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PHOTO-REACTION OF AZOXYSULFONES. A NOVEL PHOTO-REARRANGEMENT[1]

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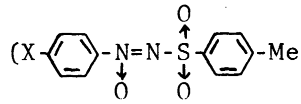
Photolysis of arylazoxy p-tolyl sulfones was investigated. A reaction mechanism proposed involves photo-rearrangement to arenediazonium sulfonates and subsequent generation of aryl free radicals.

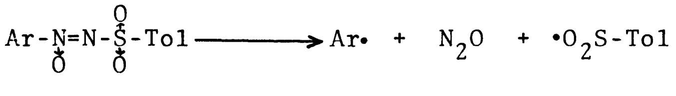
It is known that photolysis or thermolysis of an azosulfone ($R-N=N-SO_2-R'$) yields aryl and arenesulfonyl radicals with evolution of nitrogen,[2] but neither photolysis nor thermolysis of an azoxysulfone ($R-\overset{O}{N}=N-SO_2-R'$) has been reported yet. We synthesized several arylazoxy p-tolyl sulfones (**1**) from the corresponding nitrosobenzenes and chloramine-T,[3] and determined their electronic absorption spectra. Since they showed strong absorptions at 225-227 and 287-450 nm as summarized in Table 1, their photolysis appeared to be of interest.

Table 1. Absorption Maxima of Azoxysulfones () in 96%EtOH

Azoxysulfone	X	mp (°C)	λ max (nm)	ε	λmax (nm)	ε
1a	H	112	225	12,000	287	13,000
1b*	CH_3	118-120	226	28,000	307	25,000
1c	CH_3O	124-5	227	27,000	346	31,000
1d	$(CH_3)_2N$	182	227	23,000	450	43,000

*New compounds; the results of elemental analyses were satisfactory.

When an ethanolic solution of **1a** ($\sim 10^{-5}$ mol/l) was irradiated with a 500-W high-pressure mercury lamp, **1a** completely decomposed in 20 min as shown in Fig. 1, and benzene was found in a 30% yield. When a benzene solution (800 ml) of **1a** (500 mg) was irradiated with a 45-W low-pressure mercury lamp for 6 hr at room temperature, the products identified were biphenyl (35 mol%) and p-toluenesulfonic acid (30 mol%; isolated as its benzylisothiourea salt). Formation of biphenyl suggests the intermediacy of phenyl radical. When the gaseous products were analyzed with a low-temperature gas-chromatograph (with a molecular sieve) or with a gas-chromatograph-mass spectrometer, only nitrogen was found, and N_2O was not detected. This finding shows that the photolysis of **1** cannot be represented by equation (1), which is simple S-N bond fission similar to the mode of decomposition of azosulfones.



$$Ar-\underset{O}{N}=N-\overset{O}{\underset{O}{S}}-Tol \longrightarrow Ar\cdot + N_2O + \cdot O_2S-Tol \qquad (1)$$

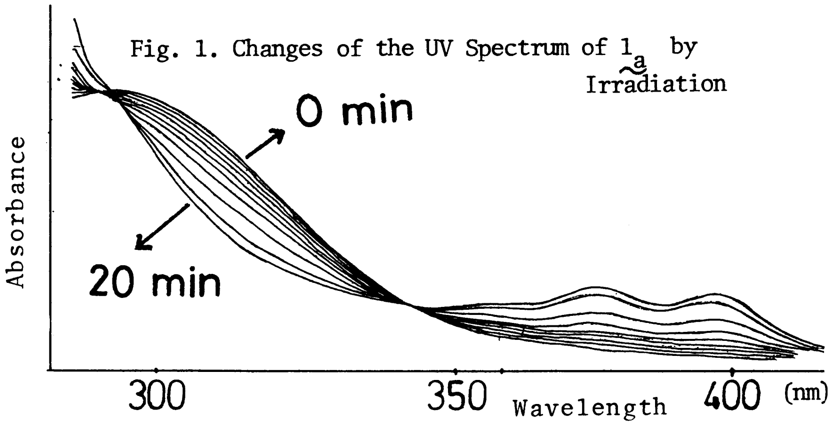
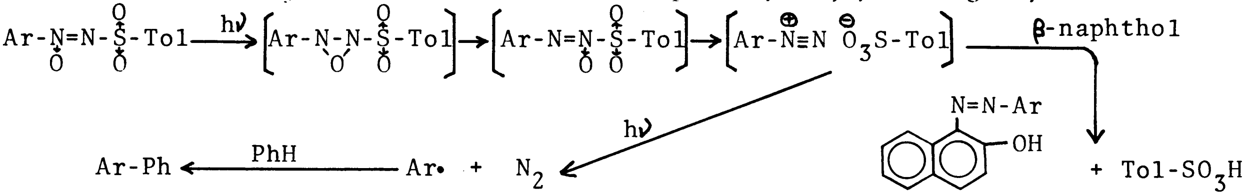


Fig. 1. Changes of the UV Spectrum of 1_a by Irradiation

Formation of nitrogen and p-TsOH suggests the intermediacy of $Ar\text{-}N_2^{\oplus}$ or $Ar\text{-}N_2\cdot$ When a benzene solution of 1_a was irradiated with a low-pressure mercury lamp in the presence of β-naphthol, the products were benzeneazo-β-naphthol(34%), p-TsOH(38%), and biphenyl(4%). When this experiment was carried out in ethanol, the products were similar; benzeneazo-β-naphthol(31%) and p-TsOH(39%).

When an ethanolic solution of 1_b, 1_c, or 1_d ($\sim 10^{-5}$ mol/l) was irradiated with a 500-W high-pressure mercury lamp, photolysis was complete in 30-40 min. When a benzene solution of 1_c was irradiated in the presence of β-naphthol (3 mol/mol 1_c) with a 40-W low-pressure mercury lamp for 120 hr, 56% of 1_c decomposed. The products isolated were $p\text{-}MeOC_6H_4\text{-}N{=}N\text{-}C_{10}H_6\text{-}OH\text{-}\beta$ (54%), p-TsOH(39%), and $p\text{-}MeOC_6H_4Ph$(7%). When a degassed benzene solution of 1_c and $Ph\text{-}CH{=}\underset{O}{\overset{}{N}}\text{-}Ph$ was irradiated with a tungsten lamp, the esr signal of $MeOC_6H_4(Ph)CH\text{-}\underset{O\cdot}{N}\text{-}Ph$ was observed($g=2.0068, a_N=10.0, a_{\beta\text{-}H}=3.2, a_{o\text{-}H}=2.4, a_{p\text{-}H}=2.4, a_{m\text{-}H}=0.9$ G).[4] In a similar manner from 1_d, $Me_2NC_6H_4(Ph)CH\text{-}\underset{O\cdot}{N}\text{-}Ph$ was obtained ($g=2.0068, a_N=10.1, a_{\beta\text{-}H}= 3.1, a_{o\text{-}H}=2.6, a_{p\text{-}H}=2.6, a_{m\text{-}H}=0.9$ G).

These results show that photo-reaction of 1 is represented by the following scheme involving the rearrangement to an arenediazonium p-toluenesulfonate. When β-naphthol is present, the majority of the salt undergo azo-coupling. When β-naphthol is absent, the diazonium ions are photolyzed, yielding aryl radicals.[5]



Azoxysulfones 1_a, 1_b, 1_c, and 1_d are thermally very stable. When a nitrobenzene solution(30 ml) of 1_a(2 mmol) was refluxed for 60 hr, about 50% decomposed and about 50% of 1_a was recovered. A chromatographic separation (Florisil) of the products yielded nitrobiphenyls (about 10mol%), which were composed of o- 49%, m- 14%, and p- 37% (glc, Apiezon L, 10%, 2 m, 180°C). This isomer ratio shows that these nitrobiphenyls are the products of free-radical phenylation. Thus it has been shown that thermolysis of azoxysulfones 1 also yields aryl radicals.

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