

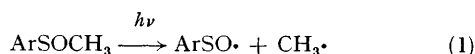
CIDNP Study of Photodealkylation in *ortho*-Substituted Aryl Methyl Sulphoxides

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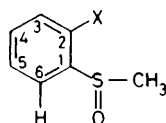
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Summary A magnetic polarization study of the photochemistry of *ortho*-substituted methyl phenyl sulphoxides indicates that *ortho*-substituents promote efficient photodealkylation, through a triplet methyl-arylsulphinyl radical pair, escape and recombination paths of which were both observed.

We report CIDNP (chemically induced dynamic nuclear polarization) results indicating a unique facilitating effect of ring *ortho*-substituents on the excited state methylsulphinyl bond cleavage in aryl methyl sulphoxides [reaction (1)]. This cleavage, inefficient in both singlet and



triplet excited states of methyl phenyl sulphoxide, becomes an important excited triplet state process on introduction of substituents at the ring position *ortho* to the MeSO group.



(1)

Typical CIDNP results obtained on u.v. irradiation of a solution of (1; X = Ph) in C₆D₆ in the presence of benzophenone as triplet sensitizer are shown in the Figure (L). Strong proton polarization is observed in methane (δ 0.18) and ethane (δ 0.78), the two escape products of the triplet-born radical pair P3, ³ArSO· + CH₃·. These two products always appear in emission (E) as predicted by the radical pair model sign rule of CIDNP.¹ Spectra recorded after completion of the u.v. irradiation indicate the predominance of process (1), chemical yields of ca. 30% of methane being obtained in this and in other systems. Owing to the considerable stability of the ArSO· species,² P3 reacts also by the collapse path, giving back (1; X = Ph), spin polarized in methyl and aromatic protons. The methyl protons show a threefold enhanced absorption (A) while the lowest field aromatic proton 6-H appears in emission. In addition to Ph a wide range of *ortho*-substituents (*e.g.* X = CO₂R, CONR¹R², CHO, NHCOR, and COSR; R = alkyl or aryl) are effective in promoting the triplet sensitized photochemical methylsulphinyl bond cleavage. In all these molecules similar nuclear polarization effects are observed indicating a common triplet state cleavage path.

The same products and the same CIDNP effects are observed on direct excitation of *ortho* substituted aryl methyl sulphoxides indicating that the triplet states in these molecules are accessible by intersystem crossing.

‡ The A effect on direct excitation is magnified by the H donors 4-methyl-2,6-di-*t*-butylphenol and benzenethiol, and is due to the escape of proton polarized CH₃· from a correlated singlet pair P1, ¹ArSO· + CH₃·. The escape path is possible in this case only owing to the stability of ArSO· (ref. 2).

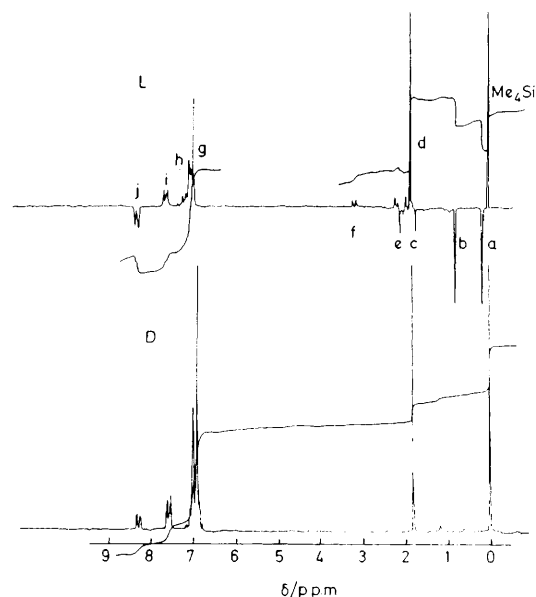


FIGURE. 90 MHz Fourier transform ¹H n.m.r. spectra of a C₆D₆ solution of (1; X = phenyl) (0.1 M) in the presence of benzophenone (0.07 M). D, dark spectrum; L, light spectrum, u.v. irradiation (2 s duration) with a 2500 W Hg-Xe lamp preceding each r.f. pulse. h, solvent; i, benzophenone; substrate protons: d, methyl; g, aromatic; j, 6-H; products: a, CH₄; b, C₂H₆. The identity of c, e, and f has not yet been definitely established.

Some molecules, however, (*e.g.* X = Ph, ROCH₂, or RO) react only by the benzophenone-sensitized route, indicating inefficient singlet-triplet intersystem crossing.

The rate of formation of ethane is considerably decreased in the presence of hydrogen donors, *e.g.*, 4-methyl-2,6-di-*t*-butylphenol³ and benzenethiol,⁴ or if CCl₃ is used as solvent. These efficient scavengers of methyl radicals prevent the bimolecular recombination involved in the formation of ethane.

In contrast to the efficient photochemical cleavage in molecules of type (1) is the relative lack of reactivity of unsubstituted aryl methyl sulphoxides. Thus direct or benzophenone-sensitized photolysis of PhSOCH₃ (or of its 4-bromo or 4-methyl derivatives) results in only weak CIDNP effects in the trace amount of proton polarized methane formed.

Here the direct photoreaction takes place in the excited singlet state giving an A effect in CH₄· while the effect in the triplet-sensitized process is similar to that in molecules of type (1). Interestingly, the parent molecule dimethyl sulphoxide shows only singlet excited state reactivity.⁵

The CIDNP technique singles out the methyl-sulphinyl bond cleavage as an efficient primary free radical photochemical process of the *ortho*-substituted aryl methyl sulphoxides. Other photoreactions observed previously in these molecules, *e.g.*, intramolecular transfer of the sulphinyl oxygen on to carbonyl functions in the *ortho*-position,⁶ originate from other primary steps.

Parallel to the facilitating effect of *ortho*-substituents on excited state dealkylation are the substantial 'neighbouring

group effects.' These are evident in ground-state reactions of sulphoxides, *e.g.*, racemization, oxygen exchange, and nucleophilic substitution.⁷

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¹ L. T. Muus, P. W. Atkins, K. A. McLauchlan, and J. B. Pedersen, *Chemically Induced Magnetic Polarization*, NATO Advanced Study Institutes Series, Vol. 34, Reidel, Dordrecht, 1977.

² Preliminary e.s.r. results for (**1**; X = CONEt₂) indicate that the photochemically formed arylsulphinyl radical is moderately stable at 150 K in 2-methyltetrahydrofuran solution; $g(\text{ArSO}\cdot) = 2.0092$. See also B. C. Gilbert, C. M. Kirk, R. O. C. Norman, and H. A. H. Laue, *J.C.S. Perkin II*, 1977, 497.

³ K. A. Muszkat and M. Weinstein, *J.C.S. Chem. Comm.*, 1975, 145; *Förster Volume, Z. phys. Chem. (Frankfurt)*, 1976, 101, 105; *J. C. S. Perkin II*, 1976, 1072.

⁴ M. Weinstein, K. A. Muszkat, and J. Dobkin, *J.C.S. Chem. Comm.*, 1975, 68.

⁵ K. Gollnick and H. U. Stracke, *Pure Appl. Chem.*, 1973, 33, 217.

⁶ R. Lüdersdorf, J. Martens, B. Pakzad, and K. Praefcke, *Annalen*, 1977, 1992; 1978, 2107; R. Lüdersdorf and K. Praefcke, *Z. Naturforsch.*, 1976, 31b, 1658; 1977, 32b, 360, and unpublished results.

⁷ D. Landini, F. Rolla, and G. Torre, *Internat. J. Sulfur Chem.*, 1972, A2, 43; S. Allenmark, *ibid.*, 1973, 8, 127; F. Montanari, *ibid.*, 1971, C6, 137; S. Allenmark, O. Bohman, C. E. Hagberg, and H. Johnson, *ibid.*, 1972, 2, 191.