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Oxidation of *N,N'*-Diarenesulfonylhydrazines

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N,N'-Diarenesulfonylhydrazine was oxidized with several oxidizing regents, but diarenesulfonyl diimide was not isolated. Diarenesulfonyl diimide produced immediately decomposed with evolution of 1 mol of nitrogen, and afforded the corresponding sulfonyl bromide, α-disulfone and sulfonic acid. Plausible mechanisms of decomposition were discussed.

By the analogy with other azo compounds such as azobisisobutyronitrile[1] and dibenzoyl diimide,[2] diarenesulfonyl diimide, $RSO_2N{=}NSO_2R$, is expected to decompose to form sulfonyl free radicals with liberation of nitrogen. Waters *et al.* made a study of the reactions of sulfonyl free radicals generated by photolysis of sulfonyl iodide.[3] Recently, Kwart and Khan reported the isolation of dibenzenesulfonyl diimide (I) by oxidation of the corresponding hydrazine (II).[4] We have been interested in the reactions of sulfonyl radicals, and attempted to produce diarenesulfonyl diimides according to their method. However, our experimental findings differ from theirs, and the diimides formed immediately decomposed in repeated experiments under various conditions. This paper will describe the results of careful products analyses and discuss the plausible mechanisms of its decomposition.

Results and Discussion

Formation of *N,N'*-di-*p*-toluenesulfonyl diimide (III) was attempted by oxidation of *N,N'*-di-*p*-toluenesulfonylhydrazine (IV) with bromine in anhydrous ethyl alcohol or aqueous acetonitrile according to the method of Kwart and Khan.[4] When an excess of bromine was dropped to the solution, 1 mol of nitrogen was instantaneously evolved and III was not isolated. Similarly, the oxidation of II resulted in evolution of 1 mol of nitrogen, and I was not isolated. Even when IV was oxidized at −40°C with bromine, the evolution of nitrogen was instantaneous. These experiments indicate that the azo compounds I and III are too unstable to be isolated as such.

Products of decomposition of I and III were analyzed. Products found were arenesulfonyl bromide, diaryl disulfone, arenesulfonic acid, and, in the case of decomposition in ethyl alcohol, ethyl arenesulfonate, as shown in Scheme 1. Amounts of these products produced under various conditions are shown in Tables 1 and 2.

1) J. P. Van Hook and A. V. Tobolsky, *J. Amer. Chem. Soc.*, **80**, 779 (1958).

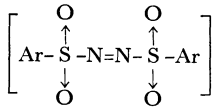
2) J. E. Leffler and W. B. Bond, *ibid.*, **78**, 335 (1956).

3) a) C. M. M. da Silva Corrêa, A. S. Lindsay and W. A. Waters, *J. Chem. Soc. C*, **1968**, 1872. b) C. M. M. da Silva Corrêa and W. A. Waters, *ibid.*, **1968**, 1874. c) C. M. M. da Silva Corrêa and W. A. Waters, *ibid.*, **1968**, 1880. d) M. McMillan and W. A. Waters, *J. Chem. Soc., B*, **1966**, 422.

4) H. Kwart and A. A. Khan, *J. Org. Chem.*, **33**, 1537 (1968).

Scheme 1

$$ArSO_2NH\text{-}NHSO_2Ar \xrightarrow[\text{aq. } CH_3CN \text{ or anhyd. EtOH}]{Br_2}$$



$$\longrightarrow N_2 + ArSO_2Br + ArSO_2\text{-}SO_2Ar$$
$$ArSO_3H + ArSO_2OEt \text{ (in EtOH)}$$

In the oxidation of II with bromine in aqueous acetonitrile and anhydrous ethyl alcohol, diphenyl disulfone was produced. Its melting point was 188—189°C, which is similar to that of diphenylsulfonyl diimide (193—194°C) reported by Kwart and Khan.[4] Diphenyl disulfone absorbed at 1300, 1325, 1345 cm^{-1} ($\nu_{as}SO_2$), 1130 cm^{-1} (ν_s-SO_2), 1580 and 1445 cm^{-1} (phenyl) in the infrared (KBr disc). Its mass spectrum (m/e) was quite similar to that reported for dibenzenesulfonyl diimide.

Various azo compounds, R–N=N–R′, are known; for instance, R=R′= $PhCO$,[2] R=R′= $(CH_3)_2$-CCN,[1] R=$PhSO_2$, R′=Ph,[5] and R=R′=Ph_2-CH.[6] In general, the more stabilized are the radicals R and R′, the more unstable is the azo compound. Sulfonyl radical is a very stable radical, and its stability is demonstrated by the fact that it does not attack a benzene ring.[3a] In view of these data, it is rather surprising that I is isolated and its melting point is as high as 193°C.

It was not possible to oxidize IV with bromine in anhydrous acetonitrile, and the starting materials were recovered. IV was not oxidized with bromine in acetonitrile under irradiation of light, and the starting materials were also recovered. Therefore, the presence of water is necessary for oxidation of diarenesulfonylhydrazines. The oxidizing species is probably the HOBr formed by the reaction of bromine and water.

IV was oxidized with chloranil, NBS (*N*-bromosuccinimide) or potassium permanganate, and di-*p*-tolyl disulfone was formed with evolution of nitrogen, as shown in Table 3. The presence of water is necessary for the oxidation of IV with NBS, as in the case with bromine. When a solution of IV and BPO (benzoyl peroxide) or AIBN (azobisisobutyronitrile) in acetonitrile was refluxed, IV was recovered. Therefore, dehydrogenation of IV to III could not be accomplished with such radicals as bromine atom, $PhCO_2\cdot$, or $(CH_3)_2\dot{C}CN$.

Waters *et al.* reported that sulfonyl radicals tended to disproportionate according to the equation;

$$6\ ArSO_2\cdot \longrightarrow 2\ (ArSO_2)_2O + ArSSO_2Ar$$

They verified the formation of $ArSO_2\cdot$ radicals by scavenging them with quinones, which converted

Table 1. Oxidation of IV with bromine

Run	Reactions mmol				Products mmol (%)				
	(TsNH–)$_2$	Br_2	Solvents	Temp.	N_2	TsBr	Ts_2	TsOH	TsOEt
1	2.60	3.15	CH_3CN	r.t.					—[a]
2	1.96	2.81[b]	CH_3CN	r.t.					—[a]
3	2.22	6.71	96% aq. CH_3CN	r.t.	2.32 (104.6)	2.51 (56.6)	0.23 (10.2)	0.87 (19.6)	—
4	2.43	2.68	96% aq. CH_3CN	r.t.	1.30 (53.7)	1.30 (26.9)	0.26 (10.7)	0.67 (13.8)	—[c]
5	2.28	6.15	97% aq. CH_3CN	−40°C	2.20 (96.5)	1.98 (42.3)	0.48 (21.2)	1.03 (22.6)	—
6	1.76	13.23	anhyd. EtOH	r.t.	1.73 (98.3)	0.75 (21.3)	0.56 (31.5)	1.07 (30.2)	0.64 (18.0)

a) The starting materials were recovered.
b) Irradiated with a tungsten lamp for 15 hr.
c) The starting materials were recovered (0.69 mmol, 28.5%).

Table 2. Oxidation of II with bromine at room temperature

Run	Reactants mmol			Products mmol				
	(PhSO$_2$NH–)$_2$	Br_2	Solvents	N_2	$PhSO_2Br$	$(PhSO_2\text{-})_2$	$PhSO_3H$	$PhSO_2OEt$
1	3.09	6.76	94% aq. CH_3CN	2.85 (92.4)	3.00 (48.7)	0.40 (12.8)	2.42 (39.2)	—
2	2.89	15.85	anhyd. EtOH	2.42 (83.5)	0.98 (16.9)	0.56 (19.5)	1.68 (29.1)	0.42 (7.2)

5) A. J. Rosenthal and C. G. Overberger, *J. Amer. Chem. Soc.*, **82**, 108 (1960); C. G. Overberger and A. J. Rosenthal, *ibid.*, **82**, 117 (1960).

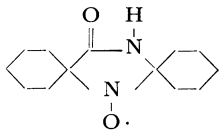
6) S. G. Cohen and C. H. Wang, *ibid.*, **77**, 2457 (1955).

Table 3. Oxidation of IV with various oxidants

Run	Reactants mmol				Products mmol (%)				
	$(TsNH-)_2$	Oxidant	Solvent	Temp.	N_2	TsBr	Ts_2	TsOH	
1	2.55	NBS 4.85	CH_3CN	80°C					a)
2	2.11	NBS 4.01	96% aq. CH_3CN	r.t.	2.19 (104.0)	2.25 (53.3)	0.22 (10.4)	1.04 (24.5)	
3	1.82	$KMnO_4$ 6.37	CH_3CN	r.t.	2.17 (118.6)	—	0.36 (19.5)	1.84 (50.3)	
4	2.06	Chloranil 4.27	CH_3CN	80°C		—	0.58 (27.9)		
5	4.1	BPO 4.1	CH_3CN	80°C		—			a)
6	3.5	AIBN 3.1	CH_3CN	80°C		—			a)

a) The starting materials were recovered.

the radicals into sulfonates of quinols.[3b] However, in our conditions, no thiolsulfonate was found. When IV was oxidized with bromine in the presence of excess *p*-benzoquinone in aqueous acetonitrile, disulfonate of hydroquinone, which was a possible product from sulfonyl radical and *p*-benzoquinone, was not detected. Attempts to scavenge the free sulfonyl radicals by cyclohexane-1-spiro-2'-(4'-oxoimidazolidine-1'-oxyl)-5'-spiro-1'-cyclohexane (V), which was stable under the reaction conditions, was also unsuccessful.



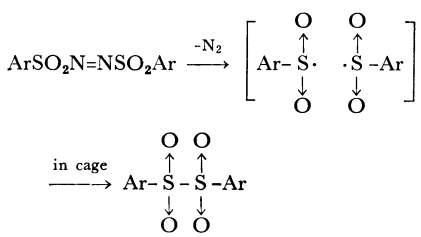
(V)

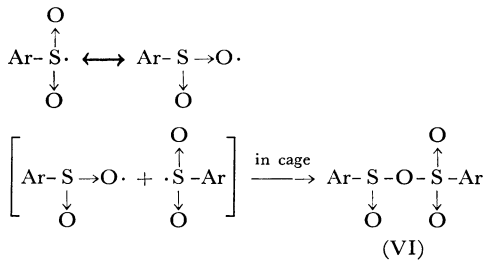
When IV was oxidized with bromine in aqueous acetonitrile in the presence of benzene or nitrobenzene, *p*-tolyl phenyl sulfone or *p*-tolyl nitrophenyl sulfone was not found. When IV was oxidized with NBS or potassium permanganate in the presence of toluene, neither *p*-tolyl benzyl sulfone nor *p*-toly tolyl sulfone was detected. These findings show that *p*-toluenesulfonyl radical does not attack benzene rings and does not abstract benzyl hydrogens.

When arenesulfonyl radicals were produced by the photolysis of arnenesulfonyl iodide, the reaction between two sulfonyl radicals always yielded a sulfinyl sulfonate (VI) without being accompanied by the formation of a disulfone.[3b] Therefore, the formation of a disulfone in our conditions can be rationalized only in terms of the recombination in a solvent cage. Oxidation of *N*-benzenesulfonyl-*N'*-*p*-toluenesulfonylhydrazine (VII) with bromine in aqueous acetonitrile gave phenyl *p*-tolyl disulfone free from any cross products, namely diphenyl disulfone or di-*p*-tolyl disulfone. This fact also supports our assumption that disulfones are the products of the recombination of the geminate sulfonyl radical pair.

Formation of other products can be explained by the reaction steps shown below.

Mechanism I





(VI)

$$VI \xrightarrow{H_2O} ArSO_3H + ArSO_2H$$

$$VI \xrightarrow{HBr} ArSO_3H + ArSBr$$

$$ArSO_2\cdot \xrightarrow{Br_2} ArSO_2Br + Br\cdot$$

$$ArSO_2H \xrightarrow{Br_2} ArSO_2Br + HBr$$

$$ArSBr \xrightarrow{H_2O,\ Br_2} ArSO_2Br$$

or

$$VI \longrightarrow ArSO_3\cdot + Ar\dot{S}O$$

$$ArSO_3\cdot \xrightarrow{RH} ArSO_3H + R\cdot$$

$$Ar\dot{S}O \xrightarrow{Br_2} ArSBr$$

Sulfinyl radicals are expected to react readily with bromine, and it is reasonable that thiosulfonate,

the disproportionation product of sulfinyl radicals, was not found in our conditions. For oxidation of II and IV more than one mole of bromine per mole of disulfonylhydrazines had to be added for evolution of the quantitative amount of nitrogen. Undoubtedly part of bromine added was used for oxidation of species containing sulfinyl sulfur. Ethyl arenesulfonate was formed as below.

$$\mathrm{VI} \xrightarrow{\mathrm{EtOH}} \mathrm{ArSO_3H} + \mathrm{ArSOEt}$$

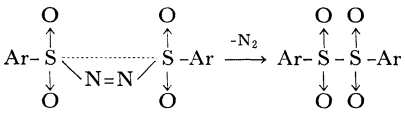
$$\mathrm{ArSOEt} \xrightarrow{\mathrm{Br_2}} \mathrm{ArSO_2OEt} + \mathrm{ArSO_2Br}$$

$$\mathrm{ArSO_2Br} \xrightarrow{\mathrm{EtOH}} \mathrm{ArSO_2OEt}$$

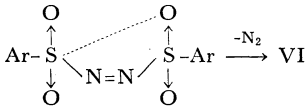
Ethyl *p*-toluenesulfonate was oxidized with bromine in ethyl alcohol at room temperature to afford *p*-toluenesulfonyl bromide and ethyl *p*-toluenesulfonate, and was produced by ethanolysis of *p*-toluenesulfonyl bromide.

The formation of the diaryl disulfone could be alternatively explained by means of a four-centered transition state:

Mechanism II



In a similar fashion intermediate VI could arise *via* a five-centered transition state.



At present it is not possible to determine which of these two mechanisms is correct.

Experimental

Materials. Acetonitrile and ethyl alcohol were purified by the usual method.[7]

Bromine, chloranil and potassium permanganate of first grade were used without further purification. NBS was recrystallized from water.

Synthesis of IV. Twelve grams of *p*-toluenesulfonylhydrazine, prepared from *p*-toluenesulfonyl chloride and hydrazine hydrate, was dissolved in 50 m*l* of ethyl alcohol. To this solution 6.5 g of *p*-toluenesulfinyl chloride was added at 60°C. After 1.5 hr, white crystals precipitated were filtered off, and recrystallized from acetone-water to afford 2.8 g of IV (20%); mp 205°C (decomp.), lit, 218—220°C (decomp.).[8]

Synthesis of II. A solution of 40 g of benzenesulfonylhydrazine and 20 g of benzenesulfonyl chloride in 50 m*l* of ethyl alcohol was refluxed for 4 hr. White crystals obtained were recrystallized from acetone-water; yield, 11 g (31%), mp 218°C (decomp.), lit, *ca.* 245°C.[9]

Synthesis of VII. VII was prepared by a modification of the procedure reported by Munshi *et al.*;[10] mp 185°C, lit, 184°C.[10]

Oxidation of IV with Bromine in Aqueous Acetonitrile. To the solution of 0.754 g of IV in 96% aqueous acetonitrile, 1.073 g of bromine was added. The evolution of nitrogen was measured by use of a gas burette. After reaction was completed, the products were extracted with methylene chloride, and dried over magnesium sulfate. Methylene chloride was removed, and the products were separated with elution chromatography on a silica gel column; *p*-toluenesulfonyl bromide was eluted with hexane-benzene (mp 93°C, lit, 96°C[11]), di-*p*-tolyl disulfone was eluted with benzene (mp 207°C, lit, 210°C[12] or 218—220°C[13]; IR: 1130 and 1340 cm^{-1}). *p*-Toluenesulfonic acid was precipitated as its *S*-benzylisothiuronium salt.

Oxidation of IV with Bromine in Anhydrous Acetonitrile. To a solution of 0.884 g of IV in 50 m*l* of anhydrous acetonitrile, 0.505 g of bromine was added drop by drop at room temperature. No evolution of nitrogen was observed even in 12 hr, and the starting materials were recovered.

Oxidation of IV with Bromine in Anhydrous Ethyl Alcohol. Oxidation was carried out in a similar way. Ethyl *p*-toluenesulfonate was isolated by elution chromatography on a silica gel column with benzene as solvent; IR: 1170 and 1360 cm^{-1}.

Attempt for Oxidation of IV with Bromine under Irradiation. A solution of 0.666 g of IV and 0.449 g of bromine in 50 m*l* of anhydrous acetonitrile was irradiated with a tungsten lamp for 15 hr. When acetonitrile was removed, the starting materials were recovered.

Oxidation of II with Bromine. Oxidation was carried out in a way similar to that of IV. Products were benzenesulfonyl bromide (IR: 1165 and 1365 cm^{-1}), ethyl benzenesulfonate (IR: 1180 and 1355 cm^{-1}), and diphenyl disulfone (mp 188—189°C, lit, mp 193°C[12]; mass spectrum, m/e (relative intensity), 282 (1.2), 250 (0.3), 234 (2.0), 218 (0.5), 154 (0.9), 153 (2.1), 152 (2.5), 151 (0.7), 141 (100), 125 (26.2), 110 (1.1), 109 (2.1), 108 (0.6) and 97 (9.3)). The mass spectrum was measured on a Hitachi mass spectrometer RMU 6E type, operated with 70 eV at 200°C.

Oxidation of IV with NBS. A solution of 0.820 g of NBS in acetonitrile was added drop by drop to a solution of 0.717 g of IV in 50 m*l* of 96% aqueous acetonitrile. The products were separated by elution chromatography.

Oxidation of IV with Potassium Permanganate. When a solution of 0.620 g of IV in 25 m*l* of anhydrous

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10) A. A. Munshi, N. M. Shah and J. P. Trivedi, *J. Indian Chem. Soc.*, **40**, (11), 966 (1963).

11) V. O. Lukashevich, *Dokl. Akad. Nauk SSSR*, **103**, 627 (1955); *Chem. Abstr.*, **50**, 5556 (1956).

12) I. M. Damson, A. McL. Mathieson and J. M. Robertson, *J. Chem. Soc.*, **1948**, 322.

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

acetonitrile was added drop by drop to a solution of 1.008 g of potassium permanganate in 50 m*l* of anhydrous acetonitrile, 0.110 g of di-*p*-tolyl disulfone was obtained.

Oxidation of IV with Chloranil. A solution of 0.700 g of IV and 1.049 g of chloranil in 85 m*l* of anhydrous acetonitrile was refluxed for 13 hr. Products were separated by chromatography on a silica gel column, and 0.178 g of di-*p*-tolyl disulfone was obtained.

Oxidation of IV with Benzoyl Peroxide. A solution of 1.4 g of IV and 1.0 g of benzoyl peroxide was refluxed for 13 hr in 5 m*l* of acetonitrile. When the solvent was removed, unchanged IV was recovered.

Oxidation of IV with Azobisisobutyronitrile (AIBN). A solution of 1.2 g of IV and 0.5 g of AIBN in 50 m*l* of acetonitrile was refluxed for 15 hr. When the solvent was removed, unchanged IV was recovered.

Oxidation of IV with Bromine in the Presence of *p*-Benzoquinone. When 1.107 g of bromine (6.93 mmol) was added at room temperature to a solution of 0.732 g of IV (2.16 mmol) and 3.1 g of *p*-benzoquinone (28 mmol) in 50 m*l* of aqueous acetonitrile, 39.2 m*l* of nitrogen was evolved. The products were extracted with methylene chloride, and an excess *p*-benzoquinone was removed by sublimation under reduced pressure. The residue was separated by elution chromatography on a silica gel column to afford *p*-toluenesulfonyl bromide, 0.226 g, and quinone mixtures. However no quinol sulfonate was found.

Oxidation of IV in the Presence of V. To a solution of 0.732 g of IV (2.15 mmol) and 1.005 g of V[14] (4.20 mmol) in 50 m*l* of acetonitrile, 0.956 g of bromine (5.98 mmol) was added drop by drop. The products were separated by elution chromatography on a silica gel column, and 0.461 g of *p*-toluenesulfonyl bromide, 0.048 g of di-*p*-tolyl disulfone and 0.750 g of unchanged V were recovered.

Oxidation of IV with Bromine in the Presence of Benzene. To a solution of 0.876 g of IV (2.58 mmol) and 2.080 g of benzene (26.6 mmol) in 50 m*l* of 96% aqueous acetonitrile, 1.353 g of bromine was added drop by drop. The products were separated by elution chromatography on a silica gel column. No *p*-tolyl phenyl sulfone was found.

Oxidation of IV with Bromine in the Presence of Nitrobenzene. To a solution of 0.702 g of IV (2.06 mmol) and 3.091 g of nitrobenzene (25.1 mmol) in 50 m*l* of 96% aqueous acetonitrile, 1.182 g of bromine (7.39 mmol) was added drop by drop. The products were separated by elution chromatography on a silica gel column. No *p*-tolyl nitrophenyl sulfone was found.

Oxidation of IV with NBS in the Presence of Toluene. A solution of 1.383 g of NBS (7.18 mmol) in acetonitrile was added drop by drop to a solution of 1.021 g of IV (3.00 mmol) and 6.6 g of toluene (71.8 mmol) in 50 m*l* of 96% aqueous acetonitrile. The products were separated by elution chromatography on a silica gel column to give 0.020 g of benzyl bromide, 0.741 g of *p*-toluenesulfonyl bromide and 0.106 g of di-*p*-tolyl disulfone, but no *p*-tolyl benzyl sulfone was detected.

Oxidation of IV with Potassium Permanganate in the Presence of Toluene. A solution of 2.197 g of IV and 13 g of toluene (141 mmol) in 50 m*l* of anhydrous acetonitrile was added drop by drop to a solution of 2.0 g of potassium permaganate (12.7 mmol) in 50 m*l* of anhydrous acetonitrile. The products were separated by elution chromatography on an alumina column. No *p*-tolyl benzyl sulfone nor *p*-tolyl tolyl sulfone was found.

Oxidation of VII with Bromine. To the solution of 0.795 g of VII (2.44 mmol) in 50 m*l* of aqueous acetonitrile, 1.066 g of bromine was added. The products were separated with elution chromatography on a silica gel column to give 0.084 g of *p*-tolyl phenyl disulfone (0.28 mmol, 11.5%); mp 162—163°C, lit, 166°C;[15] IR: 1125 and 1345 cm^{-1}. Neither diphenyl disulfone nor di-*p*-tolyl disulfone was detected.

Reaction between Ethyl *p*-Toluenesulfinate and Bromine. A solution of 1.114 g of ethyl *p*-toluenesulfinate (6.05 mmol) and 1.028 g of bromine (6.43 mmol) in 10 m*l* of anhydrous ethyl alcohol was allowed to stand at room temperature for 2 hr. Water was added to the solution and products were extracted with methylene chloride. The products were separated by elution chromatography, and 0.431 g of *p*-toluenesulfonyl bromide (1.95 mmol) and 0.094 g of ethyl *p*-toluenesulfonate (0.47 mmol) were found, and 0.217 g of unchanged ethyl *p*-toluenesulfinate (1.18 mmol) was recovered.

Reaction between *p*-Toluenesulfonyl Bromide and Ethyl Alcohol. A solution of 0.2507 g of *p*-toluenesulfonyl bromide (1.07 mmol) in 25 m*l* of anhydrous ethyl alcohol was allowed to stand at room temperature for 70 min. Water was added to the solution and products were extracted with methylene chloride. The products were separated by elution chromatography and 0.134 g of *p*-toluenesulfonyl bromide (0.57 mmol) and 0.051 g of ethyl *p*-toluenesulfonate (0.26 mmol) were found.

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