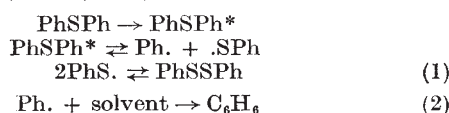


### Photolysis of Organic Sulphides

IRRADIATION of solutions of diphenylamine with ultra-violet light effects cyclization to carbazole in good yield<sup>1</sup>. It was of interest to determine if diphenyl sulphide would similarly afford 9-thiafluorene, some polymethyl derivatives of which were required. In the event, reaction took a different course, and benzene and diphenyl disulphide were produced. Trace amounts of diphenyl were also detected by gas-liquid chromatography but none of the desired 9-thiafluorene was found. The diphenyl disulphide (m.p. and mixed m.p. 57°–59°) was separated from unchanged sulphide by preparative gas-liquid chromatography; benzene was detected by gas-liquid chromatography but was not isolated. The following mechanism is adequate, assuming initial cleavage into free radicals as postulated in another case<sup>2</sup>. Free radical formation is energetically possible with light of wave-length less than 3900 Å taking the energy of the carbon-sulphur bond to be about 73 kcal/mole (ref. 3).



Reactions of type (1) and (2) are well known<sup>4</sup>. Lyons has reported<sup>5</sup> that irradiation of diphenyl disulphide in *n*-hexane and other solvents gave thiophenol by dissociation and abstraction of hydrogen from the solvent by thiophenoxyl radicals. No thiophenol could be found among the products obtained in the present experiment using light petroleum (b.p. 40°–60°) as solvent.

A number of other sulphides behaved similarly on irradiation. Thus di-*n*-butyl sulphide was smoothly converted into the disulphide, isolated by preparative gas-liquid chromatography and identified by its infra-red spectrum, and di-*n*-octyl sulphide gave the disulphide and *n*-octane (detected by gas-liquid chromatography). With benzyl phenyl sulphide, which could theoretically cleave in two ways to give either dibenzyl and diphenyl disulphide or benzene and dibenzyl disulphide, only the former reaction occurred, through the most stable pair of radicals. Similarly benzyl *n*-butyl sulphide gave mainly dibenzyl and di-*n*-butyl disulphide. In each case small amounts of phenanthrene and *trans*stilbene were detected by gas-liquid chromatography. Diallyl sulphide was decomposed and sulphur was precipitated, but the only other product was a high boiling liquid shown by gas-liquid chromatography to contain at least four components.

Dibenzyl sulphide predictably gave dibenzyl and dibenzyl disulphide, but an unexpected product was phenanthrene, which was isolated by chromatography on alumina and identified by mixed melting point. The exact sequence of reactions leading to the formation of the phenanthrene is not clear. It seemed likely that it might have been produced by photo-cyclization of stilbene<sup>6</sup>, itself formed by dehydrogenation of dibenzyl by benzylthiyl radicals<sup>7</sup>. In agreement a small amount of benzyl mercaptan was detected among the reaction products by gas-liquid chromatography. On the other hand, no more than a trace of 1,8-dimethylphenanthrene was formed when the reaction was carried out in presence of an equimolecular amount of 2,2'-dimethyldibenzyl, suggesting that there may be another route from the sulphide directly to stilbene or phenanthrene. Phenanthrene was also produced, along with some dibenzyl, by irradiation of dibenzyl disulphide, but, surprisingly, the main product of this reaction was dibenzyl sulphide. Prolonged irradiation of either the sulphide or the disulphide resulted in complete destruction of the sulphur compound and formation of a mixture of dibenzyl and phenanthrene in the ratio of approximately 2.5 : 1.

Dissociation of disulphides into radicals on irradiation with ultra-violet light is well known<sup>7,8</sup>, but there has apparently been no previous instance of sulphur extrusion

from a disulphide by light. The reaction is not general, for both diphenyl disulphide and di-*n*-butyl disulphide were unaffected under the same conditions. Measurements of bond dissociation energies show<sup>3,9</sup> that the carbon-sulphur bond in benzylic sulphides is considerably weaker than that in simple dialkyl sulphides, and it is reasonable to suppose that in dibenzyl disulphide, but not in the other disulphides examined, the usual dissociation into thiyl radicals is accompanied by cleavage of the carbon-sulphur bond, the sulphide then being formed by combination of benzyl and benzylthiyl radicals.

Reactions were conducted for 12–20 h under nitrogen (in the case of diphenyl sulphide oxygen was also used) in a quartz flask with light from a 125 W Mazda mercury vapour lamp from which the outer glass envelope had been removed, using dilute solutions (0.1–0.2 molar) in light petroleum (b.p. 40°–60°). In 'Pyrex', di-*n*-butyl and dibenzyl sulphides were unchanged, but diphenyl sulphide again gave the disulphide.

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<sup>2</sup> Walling, C., *Free Radicals in Solution*, 522 (John Wiley and Sons, London, 1957).

<sup>3</sup> Cottrell, T. L., *The Strengths of Chemical Bonds*, Second ed., 203 (Butterworths, London, 1958).  
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<sup>4</sup> See, for example, ref. 2, pp. 481, 522.

<sup>5</sup> Lyons, W. E., *Nature*, **162**, 1004 (1948).

<sup>6</sup> Mallory, F. B., Wood, C. S., Gordon, J. T., Lindquist, L. C., and Savitz, M. L., *J. Amer. Chem. Soc.*, **84**, 4361 (1962).

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<sup>8</sup> Rueggeberg, W. H. C., Cook, W. A., and Reid, E. E., *J. Org. Chem.*, **13**, 110 (1948); Kharasch, M. S., Nudenberg, W., and Meltzer, T. M., **18**, 1233 (1953).

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### Complex Formation between Transition Metal Ions and Organic Solvents: Electron Spin Resonance Investigations

THE electron spin resonance (ESR) technique provides a powerful tool for investigating transition metal complex formation in non-aqueous solutions. In recent work we have shown<sup>1</sup> that ESR and optical absorption spectra of different paramagnetic ions are changed when glycerol replaces water as a solvent. Both the variation in line width and the optical 'red shift' obtained suggest a change in crystal-field energy levels by spin-orbit mechanisms. Newer theories have linked octahedral-tetrahedral changes to these ligand-field effects on non-bonding *d* electrons<sup>2</sup>. Thus, it might be of interest to investigate the ESR spectra of the chlorides of Mn<sup>2+</sup>, Fe<sup>3+</sup> and Cu<sup>2+</sup> in different organic solvents including dimethylsulphoxide (DMSO), dimethylformamide, formamide, acetone, glycerol and ethanol. These solvents were chosen to provide a varying dielectric constant and base strength since such parameters are known to affect the equilibrium between the octahedral and tetrahedral states.

The ESR spectra were determined with a Varian V4500 100-ke ESR spectrometer using a liquid sample accessory. A DPPH standard (*g* = 2.0036 as indicated by the arrow in Fig. 1) was used as a reference for marking resonance positions. The first derivative of the absorption curve was recorded. All solvents and hydrated salts used were of reagent-grade quality.

The spectra obtained are shown in Fig. 1. In formamide a Mn<sup>2+</sup> spectrum (six-line *hf* pattern) similar to that obtained with water can be observed, while all other solvents result in a change of the spectrum. A splitting of the two outer lines and a reduction in intensity is observed with dimethylformamide and DMSO, probably due to the