The Photolysis of Aromatic Sulphones and Related Compounds

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RECENTLY, the pyrolytic decomposition of aryl sulphides and aryl sulphones has been reported.[1] While photolysis of certain cyclic aralkyl sulphones has been investigated by Cava and his co-workers,[2] apparently the photolysis of aryl sulphones has not been studied.[*] In extension of our earlier studies on the photolysis of iodoaromatic substances and certain sulphenyl compounds[2–4] we have examined the photolysis of selected diaryl sulphones and related substances.

Photolysis of diphenyl sulphone in benzene solution was studied under similar conditions as reported for iodoaromatic compounds, using a low-pressure cold-cathode mercury arc.[3] The products obtained were separated into two fractions, according to their solubility in carbon disulphide. The components of the carbon disulphide-soluble fraction are shown in Table 1.

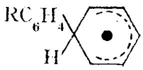
The yield of biphenyl was slightly increased in presence of oxygen or iodine. The increase, while small, was definite; and was in the expected direction, in view of earlier results on oxygen effects in phenylation reactions,[6,7] wherein oxygen (or iodine) acts to remove hydrogen from the intermediate cyclohexadienyl radical, and hence leads to product (biphenyl), rather than H-transfer to phenyl radical. Since the amounts of iodine used in these runs was small, the trapping of phenyl radicals by iodine does not interfere with the phenylation reaction. Although no appreciable amounts of iodobenzene could be detected in the reaction mixture, it may be formed and decomposed to give back phenyl radicals.[3]

The above results clearly indicate that carbon–sulphur bond cleavage of the sulphone occurs, to give phenyl radical, which then reacts with benzene to yield biphenyl. In support of this conclusion was the finding that photolysis of diphenyl sulphone in fluorobenzene gave a product which was composed at least 90% of the isomeric fluorobiphenyls. Furthermore, the photolysis of *p*-tolyl sulphone, in benzene, yielded *only* 4-methylbiphenyl and *no* 4,4′-dimethylbiphenyl, showing that the arylation reaction is *intermolecular*. However, a small amount of biphenyl was obtained, as discussed below.

The conversions found may be explained in terms of the following sequence of reactions:

(1) $RC_6H_4{\cdot}SO_2{\cdot}C_6H_4R \rightarrow RC_6H_4{\cdot} + RC_6H_4{\cdot}SO_2{\cdot}$

(2) $RC_6H_4{\cdot} + C_6H_6 \rightarrow$

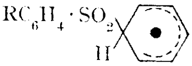


(A)

(3) $(A) + RC_6H_4{\cdot}SO_2{\cdot} \rightarrow$
or $(RC_6H_4{\cdot})$

$RC_6H_4{\cdot}C_6H_5{\cdot} + RC_6H_4{\cdot}SO_2H$ (?)
or (RC_6H_5)

(4) $RC_6H_4{\cdot}SO_2{\cdot} + C_6H_6 \rightarrow$



(B)

(5) $(B) + RC_6H_4{\cdot}SO_2{\cdot} \rightarrow$
or $(RC_6H_4{\cdot})$

$RC_6H_4SO_2{\cdot}C_6H_5 + RC_6H_5{\cdot}SO_2H$
(RC_6H_5)

(where $R = H$ or CH_3)

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[*] C. Walling and B. Miller (*J. Amer. Chem. Soc.*, 1957, **78**, 4187) reported that photolysis of diphenyl sulphone in presence of chlorine gives chlorobenzene in good yield. This reaction was demonstrated to be a free-radical process, initiated by the photochemical dissociation of chlorine molecules to chlorine atoms. The mechanism of this reaction is therefore different from that of the present work.

TABLE 1. *Products of the photolysis of diphenyl sulphone in benzene*[a]

Solvent and reaction[b] conditions	Run	Hr.	% Photo-lysis[c]	Iodine (mg./ml.)	% Yield of biphenyl[d]
Benzene[e]	(1)	19	66	—	78
Benzene	(2)	12	48	1	98[f]
	(3)	17	61	1	98[f]
Benzene saturated with nitrogen under nitrogen atmosphere	(4)	20	70	—	74
	(5)	20	70	—	70
Benzene saturated with oxygen, under oxygen atmosphere	(6)	17	52	—	69[f]
	(7)	19·5	66·5	—	92
	(8)	18	52	—	90

[a] The products shown in this Table are those which were soluble in carbon disulphide; a partially acidic material, insoluble in carbon disulphide, was also formed.

[b] In all runs, about 70 ml. of 0·015M-solution was used.

[c] Determined by estimation of the unchanged sulphone.

[d] Based on the amount which actually underwent photolysis and on the assumption that one mole of diphenyl sulphone yielded one mole of biphenyl.

[e] Reagent grade benzene was used directly from the bottle without further treatment.

[f] These results were independently confirmed in this Laboratory by Dr. T. Nakabayashi. A (W-K)^2 — 1 model, low-pressure cold-cathode mercury arc, Nuclear Supplies, Inc., Encino, California, was used in all the runs.

Steps (4) and (5) above seem unimportant, since no phenyl *p*-tolyl sulphone was detected in the photolysis of bis-*p*-tolyl sulphone. Furthermore, since only about 1% biphenyl was detected in this case, it is unlikely that the unsymmetrical sulphone (*i.e.*, $CH_3{\cdot}C_6H_4{\cdot}SO_2{\cdot}C_6H_5$) *is* formed and then decomposes.

While the components of the carbon disulphide-insoluble fractions have as yet to be established, the possibility that sulphinic acids are formed initially is suggested by the finding that acidic components were present. The investigation of these carbon disulphide-insoluble fractions is the subject of a separate study in this laboratory.

The results with diphenyl sulphone led us to investigate the photolysis of the corresponding sulphoxide and sulphide in benzene solutions. Diphenyl sulphoxide produced biphenyl (53%), diphenyl sulphide (7%), and a small amount of diphenyl disulphide. On the other hand, although it has been reported that the photolysis of diphenyl sulphide in methanol or dioxan yields polymeric materials,[8] the products obtained under our conditions are given in Table 2.

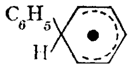
TABLE 2. *Photolysis products of diphenyl sulphide in benzene*[a]

Products	% Yield
Biphenyl	39
Diphenyl disulphide	19
Thiophenol	not determined
Starting material	less than 10%

[a] After photolysis for 7 hr., decomposition was about 90%; after 17 hr., photolysis was essentially complete as shown by disappearance of starting material.

The following reaction sequence may be suggested to rationalize these results:

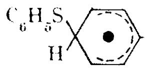
(i) $C_6H_5S{\cdot}C_6H_5 \rightarrow {\cdot}C_6H_5{\bullet} + C_6H_5S{\bullet}$

(ii) $C_6H_5{\bullet} + C_6H_6 \rightarrow$  (C)

(iii) $(C) + C_6H_5S{\cdot} \rightarrow C_6H_5{\cdot}C_6H_5 + C_6H_5SH$
$(C_6H_5{\bullet})$ (C_6H_6)

(iv) $2C_6H_5S{\bullet} \rightarrow C_6H_5S{\cdot}SC_6H_5$
or $(C_6H_5SH + O_2)$

(v) $C_6H_5SH + C_6H_5{\bullet} \rightarrow C_6H_5S{\bullet} + C_6H_6$

(vi) $C_6H_5S{\bullet} + C_6H_6 \rightarrow$  (D)

(vii) $(D) + C_6H_5S{\bullet} \rightarrow C_6H_5{\cdot}S{\cdot}C_6H_5 + C_6H_5SH$
or $(C_6H_5{\bullet})$ (C_6H_6)

Step (v) may be of some significance after accumulation of thiophenol in appreciable amounts. It is not clear, however, from the data presented in Table 2, whether steps (vi) and (vii) are of importance in these reactions. Nevertheless, by analogy to the sulphone case, these steps may be of little or no importance.

The results presented above showed that the C–S bond of aryl sulphides, sulphoxides, and sulphones cleaves under the influence of u.v. light to yield aryl radicals. Thus, it might be expected that dibenzothiophen or dibenzothiophen dioxide may lose sulphur or sulphur dioxide to yield biphenylene. However, no appreciable photolytic decomposition of these compounds could be observed under our conditions and the starting materials were recovered almost quantitatively.

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[1] W. Z. Heldt, *J. Org. Chem.*, 1965, **30**, 3897.
[2] M. P. Cava, R. H. Schlessinger, and J. P. Van Meter, *J. Amer. Chem. Soc.*, 1964, **86**, 3173.
[3] W. Wolf and N. Kharasch, *J. Org. Chem.*, 1965, **30**, 2493.
[4] W. Wolf and N. Kharasch, *J. Org. Chem.*, 1961, **26**, 283.
[5] N. Kharasch and Z. S. Ariyan, *Chem. and Ind.*, 1965, 302.
[6] N. Kharasch and R. K. Sharma, *Chem. Comm.*, 1966, 106.
[7] E. L. Eliel and M. Eberhardt, *J. Org. Chem.*, 1962, **27**, 2289.
[8] L. Horner and J. Dorges, *Tetrahedron Letters*, 1963, 757.