BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 2906—2909 (1972)

Photolyses of Diaryl α-Disulfones[1]

Michio KOBAYASHI, Koji TANAKA, and Hiroshi MINATO
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya-ku, Tokyo

(Received April 15, 1972)

Di-*p*-tolyl disulfone and diphenyl disulfone were decomposed in various arenes by irradiation of UV light. The products found were arenesulfonic acids, arenesulfonic anhydrides, thiolsulfonates, diaryl sulfones, biaryls, and sulfur dioxide. All the findings indicate that photolyses of α-disulfones yield a pair of arenesulfonyl radicals.

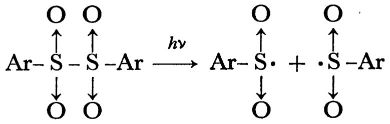
In comparison with the thiyl radicals, the sulfonyl radicals have been investigated to a much lesser extent. Some of the methods described in the literature for generation of sulfonyl radicals are thermolyses[2] and photolyses[3] of azosulfones, oxidation of sulfinic acids in water,[4] and thermolyses and photolyses of arenesulfonyl iodides.[5] It was reported that no substitution occurs from the reaction of arenes with the sulfonyl radicals formed by addition of phenyl radical to sulfur dioxide,[6] photolyses of diaryl sulfones,[7] or oxidation of *N*,*N'*-diarenesulfonylhydrazines.[8] Kice and Favstritsky studied the thermolysis of di-*p*-tolyl disulfone in bromobenzene, and the formation of phenyl *p*-tolyl sulfone was ascribed to the attack of *p*-toluenesulfonyl radical to bromobenzene.[9]

In an attempt to understand the chemistry of arenesulfonyl radicals, di-*p*-tolyl disulfone (I) and diphenyl disulfone (II) have been photolyzed in various arenes, and the products formed have been investigated. The results will be described in this paper.

Results and Discussion

Diaryl α-disulfones are very stable at room temperature, but were found to decompose fairly rapidly upon irradiation of UV light. After 30 min of irradiation, a thin layer chromatographic analysis showed the presence of diaryls, and more than 50% of disulfones were found to decompose in 2—3 hr.

Diaryl α-disulfones have an absorption maximum near 250 nm, which matches with the wavelength of the light at 253.7 nm from a mercury lamp. The recently reported value[10] for S–S bond length (2.193 Å) in diphenyl disulfone is 0.16 Å longer than the average bond length of the ordinary disulfides. The elongation of the bond length means the weakning of the S–S bond in α-disulfones, which may explain the easy splitting of these compounds by photolyses.



$$\mathrm{Ar{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}{-}Ar \xrightarrow{h\nu} Ar{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}\cdot + \cdot\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}{-}Ar}$$

The results of the photolyses of di-*p*-tolyl disulfone (I) and diphenyl disulfone (II) in aromatic solvents are shown in Table 1 and 2. It should be noted that

---

[1] Organic Sulfur Compounds. XXXVI.

[2] C. G. Overberger and A. J. Rosenthal, *J. Amer. Chem. Soc.*, **82**, 117 (1960); M. Kobayashi, H. Minato, M. Kojima, and N. Kamigata, This Bulletin, **44**, 2501 (1971).

[3] M. Kobayashi, S. Fujii, and H. Minato, *ibid.*, **45**, 2039 (1972).

[4] J. McMillan and W. A. Waters, *J. Chem. Soc.*, *B*, **1966**, 422.

[5] C. M. M. da Silva Correa and W. A. Waters, *J. Chem. Soc.*, *C*, **1968**, 1872.

[6] J. M. Squire and W. A. Waters, *J. Chem. Soc.*, **1962**, 2068; C. M. M. da Silva Correa, A. S. Lindsay, and W. A. Waters, *J. Chem. Soc.*, *C*, **1968**, 1874.

[7] N. Kharasch and A. I. A. Khodair, *Chem. Commun.*, **1967**, 98.

[8] Y. Kohara, M. Kobayashi, and H. Minato, This Bulletin, **43**, 2933 (1970).

[9] J. L. Kice and N. A. Favstritsky, *J. Org. Chem.*, **35**, 116 (1970).

[10] C. Th. Kiers and A. Vos, *Rec. Trav. Chim. Pays-Bas*, **91**, 126 (1972).

TABLE 1. PRODUCTS OF PHOTOLYSIS OF DI-*p*-TOLUENESULFONYL (I) IN BENZENE[a]

(I) (mmol)	Time irradiated hr	Extent of reaction[b] %	Products (mol/100 mol disulfone photolyzed)						
			$C_7H_7SO_3H$	$C_7H_7SO_2\text{-}SC_7H_7$	C_7H_7Ph	$C_7H_7\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}Ph$	$(C_7H_7)_2SO_2$	$(C_7H_7\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}})_2O$	$(C_7H_7S)_2$
4.06	7	84.9	113	14.2	15.1	d	d	3.3[c]	4.1
4.26	8	85.7	91.2	9.0	13.4	0.5	0.5	11.1	3.3

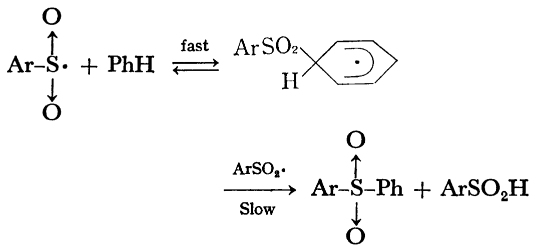
a) Irradiated in 500 m*l* of benzene with a high pressure mercury lamp.
b) On the basis of the unchanged disulfone.
c) The amount of the anhydride which was not hydrolyzed upon treatment with water.
d) Not determined.

TABLE 2. PRODUCTS OF PHOTOLYSIS OF $(PhSO_2)_2$ (II) IN TOLUENE

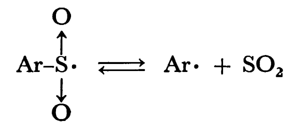
(II) (mmol)	PhMe (m*l*)	Time irradiated hr	Products (mol/100 mol disulfone used[a])							
			$PhSO_3H$	$PhSO_2SPh$	PhC_7H_7	$PhSO_2C_7H_7$	$PhSO_2\text{-}CH_2Ph$	Ph_2SO_2	$(PhS)_2$	$(PhCH_2)_2$
10.74	500	7	75.3	9.7	2.5	0.6	1.7	0.7	1.0	3.0
10.66	500	14	83.8	15.1	2.9	0.7	1.8	0.8	b)	3.0
4.05	300	7	94.9	b)	12.4	1.2	4.4	1.2	b)	3.0

a) Extent of photolysis was estimated to be 70—80%, but exact determination was not possible. Yields are based on the amount of disulfone initially added.
b) Not determined.

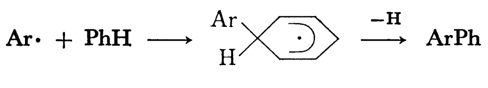
the yields of sulfones are very small. Addition of arenesulfonyl radicals to benzene is considered as a reversible step and hydrogen abstraction from an arenesulfonylcyclohexadienyl radical must be a very slow step in comparison with the dissociation of the cyclohexadienyl radicals.



Formation of methylbiphenyls shows that the following desulfonylation takes place to some extent. This reaction is known to be a reversible process.[11]

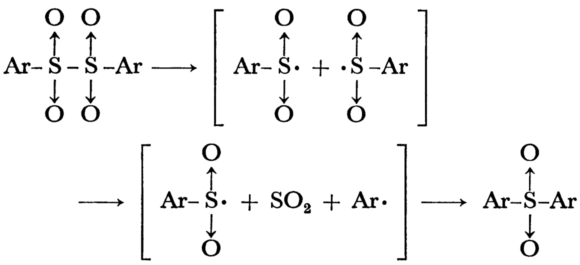


$$Ar\text{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}\cdot \rightleftharpoons Ar\cdot + SO_2$$



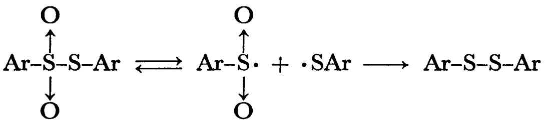
Bond dissociation energy $D(C\text{–}SO_2\cdot)$ of the related methanesulfonyl radical is estimated to be 23 kcal/mol.[12] This rather high value suggests that the cleavage of sulfur dioxide from the sulfonyl radical must be much slower than that of carbon dioxide from the corresponding aroyl radicals. In order to ascertain that arenesulfonyl radicals lose sulfur dioxide under these conditions, a benzene solution of (I) was degassed and irradiated in a quartz tube. Sulfur dioxide was found as a product; yield, 0.26 mol per mol of (I). Other products found were *p*-toluenesulfonic acid (86 mol%), *p*-tolyl *p*′-toluenethiolsulfonate (50 mol%), and *p*-methylbiphenyl (10 mol%).

Di-*p*-tolyl sulfone among the decomposition products of (I) in benzene is probably the product of combination of radicals in cage.



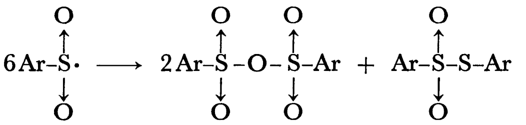
$$Ar\text{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}\text{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}\text{-}Ar \longrightarrow \left[Ar\text{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}\cdot + \cdot\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}\text{-}Ar\right] \longrightarrow \left[Ar\text{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}\cdot + SO_2 + Ar\cdot\right] \longrightarrow Ar\text{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}\text{-}Ar$$

Di-*p*-tolyl disulfide is the product of dimerization of ArS• radical, which is probably formed by photolysis of thiolsulfonates.



$$Ar\text{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}\text{-}S\text{-}Ar \rightleftharpoons Ar\text{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}\cdot + \cdot SAr \longrightarrow Ar\text{-}S\text{-}S\text{-}Ar$$

Formation of *p*-toluenesulfonic anhydride and *p*-tolyl *p*-toluenethiolsulfonate can be explained as the result of disproportionation of sulfonyl radicals as suggested by da Silva Correa and Waters.[5]



$$6Ar\text{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}\cdot \longrightarrow 2Ar\text{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}\text{-}O\text{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}\text{-}Ar + Ar\text{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}\text{-}S\text{-}Ar$$

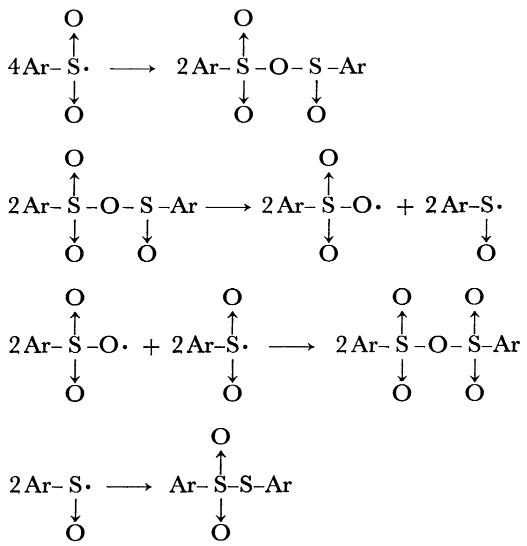
The above equation is the summary of the following

---

11) H. Goldwhite, M. S. Gibson, and C. Harris, *Tetrahedron*, **20**, 1613 (1964).

12) W. K. Busfield, K. J. Ivin, H. Mackle, and P. A. G. O'Hare, *Trans. Faraday Soc.*, **57**, 1064 (1961); A. Good and J. C. J. Thynne, *ibid.*, **63**, 2708 (1967).

multi-step reactions.



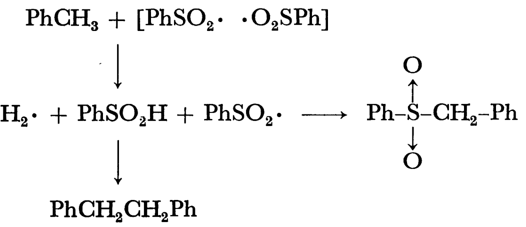
$$4\text{Ar-}\underset{O}{\underset{\downarrow}{\overset{O}{\overset{\uparrow}{S}}}}\cdot \longrightarrow 2\text{Ar-}\underset{O}{\underset{\downarrow}{\overset{O}{\overset{\uparrow}{S}}}}\text{-O-}\underset{O}{\underset{\downarrow}{S}}\text{-Ar}$$

$$2\text{Ar-}\underset{O}{\underset{\downarrow}{\overset{O}{\overset{\uparrow}{S}}}}\text{-O-}\underset{O}{\underset{\downarrow}{S}}\text{-Ar} \longrightarrow 2\text{Ar-}\underset{O}{\underset{\downarrow}{\overset{O}{\overset{\uparrow}{S}}}}\text{-O}\cdot + 2\text{Ar-}\underset{O}{\underset{\downarrow}{S}}\cdot$$

$$2\text{Ar-}\underset{O}{\underset{\downarrow}{\overset{O}{\overset{\uparrow}{S}}}}\text{-O}\cdot + 2\text{Ar-}\underset{O}{\underset{\downarrow}{\overset{O}{\overset{\uparrow}{S}}}}\cdot \longrightarrow 2\text{Ar-}\underset{O}{\underset{\downarrow}{\overset{O}{\overset{\uparrow}{S}}}}\text{-O-}\underset{O}{\underset{\downarrow}{\overset{O}{\overset{\uparrow}{S}}}}\text{-Ar}$$

$$2\text{Ar-}\underset{O}{\underset{\downarrow}{S}}\cdot \longrightarrow \text{Ar-}\underset{O}{\underset{\downarrow}{\overset{O}{\overset{\uparrow}{S}}}}\text{-S-Ar}$$

The results shown in Table 2 are generally in agreement with those in Table 1 except the formation of benzyl phenyl sulfone and bibenzyl, which can be explained as the products of combination of two radicals.



$$\begin{tikzcd}[column sep=small] PhCH_3 + [PhSO_2\cdot\ \cdot O_2SPh] \arrow[d] & \\ PhCH_2\cdot + PhSO_2H + PhSO_2\cdot \arrow[r] \arrow[d] & \text{Ph-}\underset{O}{\underset{\downarrow}{\overset{O}{\overset{\uparrow}{S}}}}\text{-CH}_2\text{-Ph} \\ PhCH_2CH_2Ph & \end{tikzcd}$$

The higher yields of these products than those of phenyl *p*-tolyl sulfones suggest that abstraction of a benzyl hydrogen from toluene is faster than substitution on the aromatic ring.

Although it has been reported that substitution of arenes with arenesulfonyl radicals does not occur,[6,7] formation of phenyl *p*-tolyl sulfone in this investigation clearly shows that an arenesulfonyl radical reacts with an arene ring to some extent. In order to study the aromatic substitution with benzenesulfonyl radical in detail, the isomer distribution of aryl phenyl sulfones were determined in toluene, anisole, and chlorobenzene. The results of benzenesulfonylation and phenylation are summarized in Table 3.

TABLE 3. ISOMER DISTRIBUTION OF SUBSTITUTED BIPHENYLS AND PHENYL ARYL SULFONES PRODUCED FROM PHOTOLYSIS OF DIPHENYL DISULFONE (II) IN ARENES

Arene	Isomer distributions %					
	PhC_6H_4X			$PhSO_2C_6H_4X$		
	o-	*m*-	*p*-	*o*-	*m*-	*p*-
PhMe	32.7	40.0	27.3	31.6	35.8	32.6
PhOMe	46.6	19.9	33.5			
PhCl	33.4	35.1	31.5			

The isomer distributions of substituted biphenyls in Table 3 are different from what is expected for phenylation with phenyl cation,[13,14] and are similar to those observed for phenylation with phenyl radical produced from thermolyses of benzoyl peroxide or *N*-nitrosoacetanilide. However, the amounts of *ortho*-substituted products are much less than those usually observed for phenylation with the phenyl radical produced by thermolyses. It is possible that the behavior of thermally produced phenyl radicals and that of photolytically produced phenyl radicals are somewhat different due to the difference of the extent of the solvation. The isomer distributions of substituted biphenyls in Table 3 are in agreement with those reported for phenylation with the phenyl radical produced from the photolysis of diphenyl sulfone (Me; *o*-, 30.4, *m*-, 43.5, *p*-, 26.1; MeO; *o*-, 32.3, *m*-, 13.5, *p*-, 55.2; Cl; *o*-, 41.8, *m*-, 28.6, *p*-, 29.6),[15] and those with the phenyl radical produced from the photolysis of phenylazo *p*-tolyl sulfone.[3]

In the photolysis of diphenyl disulfone in chlorobenzene, 176 mol chlorobiphenyls and 15.2 mol biphenyl were formed from 100 mol disulfone. These results show that chlorobenzene itself was photolyzed under these conditions.

When diphenyl disulfone was irradiated in nitrobenzene with a low pressure mercury lamp for 22 hr, almost no reaction took place. It appears that nitrobenzene absorbs light but does not transfer the energy to the disulfone.

In order to estimate the electrophilicity of sulfonyl radicals, di-*p*-tolyl disulfone was photolyzed in anisole, and the amounts of isomeric anisyl phenyl sulfones were determined. From 6.5 mmol of the disulfone, 0.031 mmol of the *p*-anisyl sulfone and 0.180 mmol of the *o*- and *m*-anisyl sulfones were formed (separation of the *o*- and *m*-isomers was not possible). Therefore, the isomer distribution is *o*+*m*, 85.3% and *p*-, 14.7%.

The isomer distribution of substituted diphenyl sulfones shown in Table 3 indicate that this benzenesulfonylation involves not benzenesulfonyl cation, but benzenesulfonyl radical. Electrophilic arenesulfonylation of arenes is known as a highly selective reaction. Cationic *p*-toluenesulfonylation of toluene gave the *o*- and *p*-(main product) sulfones exclusively, and no *m*-substituted product was found.[16]

The result of the present investigation clearly shows the occurrence of free radical arenesulfonylation of aromatic rings, whereas it was stated in the literature[6,7] that the sulfonyl radical generated in an aromatic solvent is not reactive enough to give a sulfone. This contradiction can be ascribed to the difference of the hydrogen abstracting agent from the sulfonylcyclohexadienyl radical. In the photolyses of the sulfonyl iodide, the hydrogen must be abstracted by iodine

---

[13] M. Kobayashi, H. Minato, E. Yamada, and N. Kobori, This Bulletin, **43**, 215 (1970).

[14] M. Kobayashi, H. Minato, and N. Kobori, *ibid.*, **43**, 219 (1970).

[15] T. Nakabayashi, Y. Nagata, and J. Tsurugi, III Abstracts of 23th Annual Meeting of the Chemical Society of Japan, p. 1270.

[16] M. Kobayashi, H. Minato, and Y. Kohara, This Bulletin, **43**, 234 (1970); Y. Kohara, M. Kobayashi, and H. Minato, *ibid.*, **43**, 520 (1970).

atoms which have very low reactivity for this role. In the thermolyses or photolyses of azosulfones, the sulfonyl radicals mainly act as the hydrogen abstractor from the arylcyclohexadienyls formed by the attack of aryl radicals on arene. In the photolyses of diaryl disulfones, sulfonyl radicals abstract hydrogen atom from the sulfonylcyclohexadienyl radicals produced by the attack of sulfonyl radicals on arene, and therefore, considerable amounts of diaryl sulfones are isolated.

Experimental

Materials. Benzene, toluene, anisole, and chlorobenzene were purified according to the methods described in the literature.[17] Di-*p*-tolyl disulfone was prepared by $KMnO_4$-oxidation of *p*-toluenesulfinic acid in acetic acid;[18] yield, 28%; recrystallized from acetone, and then three times from benzene; mp (decomp.) 217—219°C (lit, 211°C,[18] 218—220°C,[19] 220°C[20]). Diphenyl disulfone (II) was synthesized by $KMnO_4$-oxidation of benzenesulfinic acid in acetic acid; yield, 22%; recrystallized from acetone and then twice from benzene; mp 190—192°C (lit, 193—194°C,[18] 193°C[20]).

Photolysis of I in Benzene under Nitrogen. A benzene solution (500 m*l*) of (I) (3—5 mmol) was stirred and irradiated with a 100 W high pressure mercury lamp at 16—22°C under nitrogen. Then the reaction mixture was washed with water, and the amount of *p*-toluenesulfonic acid in the aqueous layer was determined by converting it into *S*-benzylisothiuronium *p*-toluenesulfonate. The organic layer was dried over anhydrous magnesium sulfate, concentrated under reduced pressure, and the residue was separated to its components by column chromatography (Florisil, 100—200 mesh). *p*-Methylbiphenyl (eluted with hexane), di-*p*-tolyl disulfide (hexane-benzene) and *p*-tolyl *p'*-toluenethiolsulfonate (benzene) were identified by comparison with authentic samples. Compounds containing a sulfone group (eluted with diethyl ether) were identified by use of an Ohkura Gas Chromatograph 1100 on an SE-30 column. The amount of *p*-toluenesulfonic anhydride was determined by converting it to *N*-phenyl-*p*-toluenesulfonamide and anilinium *p*-toluenesulfonate by the reaction with aniline.

Photolysis of I in Degassed Benzene. A benzene solution (60 m*l*) of (I) (0.32 mmol) in a quartz vessel was degassed by the freeze-thaw technique, and then irradiated with a 1 kW high pressure mercury lamp for 2 hr at 16—17°C. Then, the mixture was distilled at room temperature in high vacuum. Sulfur dioxide contained in the distillate was extracted with a 5% sodium hydroxide solution, and its amount was determined by iodometry. From the higher boiling fraction the unchanged (I) was filtered off, and then the rest was separated by column chromatography.

Photolysis of II in Toluene under Nitrogen. The photolysis was carried out according to the procedure described for (I). Diphenyl disulfide (eluted with hexane-benzene), phenyl benzenethiolsulfonate (benzene), diphenyl sulfone (benzene), and benzyl phenyl sulfone (benzene) were identified by comparison with authentic samples. A mixture of phenyl *o*-, *m*-, *p*-tolyl sulfones and a mixture of *o*-, *m*-, *p*-methylbiphenyls and bibenzyl (eluted with hexane) were analyzed by use of a Hitachi Gas Chromatograph K53.

Photolysis of II in Anisole under Nitrogen. An anisole solution of (II) (4.05 mmol) was stirred and irradiated with a 6 W low pressure mercury lamp under nitrogen at 16—19°C for 21.5 hr. The reaction mixture was analyzed in a manner similar to that described above.

---

[17] A. Weissberger, "Organic Solvents," Interscience Publishers, Inc., New York, (1955).

[18] T. P. Hilditch, *J. Chem. Soc.*, **93**, 1526 (1908).

[19] P. Allen, Jr. and J. W. Brook, *J. Org. Chem.*, **27**, 1019 (1962).

[20] J. M. Damson, A. M. Mathieson, and J. M. Robertson, *J. Chem. Soc.*, **1948**, 322.