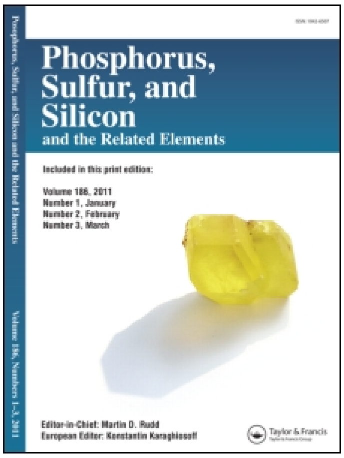

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PHOTOCHEMICAL C-S BOND CLEAVAGE IN METHYL ARYL SULFIDES AND SULFOXIDES. A CIDNP STUDY OF REACTIVITY ENHANCEMENT BY METHYLTHIO GROUPS.[1]

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PHOTOCHEMICAL C—S BOND CLEAVAGE IN METHYL ARYL SULFIDES AND SULFOXIDES. A CIDNP STUDY OF REACTIVITY ENHANCEMENT BY METHYLTHIO GROUPS.[1]

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Proton photo CIDNP studies indicate that ring substitution of the methylthio group in methyl phenyl sulfoxide or in methyl phenyl sulfide results in a strong enhancement of the methyl-S bond cleavage reactivity. In sulfoxides bond cleavage originates from the triplet state born radical pair ^{3}RP1 ($\overline{^3\mathrm{ArSO}^{\cdot} + \mathrm{CH}_3^{\cdot}}$) formed by direct excitation or by ketone triplet sensitization. Strong emission is observed in the methyl protons of the escape products of ^{3}RP1, CH_4, C_2H_6 and $ArSCH_3$. The polarization in the sulfide product establishes that photodeoxygenation of sulfoxides takes place in the arylsulfinyl radical following the C—S photocleavage step. The collapse path of ^{3}RP1 (giving back the parent molecule) is readily recognized, giving rise to enhanced absorption in the methyl protons of the methylsulfinyl group and emission in the ring protons ortho to that group. In the di(methylthio) benzenes C—S bond photocleavage has now been clearly established giving rise to polarized ethane and methane by the escape path.

INTRODUCTION

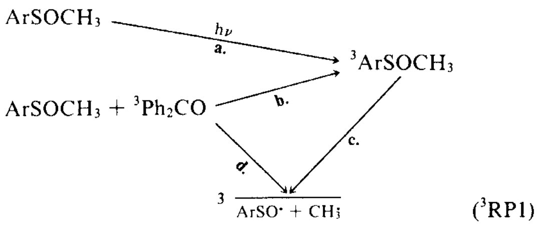
As shown earlier,[2-4b] free radical paths in sulfur photochemistry[5] are directly amenable to investigation by the CIDNP[6] method which is product specific and usually can provide significant mechanistic information. In addition, CIDNP studies are also of direct relevance to the characterization of the complementary concerted electrocyclic counterparts of free radical paths. Thus far, among the free radical paths of photoreactions of organo-sulfur compounds we have investigated the photodecarboxylation of arylthioacetic acids[2] and the carbon-sulfur photocleavage process.[3,4b] Concerning this last process we have recently observed large variations in the C—S bond photocleavage reactivity in sulfoxides.[3,4b] In the common case, as in methylphenylsulfoxide and in its 4-substituted derivatives $ArSOCH_3$, the C—S bond photocleavage is a very inefficient process which can be detected by ^{1}H NMR through the formation of trace amounts of polarized methane (CH_4^*). This product is obtained from the escape path of the triplet state born (and electron spin correlated) radical pair $^3\overline{\text{ArSO}^{\cdot} + \text{CH}_3^{\cdot}}$(^{3}RP1). The free radical photochemical paths of the photoreactive sulfoxides (see below) are summarized in Scheme 1. Step (1) of Scheme 1 takes place on triplet sensitization while direct excitation (whenever effective) leads to photocleavage from both triplet- or singlet-state born radical pairs, through the escape paths of ^{3}RP1 or ^{1}RP1.

We have observed a considerable enhancement of the triplet state C—S bond photocleavage reactivity in the following special classes of sulfoxides:

A. *Ortho-substituted methyl-phenyl sulfoxides,* 2-X-$C_6H_4SOCH_3$, e.g., X = —COOR, —CONHR, —CONR$_1$R$_2$, —NHCOR, —CHO, and —C_6H_5.[3,4b] In these compounds escape path (1a) leads to the formation of methane in considerable yields and with a large nuclear polarization. Proton polarized ethane is also formed by escape path (1b) as are the corresponding methyl-polarized methylsulfides 2-X-$C_6H_4SCH_3^*$, obtained by scavenging of $CH_3^{\cdot *}$ by thiyl radicals 2-X-$C_6H_5S^{\cdot}$ (path 1c) formed in the deoxygenation process of the arylsulfinyl radicals.

However, in addition to the escape paths (1a–1c) these molecules show also evidence for a significant extent of recombination in ^{3}RP1, leading to methyl- and ring-polarized $ArSOCH_3$ (path 2). The whole degenerate photochemical cycle described in Scheme 1, e.g. formation of ^{3}RP1 (by steps **a.** and **c.**, or **b.** and **c.**, or by step **d.**), followed by (2), provides a 'no-reaction' dissipation path for electronic excitation energy as well as one possible mechanism for photoracemization of sulfoxides (cf. Ref. 5b), the exact weight and scope of which remain yet to be fully evaluated.

Other ortho substituents (X=Cl, Br, I, CH_3, COOH, NH_2, CH_2OH) do not exert any significant effects on the reactivity pattern described above for 4-X-$C_6H_4SOCH_3$(X=H, CH_3, Br).[3,4b]



(1) escape paths of $CH_3^{\cdot *}$
$\epsilon = -$

$$\text{a.} \xrightarrow[\text{H abstraction from R'H}]{} CH_4^* \qquad \Gamma = -$$

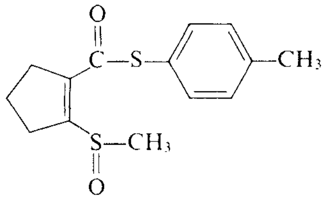
$$\text{b.} \xrightarrow[\text{dimerization}]{} CH_3CH_3^* \qquad \Gamma = -$$

$$\text{c.} \xrightarrow[\text{(by loss of O)}]{\text{ArS}^{\cdot}} ArSCH_3^* \qquad \Gamma(CH_3) = -$$

$$(2) \xrightarrow[\text{recombination } (\epsilon +)]{} Ar^*SOCH_3^* \qquad \begin{array}{l}\Gamma(CH_3) = + \\ \Gamma(6\text{-H}) = -\end{array}$$

SCHEME 1

B. *Methyl-Vinyl Sulfoxides.*[4b] Closely related to the reactive sulfoxides of group A are the methyl cyclopentenyl sulfoxide **1**, and its cyclohexenyl homolog. Thus **1** gives rise to polarized methane, ethane and methyl sulfide R_aSCH_3 by the escape path, and to polarized **1** through recombination.[4b]



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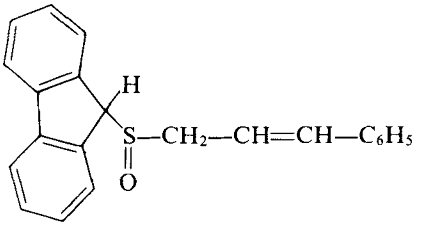
C. *Benzyl, Allyl, and Pentadienyl Sulfoxides.*[4b] Strong C—S bond photocleavage reactivity has also been observed in sulfoxides with especially weak bonds such as cinnamyl-fluorenyl sulfoxide **2** and the phenyl-pentadienyl sulfoxide **3**. The CIDNP experiments indicate that the fluorenyl-sulfinyl and cinnamyl-sulfinyl bonds of **2** and the pentadienyl-sulfinyl bond of **3** undergo photocleavage which in this group is largely reversible (see Scheme 1).[4b]



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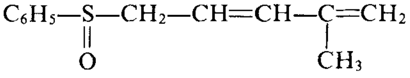


3

$$C_6H_5-\underset{\overset{\|}{O}}{S}-CH_2-CH{=}CH-\underset{CH_3}{\underset{|}{C}}{=}CH_2$$

Methyl aryl sulfides corresponding to the sulfoxides discussed in A and B show usually little *own* free radical photochemical reactivity.[8] Thus the ortho type facilitating effect[9] acting on sulfoxides is not sufficient to promote significant bond cleavage reactivity in the corresponding methyl aryl sulfides. However, methyl aryl sulfides undergo readily a reversible H atom photoabstraction by triplet benzophenone[8] (cf. Scheme 3 and also Refs. 2 and 10). In the present paper we wish to describe an additional type of structural element which strongly enhances C—S bond photocleavage reactivity in both sulfoxides and sulfides. Substitution of the methylthio group (CH_3S) at the benzene ring of methylphenyl sulfoxide (**4**) as in compounds **5**, **6** and **7** results in significant photocleavage reactivity and surprisingly enough the same group shows also a strong facilitating effect on the parallel photoprocess of methylphenyl sulfide (**8**) which is otherwise almost completely inert to C—S cleavage by either direct excitation or triplet benzophenone sensitization.[8]

RESULTS AND DISCUSSION

(*Methylthio*)*Methylsulfinyl Benzenes.* Methylthio-group substitution at the three ring positions leads to significant methyl-sulfinyl bond cleavage reactivity for both direct excitation (Figures 1, 3 and 5) as well as for triplet benzophenone (BP) sensitization (Figures 2, 4 and 6).[11] The free radical photochemical processes involved

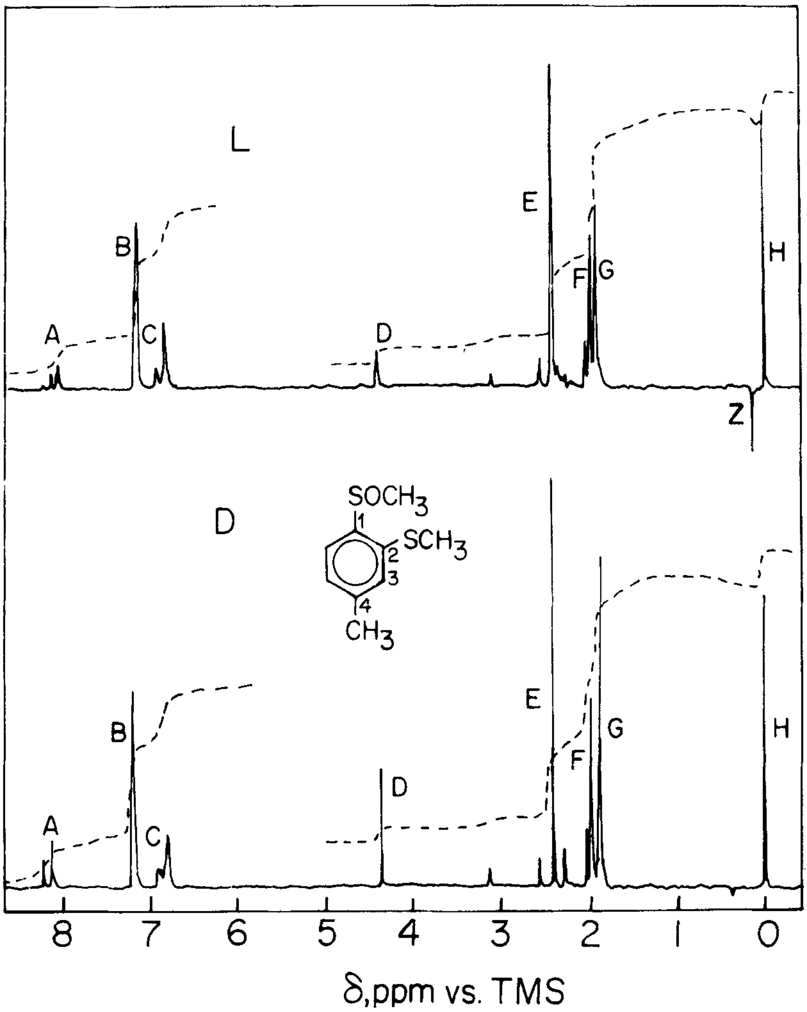


FIGURE 1 90 Mhz ^{1}H photoCIDNP in 4-methyl-1-methylsulfinyl-2-methylthiobenzene (**5**, 0.2M) benzene-d_6 solution, direct excitation. **D**, dark spectrum; **L**, light spectrum (see Experimental). Assignment: A, 6-H; B, solvent; C, 3-H and 5-H; D, impurity; E, $SOCH_3$; F, SCH_3; G, $ArCH_3$; H, TMS; Z, CH_4.

are summarized in Scheme 1. Polarized methane (signal Z in Figures 1–6, δ 0.18 in C_6D_6) is observable in emission, in every case. Polarized ethane (signal Y, δ 0.68, E effect) is observable, both on triplet benzophenone sensitization (Figures 2 and 6) and on direct excitation (Figures 3 and 5). Signals X (Figures 2, 4–6) are the negatively polarized methyl protons of the sulfide product (e.g. **9**, **10**, **11**) formed by the deoxygenation process (cf. Ref. 5*l*) of the corresponding sulfoxide (**5**, **6**, and **7**) according to the general path of deoxygenation, (1a) followed by (3) and (1c) (cf. Scheme 1),

$$\mathrm{ArSO}^{\bullet}\xrightarrow{-[\mathrm{O}]}\mathrm{ArS}^{\bullet} \qquad (3)$$

The observed negative polarization of the methyl protons of the three escape products of ^{3}RP1 (methane, ethane and $Ar'SCH_3$) is in agreement with the predic-

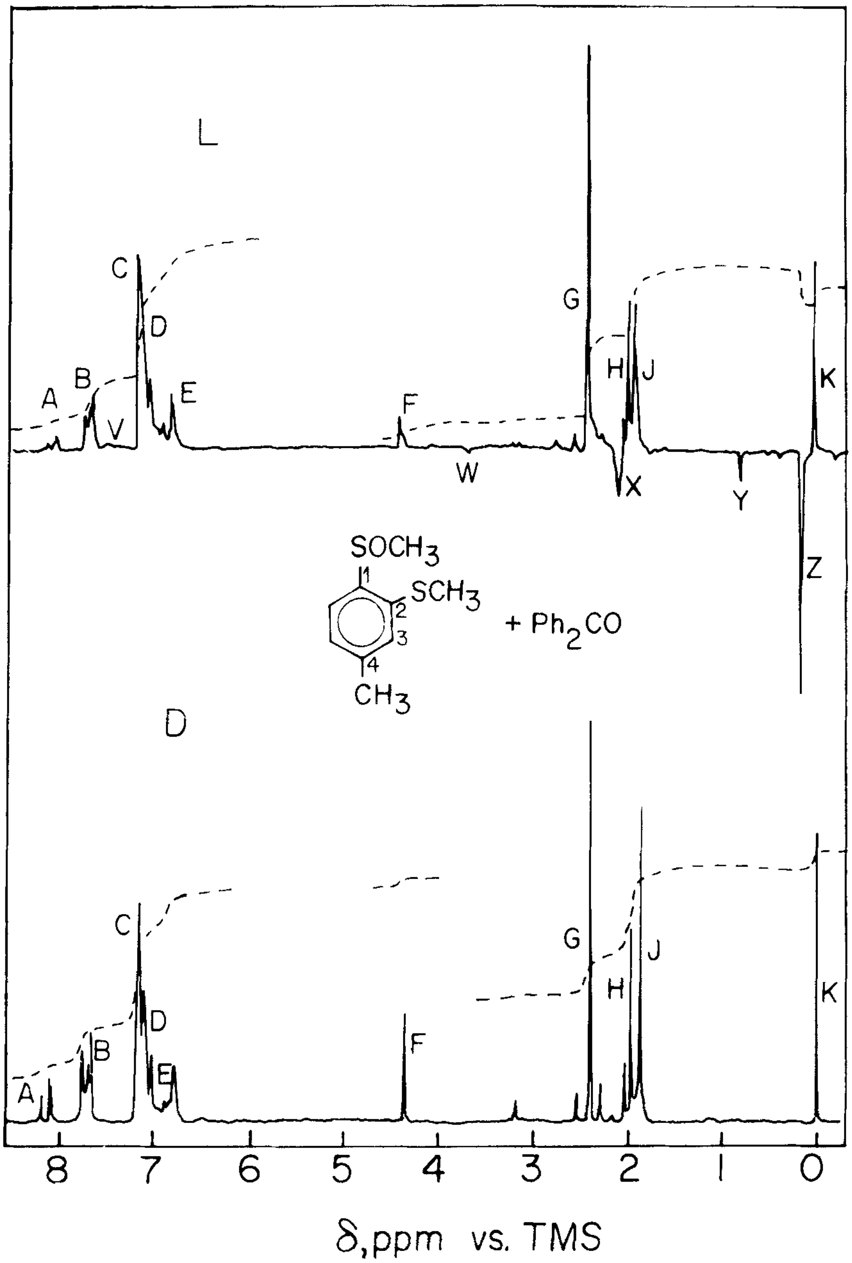


FIGURE 2 90 Mhz ^{1}H photoCIDNP in **5**, 0.2M in benzene-d_6 in the presence of benzopnenone (BP, 0.1M) see caption to Figure 1. Assignment: **5**-A, 6-H; E, 3-H and 5-H; G, SOCH$_3$; H, SCH$_3$; J, ArCH$_3$. BP—B, H ortho; D, other aromatic H. K, TMS; C, solvent. Products: Z, CH$_4$; Y, C$_2$H$_6$; X, probably Ar'SCH$_3$; W, methylene of Ph$_2$COH—CH$_2$SAr'; V, probably ortho H of Ph (of same); F, impurity.

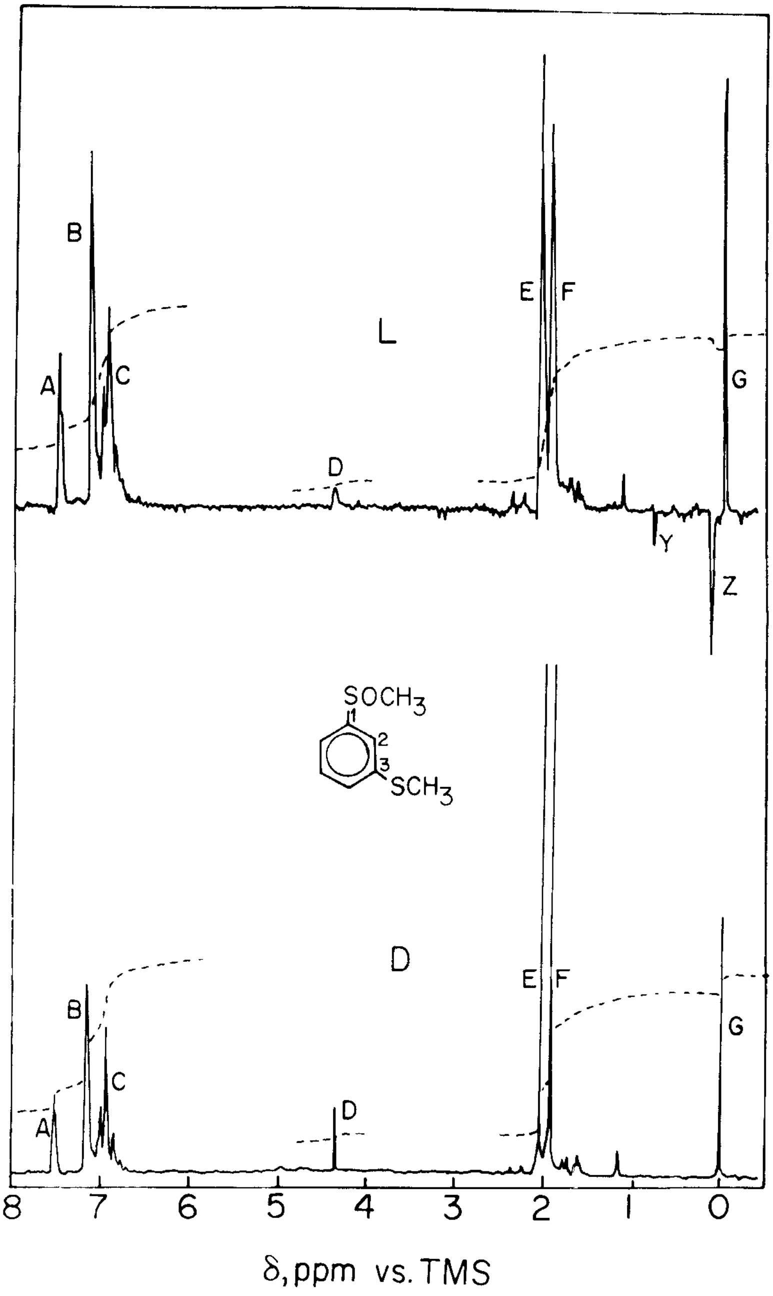


FIGURE 3 ^1H photoCIDNP in 1-methylsulfinyl-3-methylthiobenzene, **6**, 0.2M in benzene-d_6, direct excitation. See caption to Figure 1. Assignment: **6**-A, 2-H; C, other aromatic H; E, $SOCH_3$, F, SCH_3. B, solvent; D, impurity; G, TMS; Y, C_2H_6; Z, CH_4. Signal at δ 1.2 is due to HDO.

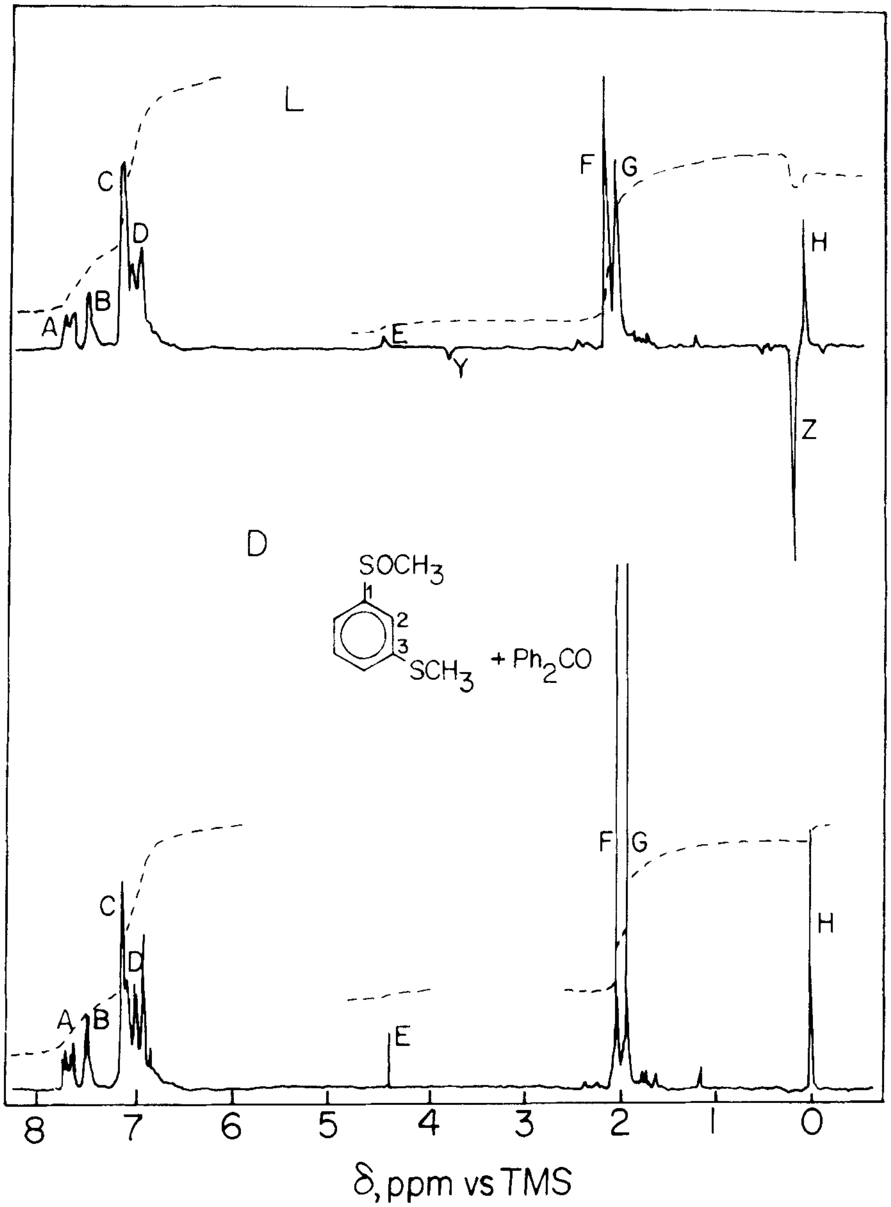


FIGURE 4 ^{1}H photoCIDNP in **6**, 0.2M in benzene-d_6 in the presence of BP, 0.1M (see caption to Fig. 1) **6**: B, 2-H; D, Ar-H; F, $SOCH_3$; G, SCH_3. H, TMS; A, H ortho of BP. C, solvent; E, impurity; Y, methylene of $Ph_2COH—CH_2SAr'$; Z, CH_4.

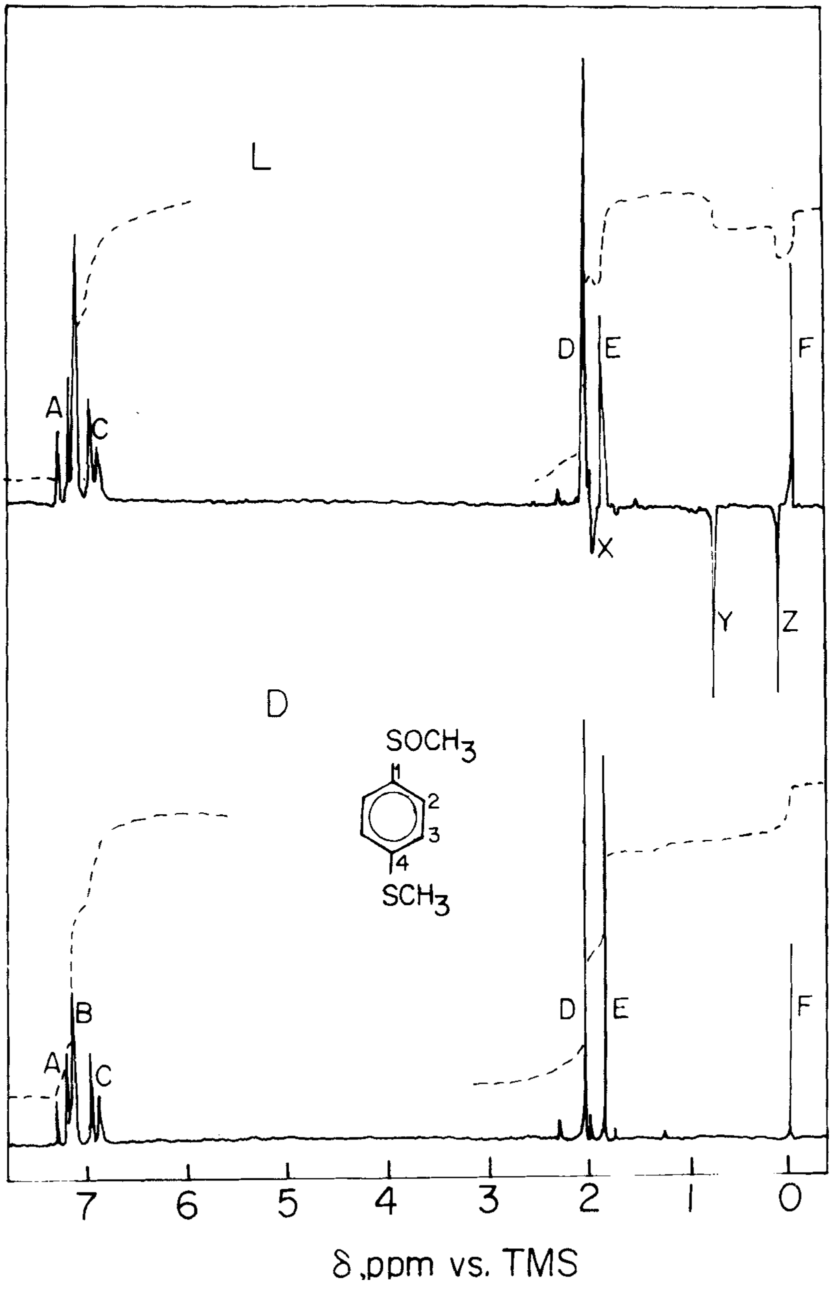


FIGURE 5 ^1H photo CIDNP in 1-methylsulfinyl-4-methylthiobenzene (**7**, 0.2M) in benzene-d_6 solution, direct excitation (see caption to Figure 1). **7**: A, 2-H and 6-H; C, 3-H and 5-H; D, $SOCH_3$; E, SCH_3. B, solvent; F, TMS. Products: X, SCH_3 of **11**; Y, C_2H_6; Z, CH_4.

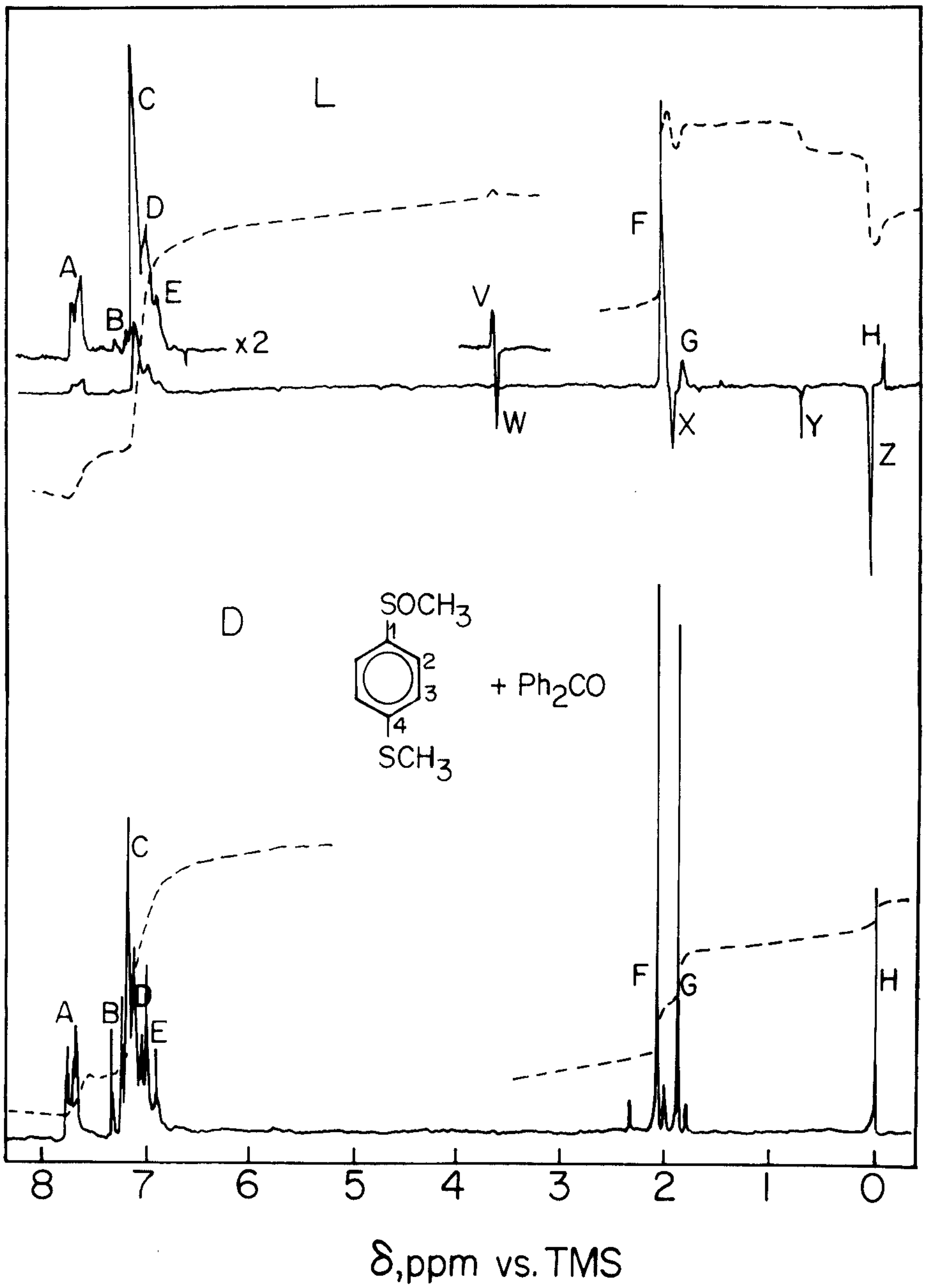
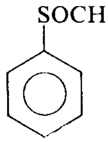


FIGURE 6 ^{1}H photo CIDNP in **7** (0.2M in benzene-d_6) in the presence of BP (0.1M). See caption to Figure 1. **7**: B, 2-H and 6-H; E, 3-H and 5-H; F, $SOCH_3$; G, SCH_3. BP: A, H ortho; D, other Ar-H. C, solvent; H, TMS. Products: W, methylene of $Ph_2COH—CH_2SAr'$; X, SCH_3 of **11**; Y, C_2H_6; Z, CH_4; V, unassigned.

tion of the Radical Pair model[7] [$\mu+$, $\epsilon-$, $A(\mathrm{CH}_3^\bullet)-$ and $\Delta g-$, as $g(\mathrm{CH}_3^\bullet) < g(\mathrm{ArSO}^\bullet)$, cf. Ref. 2–4b, 8, 12 so that Γ, according to $\Gamma = \mu \cdot \epsilon \cdot \Delta g \cdot A_i$ is negative]. The total electronic spin state is a triplet for all radical pairs involved as the nuclear polarization in all products formed by both direct excitation and triplet sensitization is of the same sign. The polarization of methane obtained from singlet ^{1}RP1 shows an opposite (positive) sign.[3,4b,13]



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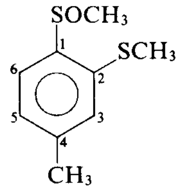

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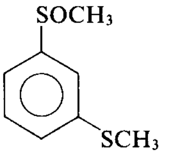

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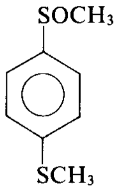

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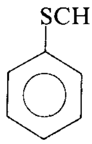

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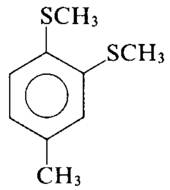

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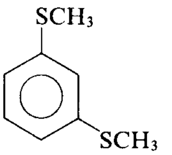

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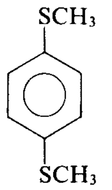

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The present systems show ample evidence for the recombination path (2), Scheme 1, of the *triplet* born ^{3}RP1, $\overline{^3\mathrm{ArSO}^\bullet + \mathrm{CH}_3^\bullet}$. Strong enhanced absorption is observed in the sulfinyl methyl protons of **5** (G in Figure 2), of **6** (F in Figure 6) and of **7** (D in Figure 5) while a negative effect is observed in the 6-H protons of **5** (A in Figure 2). The direct excitation results indicate that the 4-methylthio compound is the most reactive as far as photocleavage is concerned, and the fact that significant additional reactivity is evoked by the triplet benzophenone excitation of the 2- and 3- methylthio compounds (e.g. cf. Figure 1 with Figure 2) indicates that in both the photochemical reactivity is controlled (and limited) by the rate of intersystem crossing.

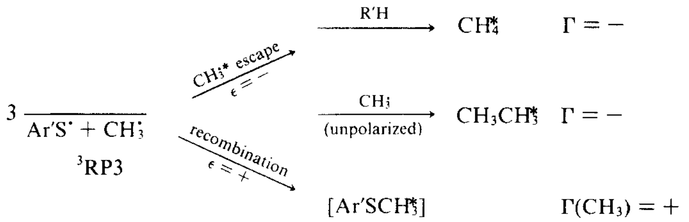
The enhanced absorption effect observed in the methyl protons of the ^{3}RP1 recombination product is also well reproduced by the Radical Pair model. With the exception of $\epsilon+$ the other three parameters are as for the escape path so that Γ [Eq. (a) footnote 6] $= ++-- = +$. The CIDNP effects described here, especially those of Figures 2, 4, 5 and 6, leave little doubt that the C—S photocleavage taking place in these systems is at the methylsulfinyl groups

$$^3\mathrm{ArSOCH_3} \longrightarrow \overline{^3\mathrm{ArSO}^\bullet + \mathrm{CH}_3^\bullet} \qquad (1)$$

and not at the methylthio groups

$$^3\mathrm{Ar'SCH_3} \longrightarrow \underset{^3\mathrm{RP3}}{\overline{^3\mathrm{Ar'S}^\bullet + \mathrm{CH}_3^\bullet}} \qquad (4)$$

The recombination process of $\overline{^3\mathrm{Ar'S}^\bullet + \mathrm{CH}_3^\bullet}$ (^{3}RP3), Scheme 2, would lead to polarization in the methyl protons of the methylthio groups which has not been observed in these compounds. The methyl sulfinyl path seems to be preferred over the methylthio path for energetic reasons (see below). Factors of direct electronic origin also play an important role in directing the reaction to this path. Preliminary results obtained by studying low temperature effects on the absorption spectra in ethanol of **5–7** and **9–11** indicate that the first transition in both types of molecules is a necessarily locallized $n \rightarrow \pi^*$ transition involving the sulfur atom.[14]



SCHEME 2

In **9–11** this transition is at higher energies than in the corresponding sulfoxides, a fact which indicates that the lowest electronic transition in **5–7** is a $n - \pi^*$ transition largely locallized at the methylsulfinyl group.[15] The results of the triplet benzophenone sensitization of the photocleavage of **5** and **6** (Figures 2 and 4) show evidence for traces of H atom abstraction by triplet benzophenone. This abstraction is probably from the methylthio group (path 5a) as in arylmethylsulfides, cf. Scheme 3,

$$Ar'SCH_3 + {}^3Ph_2CO \longrightarrow \underset{^3RP5}{{}^3\overline{Ar'SCH_2^{\cdot} + Ph_2COH^{\cdot}}} \tag{5a}$$

and not from the methylsulfinyl group, path 5b,

$$ArSOCH_3 + {}^3Ph_2CO \longrightarrow {}^3\overline{ArSOCH_2^{\cdot} + Ph_2COH^{\cdot}} \tag{5b}$$

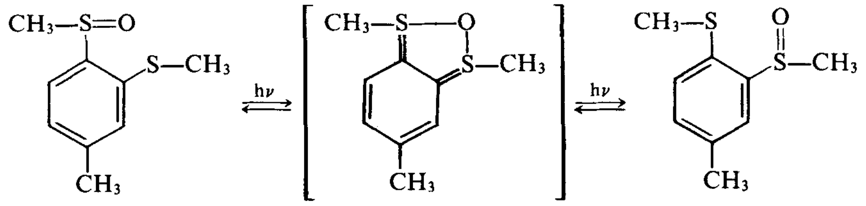
${}^3\overline{Ar'SCH_2^{\cdot} + Ph_2COH^{\cdot}}$	(³RP5)	Γ, calculated eq (a)
(6) $\xrightarrow{\text{recombination } (\epsilon+)} Ar'SCH_2^{*}\underset{\underset{OH}{\vert}}{C}Ph_2^{*}$ (12*)	$\Gamma(CH_2) = -$ $\Gamma(Ph,ortho\text{-}H) = +$	$+++- = -$ $++-- = +$
(7) $\xrightarrow[\text{H transfer}]{\text{recombination } (\epsilon+)} Ar'SCH_3^{*} + [Ph_2^{*}CO]$	$\Gamma(CH_3) = -$ $[\Gamma(Ph,ortho\text{-}H) = +]$	$+++- = -$ $[++-- = +]$
(8) $\xrightarrow[\text{dimerization}]{\text{escape of } Ar'SCH_2^{*\cdot}\ (\epsilon-)} Ar'SCH_2^{*}CH_2SAr'$ (13*)	$\Gamma(CH_2) = +$	$+-+- = +$
(9) $\xrightarrow[\text{H loss}]{\text{escape of } Ph_2^{*}COH^{\cdot}\ (\epsilon-)} Ph_2^{*}CO$	$\Gamma(Ph,ortho\text{-}H) = -$	$+--- = -$
(10) $\xrightarrow[\text{H abstraction}]{\text{escape of } Ar'SCH_2^{*\cdot}(\epsilon-)} Ar'SCH_3^{*}$	$\Gamma(CH_3) = +$	$+-+- = +$

SCHEME 3

Signals W in Figure 2, Y in Figure 4, and W in Figure 6 are from the methylene protons of the collapse product 12* of ^{3}RP5 (see below).

Photo CIDNP studies indicate that process (5a) is a general path of triplet quenching by arylthioacetic acids,[2] methylthioaromatics[8] and higher alkyl arylsulfides.[10] Thus in the present cases triplet energy transfer to the methylsulfinyl group of **5** and **6** should be considerably faster than both energy transfer to the methylthio group[16] or H atom abstraction by the triplet benzophenone from that group. Compounds **5**, **6** and **7** [unlike the di(methyl thio) benzenes **9–11**, see below] show only a limited extent of H atom abstraction as evidenced from emission signals W (Figure 2 and 6) and Y (Figure 4), assigned to the methylene of the recombination product $Ph_2COHCH_2^*SAr'$(**12***) of ^{3}RP5.

The photocleavage of compound **5** shows the reactivity expected as a result of the introduction of a facilitating substituent, much in common with the effect of substitution at the 3 and 4 ring positions. However the present results do not point to a special ortho type (neighboring group) effect as in the reactive systems of group A (cf. Introduction and Ref. 3, 4b) nor do they indicate any evidence for an intramolecular oxygen transfer from the methylsulfinyl group to the methylthio group, to give **5′**.



5 **5a** **5′**

Because of the photodealkylation, this process would result in nuclear polarization in the 3-H ring proton of **5**.

DI(METHYLTHIO)BENZENES

The most reactive molecule of this series with respect to the C—S bond cleavage in the methylthio group is the ortho di(methylthio) derivative **9**, which undergoes significant photocleavage on direct excitation (Figure 7) as well as on triplet benzophenone sensitization (Figure 8). In the first instance both negatively polarized methane and ethane are formed, as expected for the methyl-sulfur methylthio group cleavage (process 4). Triplet sensitization (Figure 8) leads to polarized methane and to the photo abstraction signal Y of the methylene protons in the collapse product $(C_6H_5)_2COH—CH_2^*$ SAr′ (see Scheme 3). The fate of the arylthiyl radical Ar′S$^\bullet$ is obscure.

The lack of methyl polarization in Ar′SCH$_3$ due to the recombination path of ^{3}RP3 (Scheme 2) could be the result of cancellation by the opposite sign polarization from the collapse process (7) of ^{3}RP5 in Scheme 3. This finding in **9** is in contrast with the effect observed in **5** for ^{3}RP1 (see Figure 2). The ArSOCH$_3$ and Ar′SCH$_3$ bond dissociation energies (55 vs. 67 Kcal/mole)[15] suggest that recombination in ^{3}RP3 would be faster than in ^{3}RP1. Lack of polarization in ^{3}RP3 would

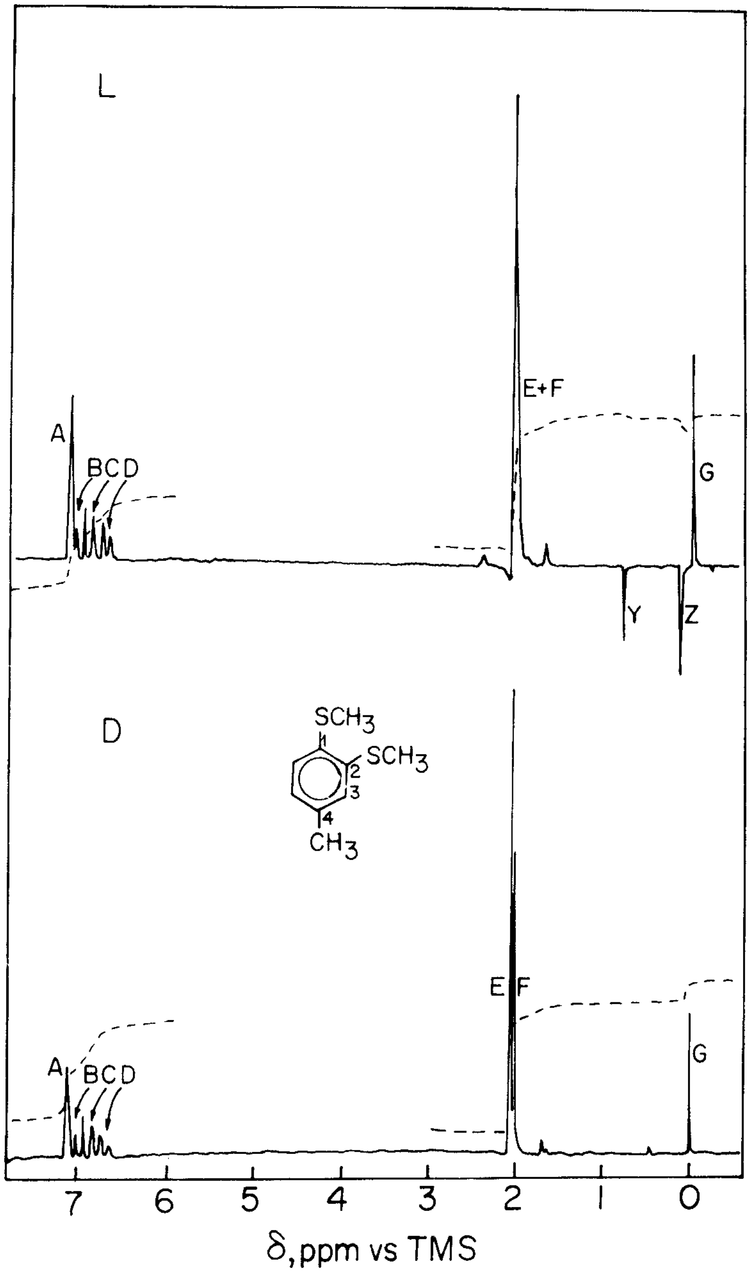


FIGURE 7 ^{1}H photo CIDNP in 4-methyl-1,2-di(methylthio) benzene (**9**, 0.2M) in benzene-d_6 solution. See caption to Figure 1. **9**: B, 6-H; C, 3-H; D, 5-H; E or F, SCH_3 or $ArCH_3$. G, TMS; Y, C_2H_6; Z, CH_4.

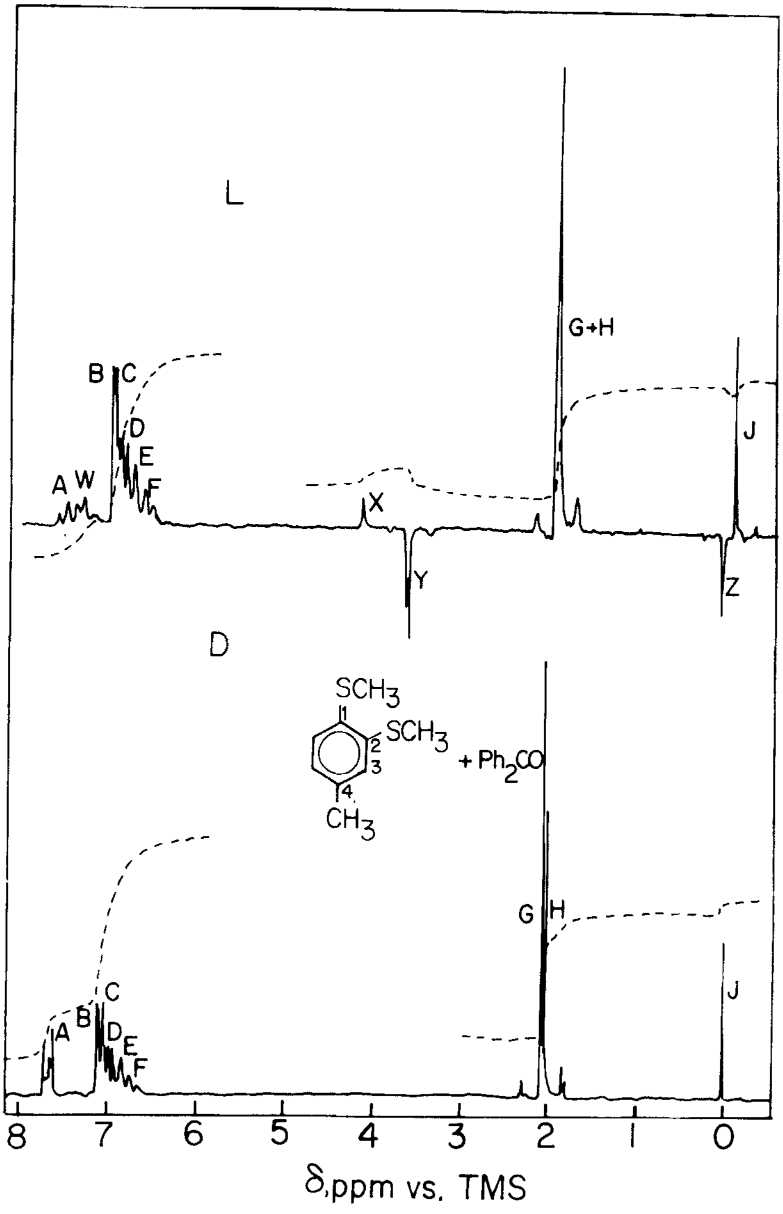


FIGURE 8 ^1H photo CIDNP in **9** (0.2M) in benzene-d_6 in the presence of BP (0.1M). See caption to Figure 1. **9**: D, 6-H; E, 3-H; F, 5-H; G or H, SCH_3 or $ArCH_3$. BP: A, H ortho; and C, other aromatic protons. B, solvent; J, TMS. $Ph_2COH—CH_2SAr'$: Y, methylene; W, possibly ortho phenyl protons. Z, CH_4; X, unassigned.

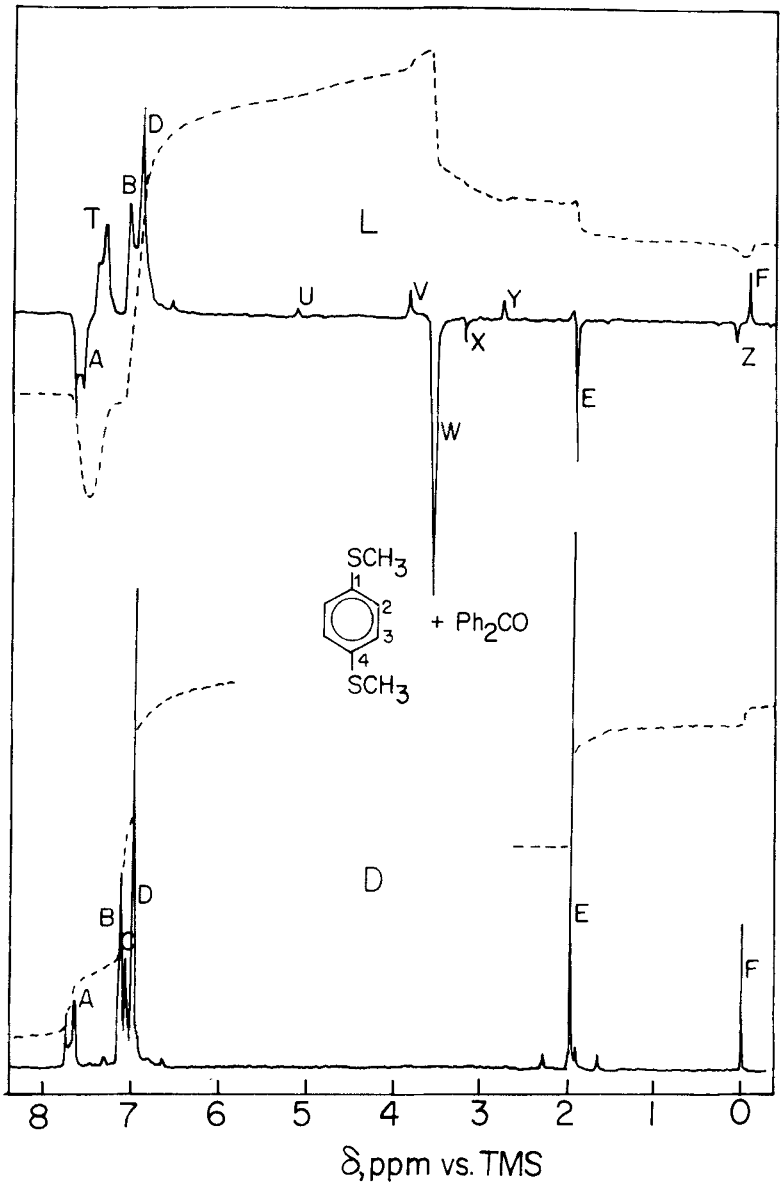
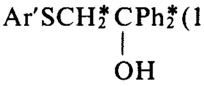


FIGURE 9 ^{1}H photo CIDNP in 1,4-di(methylthio)-benzene (**11**, 0.2M) in benzene-d_6 solution in the presence of BP (0.1M). **11**: D, aromatic protons, E, SCH_3. BP: A, H ortho; C, other protons. B, solvent; F, TMS. Products: Z, CH_4; Y, methylene of Ar′SCH_2CH_2SAr′; W, methylene of $Ph_2COH—CH_2SAr$′, T, ortho phenyl protons of same. U, V and X, unassigned.

indicate that other competing processes such as H abstraction or dimerization intervene.

In the para-di(methylthio) compound **11** no C—S photocleavage is observed on direct excitation. Benzophenone sensitization (Figure 9) leads to H atom abstraction from the methylthio group as the most prominent process which results in polarization in both collapse and escape products of ^{3}RP5 (Scheme 3), e.g.



$\mathrm{Ar'SCH_2^*\underset{OH}{\underset{|}{C}}Ph_2^*}$ (12*) (path 6, signals W and T), $\mathrm{Ar'SCH_3^*}$ (path 7, emission, $\mathrm{Ar'SCH_2^*CH_2SAr'}$ (**13*** path 8, signal Y) and $\mathrm{Ph_2^*CO}$ (path 9, signal A). Path 10, leading to the parent molecule by the escape route is observable in the presence of thiophenol. In **11** the photocleavage can be observed only as a minor path leading to polarized methane. In the meta di-(methylthio) benzene **10** no C—S photocleavage takes place, either by direct excitation or by triplet sensitization, the only photochemical process observed being the H atom photoabstraction by triplet benzophenone (Scheme 3).

The signs of the polarized protons of all the recombination and escape products of ^{3}RP5 are fully accounted for by Eq. (a),[6] $\Gamma = \mu \cdot \epsilon \cdot \Delta g \cdot A_i$. Here $\mu +$ and $g(\mathrm{Ar'SCH_2^{\bullet}}) > g(\mathrm{Ph_2COH^{\bullet}})$. All polarized protons have negative hfs factors ($A-$).[2-4b,6,7,8,12] The polarization signs derived from Eq. (a) are shown in the right-hand side of Scheme 3.

THE ENERGETICS OF C—S CLEAVAGE

The photo polarization pattern in the methyl aryl sulfoxides $\mathrm{ArSOCH_3}$ observed in this and in the previous work[3,4b] is compatible only with cleavage of the methyl-sulfur bond but not with a cleavage of the aryl-sulfur bond. The same conclusion holds for the methyl-aryl sulfides.[8] This cleavage mode is a natural outcome of the different bond strengths of the $\mathrm{CH_3}$—S and of the Ar—S bonds.[15] The estimates for these (in Kcal/mole) are $\mathrm{D(CH_3{-}SOC_6H_5)} < 55$, $\mathrm{D(CH_3SO{-}C_6H_5)} \simeq 66$; $\mathrm{D(CH_3{-}SC_6H_5)} = 67$ and $\mathrm{D(CH_3S{-}C_6H_5)} = 89$.[15] Much the same can be said concerning the preference for C—S photocleavage in the methylsulfinyl group over the C—S photocleavage of the methylthio group in compounds **5**–**7**, as the methyl-arylsulfinyl bond is weaker by some 10 Kcal/mole than the methyl-arylthio bond.

These bond dissociation energy data thus indicate that the triplet state energy of benzophenone, $\mathrm{E_T} = 69$ Kcal/mole[17b] is sufficient for a fast direct cleavage process in many sulfoxides, e.g. path **d** of Scheme 1

$$^3\mathrm{Ph_2CO} + \mathrm{ArSOCH_3} \longrightarrow \overline{^3\mathrm{ArSO^{\bullet}} + \mathrm{CH_3^{\bullet}}} + \mathrm{Ph_2CO} \qquad (\mathbf{d})$$

as $\mathrm{D(CH_3{-}SOAr)} < 55$ Kcal/mole.

However it seems now that in several methylphenyl sulfoxides the $\mathrm{E_T}$ of benzophenone is too low to reach $^3\mathrm{ArSOCH_3}$ as intermediate in the formation of ^{3}RP1 (path **b** in Scheme 1, followed by **c**). Thus in a polar medium $^3\mathrm{p\text{-}BrC_6H_4SOCH_3}$ is at 79 Kcal/mole,[18] and similar values are obtained for several other p-substituted phenyl sulfoxides.[13] It is at present unclear whether the same situation holds in the case of ortho substituted or methylthio-substituted methyl-phenyl sulfoxides.

For the parallel sensitized cleavage of methyl phenyl sulfide and most of its derivatives,

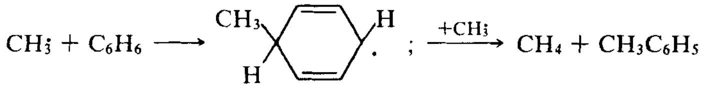
$$^3\mathrm{Ph_2CO} + \mathrm{Ar'SCH_3} \longrightarrow \overline{^3\mathrm{Ar'S^{\bullet}} + \mathrm{CH_3^{\bullet}}} + \mathrm{Ph_2CO} \qquad (\mathbf{e})$$

the triplet energy of benzophenone seems to be insufficient to guarantee a fast process (as $\mathrm{D(Ar'S{-}CH_3)} = 67$ Kcal/mole) in agreement with the experimental findings for these molecules. Thus it seems certain that the methyl-S bond dissociation energies of the di(methylthio) benzenes (e.g. of **9**) are below 69 Kcal/mole.

Very recently obtained results with the acetone triplet ($\mathrm{E_T} = 78$ Kcal/mole[17b]) indicate that this energy is sufficient for the cleavage of most methyl-S bonds in methyl aryl sulfides and sulfoxides.[14b]

H ATOM SOURCES

The methyl radicals formed in the photocleavage processes of sulfoxides and of sulfides give polarized methane by an H atom abstraction step. As the present studies were mostly carried out in perdeuterated benzene the absence of H—D splitting in the methane signal indicates that the abstracted H atoms originate from the substrate molecules. In this solvent direct abstraction would be unlikely, but an addition-abstraction mechanism, e.g.,



(12)

would be still energetically feasible. Abstraction from solvent has also not been observed in other solvents such as acetonitrile, acetone and chloroform. H—D splitting is however evident in methane formed in methanol-d_4 solution.

While no detailed data are available on the hydrogen abstraction step beyond the evidence that the H atom originates usually from the substrate molecules it seems that the abstraction follows an addition-abstraction path analogous to (12). This mechanism was indeed invoked in our previous studies of Norrish type I processes.[19]

EXPERIMENTAL

For the preparation of **5**, **6**, and **9** see Ref. 20, for that of **10**-Ref. 21, and for the preparation of **7** and **11** see Ref. 22. All ^1H photo-CIDNP measurements were carried out at 90 Mhz on a Bruker HFX-10 NMR spectrometer operating in the Fourier-transform mode. A 2500 W mercury-xenon lamp was used as a light source. Each radio frequency pulse was preceded by a 1-2 sec light period. For full experimental details, see previous publications.[4b,23] Typically 0.2 M solutions in benzene d_6 were used, tetramethylsilane (TMS) serving as chemical shift standard; each spectrum was obtained from 8 free-induction decay accumulations.

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$$\Gamma = \mu\cdot\epsilon\cdot\Delta g\cdot A_i \qquad \text{(a)}$$

μ is the total electron spin state of $A^\cdot + B^\cdot$. $\mu+$ (triplet), $\mu-$ (singlet). ϵ is the path parameter. $\epsilon+$ (collapse), $\epsilon-$ (escape). Δg is the sign of the g-factor difference $g(A^\cdot) - g(B^\cdot)$, and A_i is the sign of the hyperfine nuclear spin-electron spin interaction of atom i in $A^\cdot$. Nuclear polarization is denoted by an asterisk (*).

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