their assignment to a (5b) type structure. The absence of the SO group taken together with a negative methyl ^1H polarization indicate that this is an escape product from RP3, formed by $R^2SO{-}CH_3$ bond cleavage.

$$R^2SOCH_3 \xrightarrow{^3(C_6H_5)_2CO} {}^3\overline{R^2SO^{\bullet} + CH_3^{\bullet}}\ (^3RP3 \qquad (7)$$

$$\xrightarrow{\text{(escape)}} CH_3^{\bullet *} + R^2SO^{\bullet} \xrightarrow{-SO} R^{2\bullet} \qquad (8)$$

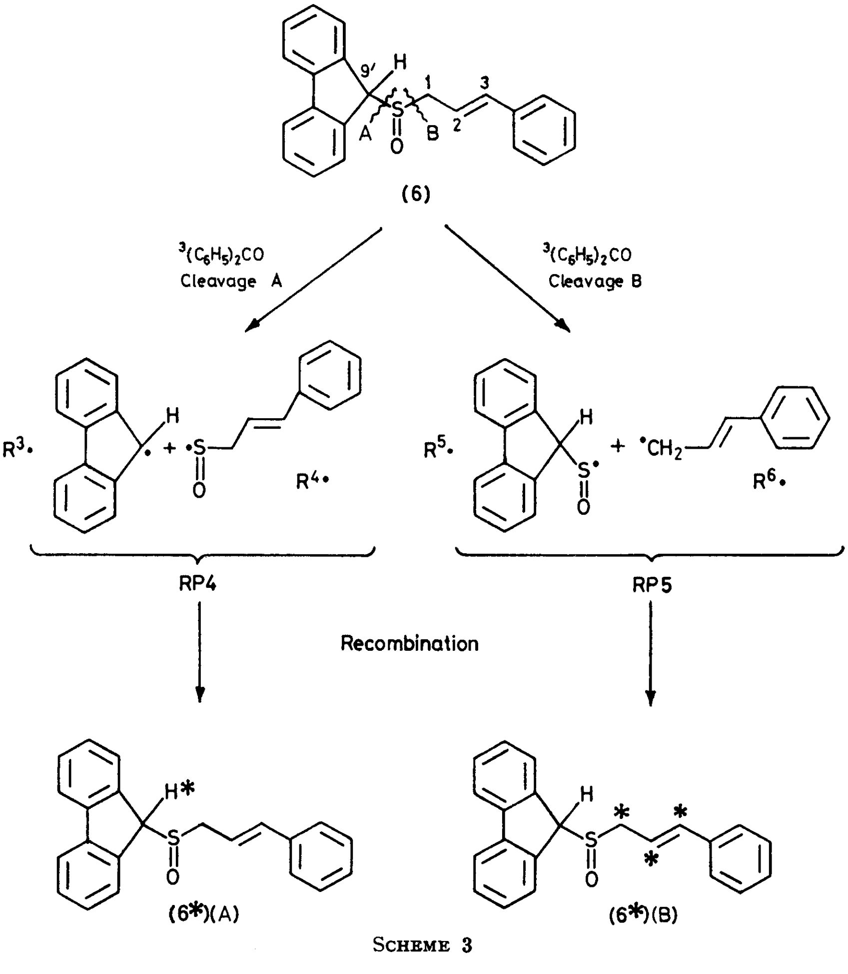
$$CH_3^{\bullet *} + R^{2\bullet} \longrightarrow R^2CH_3{*}\ (5b{*}) \qquad (9)$$

SCHEME 2

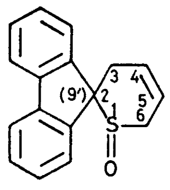
The loss of SO from $R^2SO^{\bullet}$ in reaction (8) should be fast as in this case (5b) is the only polarized product of the methyl group. On the other hand, the recombination from RP3 in (7) has to be slow enough in order to explain this process and the lack of polarization on the methyl protons of (5a). The elimination of SO in path (7)—(9) as observed for (5a) seems to be quite a rare process (*cf.* ref. 7*c*).

IV *The Allyl Benzyl System.*—A number of such systems, *e.g.* (6) (Scheme 3) and (7a—f), were examined for CIDNP effects by both direct excitation and by triplet benzophenone sensitization. The search for free radical paths in (7a—f) was of particular interest as they undergo uniformly by direct excitation in benzene solution a complex reaction which results in intramolecular hydrogen transfer as established by labelling [see (10)], migration of an oxygen atom, elimination of sulphur, and ring opening with formation of (8) and related compounds from (7a and c—f).[7c] Cinnamyl fluorenyl sulphoxide (6) was the only compound in these series which gave a clearcut indication for a free-radical path photoreaction (Figure 7L), but only by triplet benzophenone sensitization. Taken together with the existing data on free radical processes in sulphoxides (*cf.* refs. 5—7), this result indicates that reaction (10) and the corresponding process in (7a—f) is a concerted electrocyclic process (or rather several of these processes) and not a free radical reaction.

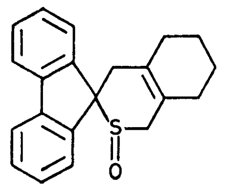
The photo-CIDNP results obtained for (6) indicate that in this molecule two C–S bond cleavage processes take place side by side: the fluorenyl–sulphinyl cleavage (A in Scheme 3) and the cinnamyl–sulphinyl cleavage (B in Scheme 3). Two triplet-born radical pairs, ^{3}RP4 and ^{3}RP5, are formed accordingly, the recombination



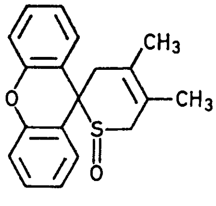
SCHEME 3



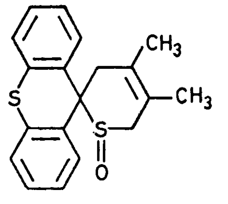
(7a)



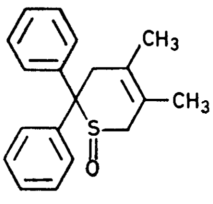
(7c)



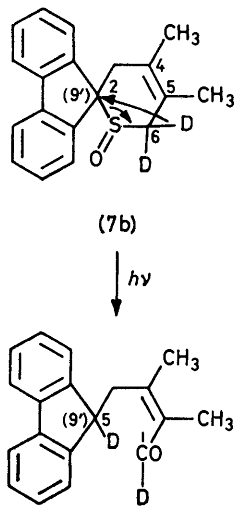
(7d)



(7e)



(7f)



(10)

(8)(*cis-trans* mixture)

path of which give rise to two different patterns of ^{1}H polarization in (6),† (6*)(A) and (6*)(B).

Polarization pattern (6*)(A) involves mainly an enhanced absorption effect on the benzyl proton 9'-H [A(9'-H) $-$,[11] $\Delta g(R^{3\cdot})$ $-$,[9] $\mu +$, $\varepsilon +$, $\Gamma +$]. As the effect on 9'-H is stronger than on 1-, 2-, or 3-H (see below), one is tempted to conclude that cleavage mode A is preferred to B, possibly because of a corresponding difference in the C-9'-S and C-1-S bond dissociation energies. This result would be in line with the course of reaction (10).[7c]

The polarization pattern (6*)(B) involves enhanced absorption effects on both 1- and 3-H, and an emission effect on 2-H [signals, G, D, and E, respectively in Figure 7(L)]. This pattern is the one expected for the recombination path of the allyl radical $R^{6\cdot}$ with an arylsulphinyl radical as in ^{3}RP5. For the recombination path of $R^{6\cdot}$ in ^{3}RP5 we have $\mu +$, $\varepsilon +$, $\Delta g -$. A is negative for both 1- and 3-H, but positive, because of negative spin density, for 2-H.[11b] Thus the RP model requires that Γ be positive for both 1- and 3-H but negative for 2-H for the recombination path of ^{3}RP5, in agreement with the experimental results of Figure 7(L).

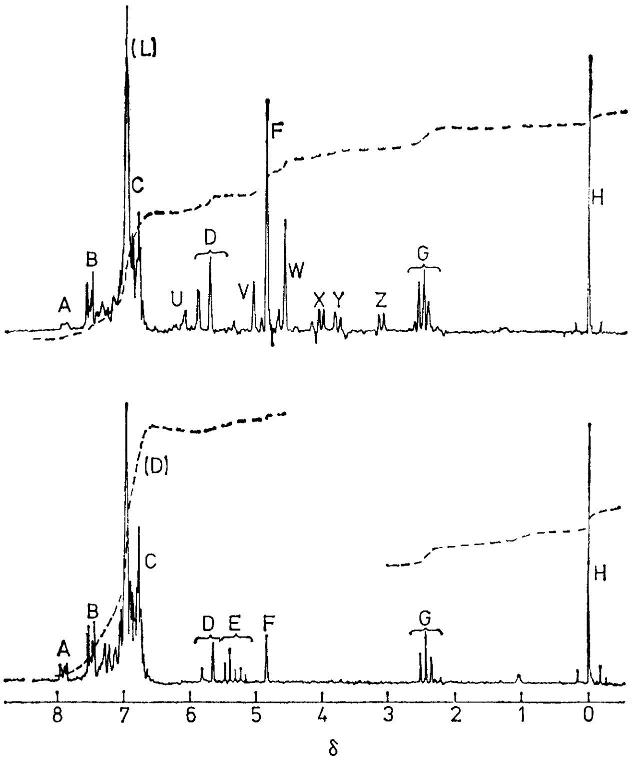


FIGURE 7. (L), Photo-CIP effects in 0.1M-(6) in [$^2H_6$]benzene solution, in the presence of 0.05M-benzophenone. See caption to Figure 1. (D), Dark spectrum. See also footnote on this page. Assignment: A (δ 7.84—7.92), aromatic protons; B (δ 7.46—7.55), benzophenone *ortho*-H, C (δ 6.72—7.25), other aromatic protons of (6), of benzophenone and solvent; D (δ 5.74), 3-H; E (δ 5.33), 2-H; F (δ 4.83), 9'-H, G (δ 2.44), 1-H; H, Me_4Si Products: U—Z

We have not considered up to now the CIDNP effects on 1-H in (6*)(A) and on 9'-H in (6*)(B). 1-H in $R^{4\cdot}$ as well as 9'-H in $R^{5\cdot}$ are β-protons (two bonds away from the free electron centre). For both, A is positive.[9] However Δg is also positive for both $R^{4\cdot}$ in ^{3}RP4 and for $R^{5\cdot}$ in ^{3}RP5. Therefore on this account both 1-H in (6*)(A) and 9'-H in (6*)(B) should also show enhanced absorption effects.

In addition to these two virtual photochemical paths,

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† The ^{1}H n.m.r. spectrum of (6) in a [$^2H_6$]benzene solution (Figure 7) warrants some special comments. Due to the chiral sulphinyl centre the two C-1 methylene protons are magnetically non-equivalent and give rise to an observable geminal coupling which is not observed (as it should be) in the corresponding non-chiral sulphide and sulphone molecules. In [$^2H_6$]benzene solution the C-1 methylene protons (signal G) appear as a 'deceptive simple' triplet because then δ(1-H) ~ δ(1-H'), J(geminal) ~ J(1,2), and the allylic coupling J(1,3) is small. {In [^{2}H]chloroform solution this degeneracy is removed and 1-H and 1-H' show the full structure of a 16 line multiplet, J(geminal) ~ 13, J(1,2) ~ 8, J(1,3) ~ 1.5 Hz and |δ(1-H) − δ(1-H')| at 100 MHz ~ 26 Hz}.[7c] The 3-H signal (D) is a doublet showing some broadening due to 1,3 coupling.

Table 3

270 MHz ^{1}H N.m.r. spectrum of (9a and b) in $CDCl_3$. Chemical shifts (δ) and spin–spin coupling constants (J) for olefinic and aliphatic protons

	(9a)			(9b)		
Proton	δ [a]	δ(calc.) [b]	J/Hz	δ	δ(calc.) [b]	J/Hz
1-H, 1-H′	3.57 (m)		1-H, 1-H′ 13 1-H, 2-H 7 1-H′, 2-H 7	3.42 (d), 3.81 (d)		1-H, 1-H′ 13
2-H	5.43 (dt)	5.96	2-H, 3-H 18 2-H, 1-H 7 2-H, 1-H′ 7			
3-H	6.17 (d)	6.41	3-H, 2-H 18	5.8 (d)	6.13	3-H, 4-H 10
4-H				6.51 (dt)	6.49	4-H, 5-H′ 17 4-H, 3-H 10 4-H, 5-H 10
5-H	4.94 (s)	4.98		5.14 (t)	5.20	5-H, 5-H′ 10 5-H, 4-H 10
5-H′	4.99 (s)	4.99		5.12 (dd)	5.27	5-H′, 5-H 10 5-H′, 4-H 17
$2-CH_3$				1.82 (s)		
$4-CH_3$	1.78 (s)					

[a] s = Singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet. [b] According to ref. 15.

Figure 7L indicates the formation of nuclear polarized products (signals U—Z). These products have not been yet identified. Comparison with authentic samples rules out the escape products R^3H, $R^3–R^3$, R^3SR^6, and $R^3SO_2-R^6$, while R^6H is excluded on other grounds.

V *The Penta-*2,4-*dienyl System.*—The sample of 4-methylpenta-2,4-dienyl phenyl sulphoxide (9a) used [*,14] was shown by 270 MHz ^{1}H n.m.r. to contain *ca.* 20% of the 1,5-rearrangement product (9b). The interpretation of the ^{1}H 270 MHz spectra of both isomers is given in Table 3.

The CIDNP results [Figure 8(L)] show that this is certainly a complicated photochemical system. The strong CIDNP effects undoubtedly reflect a significant photochemical reactivity, and the large number of polarized signals indicates that several free radical processes take place in parallel. In light of the results for the other systems the gross features of the free radical reactivity here seem to be clear even though a complete interpretation of the photo-CIDNP effects has to await, *inter alia*, the results of a detailed photoproduct study. Thus in Figure 8(L) signals E, F, H, J, X, and K of the pentadienyl protons of (9a and b) show a significant enhancement (A effect). The enhancement of signals E, J, and K is due to the recombination path of the triplet-born radical pair ^{3}RP6, while the enhanced signals F, H, and X would arise from the recombination in ^{3}RP6′.

The enhanced absorption in the protons of (9a and b) at C-1, -3, and -5 is accounted for in the usual way: μ and ε are both positive and Δg is negative for $RZ_1^{\bullet}$ and $RZ_2^{\bullet}$. In the odd–alternant pentadienyl π-system, the sign of the hyperfine constant is negative for protons on the starred set of π centres.[10,11] Thus A is negative for the C-1, -3, and -5 protons and therefore for these Γ is positive in the product of the recombination path, in agreement with the experimental results. The protons attached to carbons of the unstarred set of (9a and b), 2- and 4-H, have a positive A. These should appear in emission (Γ —). Indeed several emission signals can be

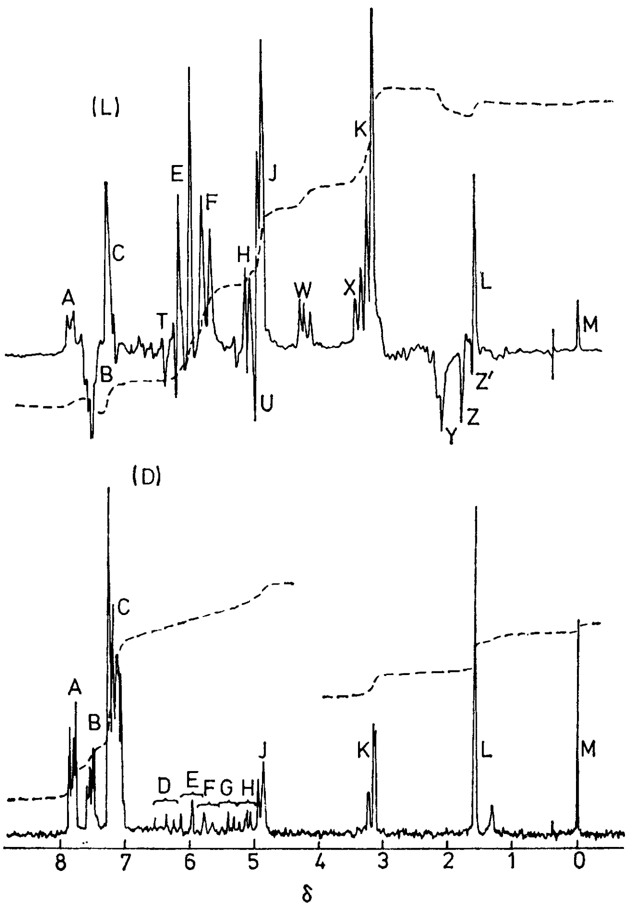

FIGURE 8 (L), Photo-CIDNP effects in 0.1M-(9a) in [$^2H_6$]benzene solution, in the presence of 0.05M-benzophenone. See caption to Figure 1, text, and Table 3. (D), Dark spectrum. (9a): B (δ 7.41—7.58), 2′- and 6′-H; E (δ 5.96—6.13), 3-H; G (δ 5.22—5.47), 2-H; J (δ 4.84—4.93), 5-H; K (δ 3.13), 1-H; L (δ 1.60), $4-CH_3$. (9b): D, F, H, X. M, Me_4Si A, Benzophenone *ortho*-H. Products, unidentified, T, U, W, Y, Z

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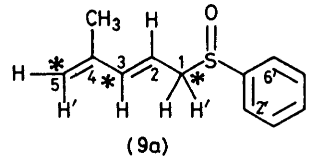
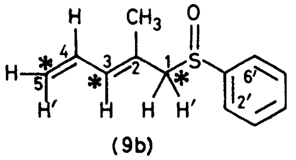
[*] We are greatly indebted to Professor Y. Gaoni, Department of Organic Chemistry, The Weizmann Institute, Rehovot, for providing a sample of this compound.

seen in Figure 8(L) which correspond to sets D and E in the dark spectrum of Figure 8(D).

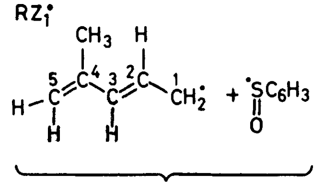
The present considerations indicate that on account of their negative sign in Figure 8(L), signals Y, Z, and Z′ cannot be due to the 2-methyl protons in the recombination product from $RZ_2^\bullet$. In this case the β-hyperfine interaction because of the hyperconjugative mechanism would result in a negative *A* for these protons. Interestingly enough, the 1,3-sigmatropic rearrangement product of (9a) [or (9b)], 2-methyl-1-vinylprop-2-enyl phenyl sulphoxide (10) has not been observed, even as a nuclear polarized species.



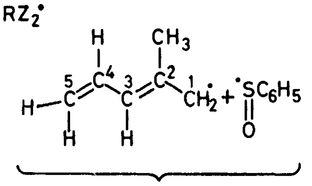
(9a)



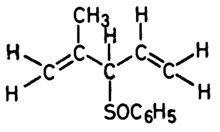
(9b)



RP6
(from 9a)



RP6′
(from 9b)



(10)

VI 270 MHz *Photo-CIDNP Study of the* 4-*Methylpenta*-2,4-*dienyl Sulphoxide*.—Following the completion of the 90 MHz photo-CIDNP work, the same system {(9a), benzophenone photosensitization, [$^2H_6$]benzene solution} was re-examined using our very recently developed 270 MHz photo-CIDNP setup.* The results obtained are shown in Figure 9. The light intensity available at the sample is lower in this setup than that obtained with the optical system of the 90 MHz spectrometer.[12] For this reason fewer product photo-CIDNP signals are observable than at 90 MHz. The assignment of the proton photo-CIDNP signals of (9a and b) is now unambiguous and in complete agreement with the interpretation of the previous section. In (9a), 3-H (signal E), 5-H, and 5-H′ (signal J) show strong enhancement, while 2-H (signal G) appears in emission. In (9b), 3-H (signal F) and 5-H and 5-H′ (signal H) show enhanced absorption while 4-H (signal D) shows indication of negative polarization. B, the aromatic 2′-, 6′-protons signal of (9a) [and (9b)], appears in emission. K and X, the methylene 1-H and 1-H′ signals of (9a and b), respectively, appear in enhanced absorption.

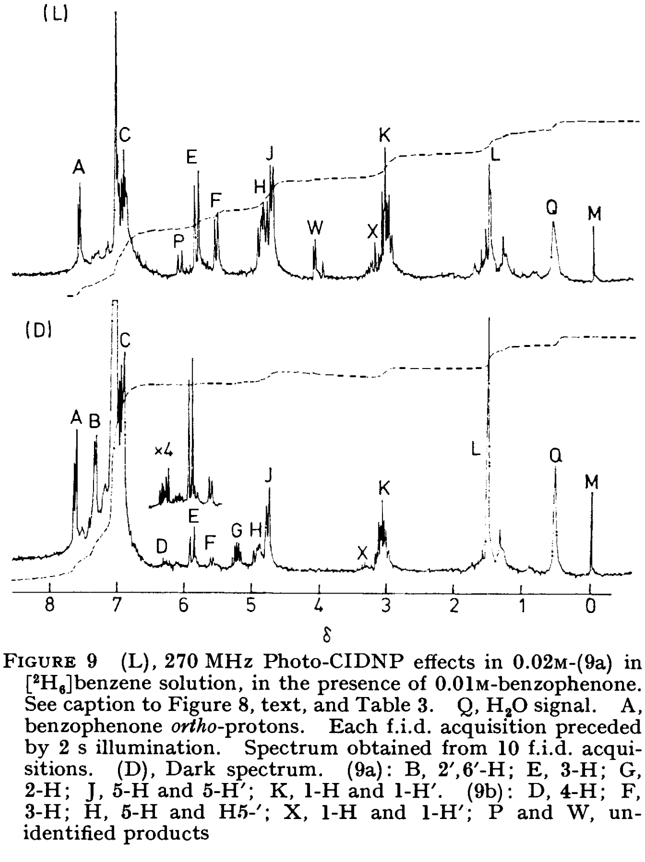


FIGURE 9 (L), 270 MHz Photo-CIDNP effects in 0.02M-(9a) in [$^2H_6$]benzene solution, in the presence of 0.01M-benzophenone. See caption to Figure 8, text, and Table 3. Q, H_2O signal. A, benzophenone *ortho*-protons. Each f.i.d. acquisition preceded by 2 s illumination. Spectrum obtained from 10 f.i.d. acquisitions. (D), Dark spectrum. (9a): B, 2′,6′-H; E, 3-H; G, 2-H; J, 5-H and 5-H′; K, 1-H and 1-H′. (9b): D, 4-H; F, 3-H; H, 5-H and H5-′; X, 1-H and 1-H′; P and W, unidentified products

VII *Photocleavage Reactivity of Sulphoxides*.—The photo-CIDNP data available thus far (present paper and refs. 5 and 6) indicate that the photocleavage of sulphoxides follows closely general ground-state reactivity trends. As expected the aryl–sulphinyl and vinyl–sulphinyl C–S bonds, being part of heterobenzylic or heteroallylic systems are much less susceptible to photocleavage than are the corresponding bonds of the methyl, benzyl, allyl, and pentadienyl sulphoxides. This fact is in agreement with the greater bond dissociation energies of the C–sulphinyl bond in the former group, a result of bonding $2p_z(C)$–$3d_{z'}(S)$ (and other) orbital interactions. The CH_3–SO bond dissociation energy $D(CH_3–SO)$ is estimated as *ca.* 55 kcal mol^{-1},[16] while in $(C_6H_5)_2SO$ *D* is 66 kcal mol^{-1}.[16] However, in the benzyl, allyl, and pentadienyl sulphoxides the respective bond dissociation energies are lower than the $D(CH_3–SO)$ value by the extra stabilization energy specific to each system. This can be best seen by comparison with the corresponding sulphones for which bond dissociation energy estimates are available,[16] *i.e.* $D(CH_3SO_2–CH_3)$

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* This setup consists of a Bruker WH 270 spectrometer provided with the standard 5 mm ^1H probe. The light source is a 5 000 W Hg–Xe lamp. A quartz optical system is used. The i.r. component is filtered out with a 150 mm long water cell. Light is admitted to the sample region along the magnet axis, through a vertical light guide. The light guide is connected rigidly to the sample cell which is rotated at the usual rate (K. A. Muszkat and I. Khait, in preparation).

68, $D(CH_3SO_2{-}CH_2CH{=}CH_2)$ 55, $D(CH_3SO_2{-}CH_2C_6H_5)$ 56, and $D(CH_3SO_2{-}C_6H_5)$ 83 kcal mol^{-1}. Thus the allyl, benzyl, and pentadienyl groups promote photocleavage reactivity as would be expected for such systems. Some independent evidence for the above mentioned difference of bond dissociation energies may be had by comparing the bond lengths in the two groups, *e.g.*, in dimethyl sulphoxide the C–S bond length is 1.82 Å [17a] compared to 1.7 Å in diphenyl sulphoxide.[17b] The recombination–escape competition of the radical pair $^3\overline{R^\cdot + R^1SO^\cdot}$, much as the photocleavage process, is determined by bond dissociation energy considerations (though other factors such as diffusion coefficients play here an important role). Thus the hydrogen atom abstraction by an escaping methyl radical is much faster [$D(CH_3{-}H)$ 104 kcal mol^{-1}] than the corresponding process of the allyl radical [$D(CH_2{=}CHCH{-}H)$ 85 kcal mol^{-1}], the benzyl radical (same D), or the pentadienyl radical [$D(C_5H_7{-}H)$ 80 kcal mol^{-1}].[16c] The bimolecular recombination of the escaped methyl radical is similarly preferred over the corresponding processes of the other radicals because of the significantly larger D of the newly formed C–C bond. These seem to be the factors responsible for the lack of polarized hydrocarbon escape products in the triplet sensitized photocleavage of cinnamyl fluorenyl sulphoxide (6).

VIII *The Sensitization–Excitation Process*.—The triplet energy transfer process by itself should not result in nuclear polarization (due to the radical pair mechanism) in the benzophenone nuclei proper. This is indeed observed for the methyl phenyl sulphoxides of Tables 1 and 2 and for the reactions of (3), (5a), (6), and (9a).

The formation of the triplet-born radical pair $^3\overline{R^\cdot + R^1SO^\cdot}$ by triplet benzophenone sensitization can proceed by two different mechanisms, (a) by energy transfer to form first the triplet state of the sulphoxide [reactions (11) and (12)] or (b) by direct formation of the radical pair, without going through the sulphoxide triplet state [reaction (13)], a process which also obeys the electronic spin conservation rules.

$$^3(C_6H_5)_2CO + RSOR^1 \longrightarrow {}^3RSOR^1 + (C_6H_5)_2CO \quad (11)$$

$$^3RSOR^1 \longrightarrow {}^3\overline{R^\cdot + R^1SO^\cdot} \quad (12)$$

$$^3(C_6H_5)_2CO + RSOR^1 \longrightarrow (C_6H_5)_2CO + {}^3\overline{R^\cdot + R^1SO^\cdot} \quad (13)$$

Whenever the triplet energy of the sulphoxide is above 69 kcal mol^{-1} (the triplet energy of benzophenone) [8] path (13) is still possible as for methyl sulphoxides and for the other sulphoxides examined in the present paper, for which $D(CH_3{-}SO) \leq$ 55 kcal mol^{-1}, as discussed above.

IX *Singlet* versus *Triplet Reactivity*.—The results obtained with methyl 4-methylphenyl sulphoxide (*i.e.*, A effect on CH_4* by direct excitation, E effect by triplet sensitization) point out to an interesting duality of photoreactivity in the two spin states, which extends through all the photoreactions of sulphoxides.[18-21] Thus singlet state reactivity is indicated for dimethyl sulphoxide [22] while the triplet state is involved in the photoprocesses of many other systems.[20,21]

The methyl phenyl sulphoxides (1i—l) as well as compounds (3) and (4) are systems in which singlet–triplet intersystem crossing rates play a critical role in determining the reactivity of sulphoxides to C–S bond cleavage. These compounds are inert by direct excitation but react readily (*cf.* Figure 3) by triplet benzophenone excitation. It seems thus that in these cases intersystem crossing is too inefficient and only triplet energy transfer can lead to significant reaction rates.

The recently observed strong facilitating effect of the 4-methylthio-group [6b] on the sulphoxide C–S bond cleavage could be due to the operation of the same factor. By its increase of spin–orbit coupling this group would enhance the rate of singlet–triplet intersystem crossing to an extent sufficient to result in a reactivity similar to that of the most reactive compounds of Tables 1 and 2.

X *The Oxygen Transfer Process in Sulphoxides*.—The photochemical conversion of sulphoxides to sulphides has been observed in the dialkyl, alkyl aryl, diaryl, and in cyclic compounds.[18b,19,20,22] Little information is available about this process and the oxygen receiving species is often unknown. Sulphones,[22] alcohols, and ethers have been however detected in some systems.[20,21] In some 2-substituted phenyl sulphoxides $2\text{-}RC_6H_4SOCH_3$ (R = CHO or $COXC_6H_4CH_3$, X = O, S, or Se) an intramolecular mechanism for oxygen transfer could be deduced in the previous investigation.[7a,h]

The present study provides a rather detailed picture of several of the aspects concerning this reaction.

As mentioned above, the methyl protons of the 2-substituted thioanisoles (2a—l) and of the methyl vinyl sulphide product (3′) are all negatively polarized. The aromatic protons of (2a—l) and the vinyl protons of (3′) are unpolarized. This finding leads to the conclusion that the sulphide is formed as an immediate result of the primary photochemical event, by the escape path of RP1. This path is favoured by the relative inertness of the aryl- and alkenyl-sulphinyl radicals $R^1SO^\cdot$ [*,9] and by the triplet spin state of the radical pair. The escaped sulphinyl radical transfers the oxygen atom and loses its nuclear polarization and then recombines with a polarized methyl radical to give the corresponding methyl sulphide derivative R^1SCH_3. Thus the present study shows that the deoxygenation process actually involves a sulphinyl radical and is certainly not [at least for molecules (1a—l) and for (3)] an electrocyclic process of the intact singlet ground state molecule. Also, the parallel study of the photo-CIDNP effects in benzophenone triplet sensitized photoreactions of the R^1SCH_3 compounds (2a—l) and (3′) [6] leads us to conclude that the

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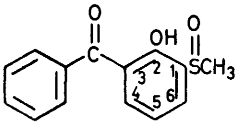
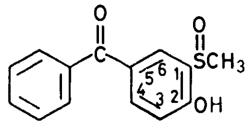
[*] Our e.s.r. results indicate that the $2\text{-}Et_2NCOC_6H_4SO^\cdot$ radical formed photochemically from (1b) is moderately stable in 2-methyltetrahydrofuran solution at 150 K. Its g factor is 2.0092.

observed polarization in the methyl nuclei of the sulphide molecules is not obtained in another secondary photochemical process, involving hydrogen atom transfer between triplet benzophenone and an aryl or vinyl methyl sulphide. This process is known [6] and always leads to *three* polarized signals originating from the sulphide methyl protons, (a) the benzophenone–sulphide addition compound, $R^1SCH_2{}^*COH(C_6H_5)_2$ (E), (b) the sulphide 'dimer' $R^1SCH_2{}^*CH_2SR^1$ (A), and (c) the methyl sulphide, $R^1SCH_3{}^*$ (E). In the present case both (a) and (b) are not observed, pointing to the primary origin of the sulphide methyl polarization.

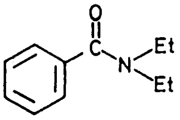
XI *Other Photochemical Processes of Sulphoxides*.—The photo-CIDNP study of compounds (1a—l) indicates that in addition to methyl-sulphinyl cleavage and to deoxygenation other free radical photochemical processes may at times be of importance. Thus the irradiation of (1j) ($X = C_6H_5CO_2{}^-$) in the presence of benzophenone leads to new signals, at δ 6.4 and δ 6.6, in emission. As no new aliphatic proton signals related to these appear, the photo-Fries rearrangement products (1ja and 1jb) (*cf*. refs. 7*a* and 23) seem to be a tentative possibility. In $[^2H_6]$benzene solution the chemical shift of 5-H in (1ja) is δ 6.6 (t, *J* 8 Hz). The observed negative polarization would be expected for 5-H in a recombination product of a triplet-born radical pair of phenoxyl and benzoyl radicals (μ +, ε +, Δ*g* +, A_5 −).



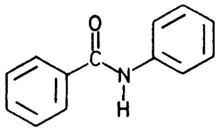
(1ja)



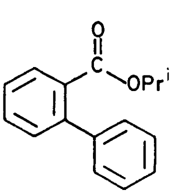
(1jb)



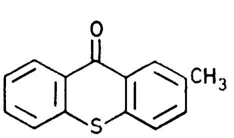
(11b)



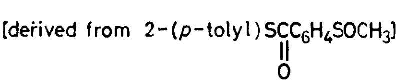
(11f)



(11h)



(11m)



$[\text{derived from 2-(}p\text{-tolyl)S}\underset{\underset{\displaystyle O}{\|}}{C}C_6H_4SOCH_3]$

A number of products (11) [(11b, f, h, and m)] which formally would be obtained by an aryl–sulphinyl bond cleavage have been previously observed.[7a,h] However, the path leading to these products could not be identified by photo-CIDNP nor could clearcut evidence be obtained by n.m.r analysis for possible methylsulphinyl group end-products such as CH_3SCH_3 or CH_3SSCH_3 (δ 1.82 and δ 2.06, respectively, in C_6D_6).

EXPERIMENTAL

The 90 MHz ^1H photo-CIDNP measurements were carried out in the Fourier transform mode on a Bruker HFX-10 spectrometer. The optical irradiation set up used (2 500 W Hg–Xe lamp, quartz lenses system, 50 cm long quartz light guide) was the same as in previous studies.[3,5,12] A quartz water filter for removing the i.r. radiation (8 cm path length) was used, followed by an electromagnetic shutter. The spectra were obtained from the accumulation of 8—16 free induction decay (f.i.d.) measurements. The photo-CIDNP results were obtained by a light-radiofrequency pulse–f.i.d. acquisition sequence (*cf*. ref 24). The duration of the optical irradiation (light) period in each cycle was usually 2 s. The operation of the whole setup (*i.e*., shutter, radiofrequency transmitter, f.i.d. acquisition) was controlled by a multi-trigger unit. Similar results (with slightly higher extents of polarization) could be obtained in several cases by continuous optical irradiation. Most measurements were carried out on non-deaerated 0.1M solutions of the compounds in $[^2H_6]$benzene. Tetramethylsilane was used as the chemical shift standard. Benzophenone was usually at 0.05—0.02M concentrations. For typical optical absorption spectra of sulphoxides, see ref. 25. The concentration of benzophenone in the sensitization experiments was adjusted so that the near u.v. region of the lamp emission would be almost completely absorbed by the sensitizer. In Figures 1—9, D denotes the dark spectrum, L the photo-CIDNP spectrum. The compounds were prepared as described previously, *e.g*. (1a—l), refs. 7*a*, *h*; *S*-4-methylphenyl 2-(methylsulphinyl)cyclopentanethiocarboxylate (3) and S-4-methylphenyl 3-(methylsulphinyl)thiopropionate (5a), ref. 7*a*; *S*-4-methylphenyl 2-(methylsulphinyl)cyclohex-1-enethiocarboxylate (4), ref. 7*d*; α-cinnamyl fluoren-9-yl sulphoxide (6) and *cis*- and *trans*-4-(fluoren-9-yl)-2,3-dimethyl$[1,5\text{-}^2H_2]$but-2-enal (8), ref. 7*c*; 3′,6′-dihydrospiro-(fluorene-9,2′-2*H*-thiopyran) 1′-oxide (7a), ref. 7*e*; 3′,6′-dihydro-4,5′-dimethylspiro(fluorene-9,2′-$[6,6\text{-}^2H_2]$-2*H*-thiopyran) 1-oxide (7b), ref. 7*g*; 3,4,5,6,7,8-hexahydrospiro-(1H-2-benzothiopyran-3,9′-fluorene) 2-oxide (7c), 3,6-dihydro-4,5-dimethylspiro(xanthen-9,2′-2*H*-thiopyran) 1-oxide (7d), 3,6-dihydro-4,5-dimethylspiro-(2*H*-thiopyran-2,9′-thioxanthen) 1-oxide (7e), 3,6-dihydro-4,5-dimethyl-2,2-diphenyl-2*H*-thiopyran 1-oxide, (7f), ref. 7*e*.

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