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PHOTO-REACTIONS OF SULFINAMIDES[1]

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p-Toluenesulfinamides were irradiated with a low-pressure mercury lamp. In methanol, photo-alcoholysis took place, yielding methyl sulfinates. In aprotic solvents (benzene, acetonitrile), homolysis of the S-N bond took place, and the products of recombination and disproportionation of sulfinyl radicals were found. Photo-isomerization to a sulfoxide was also observed.

A previous paper from our laboratories described that irradiation of alkyl sulfinates with a low-pressure mercury lamp causes the homolysis of the sulfinates, yielding sulfinyl and alkoxy radicals.[2] However, this method is not suitable for production of sulfinyl radicals, since the photolysis of sulfinates is very slow and the primary products of the photolysis undergo further changes by long irradiation. Therefore, in an attempt to find a better sulfinyl radical generator, the photo-reactions of sulfinamides were investigated.

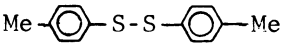
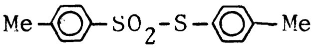
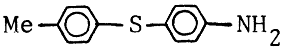
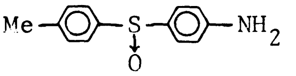
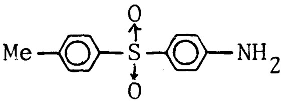
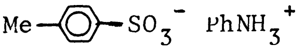
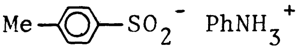
N-Phenyl-p-toluenesulfinamide (**1**) was prepared by mixing p-toluenesulfinic acid (6.8 g, 43 mmol), aniline (4.0 g, 43 mmol), and dicyclohexylcarbodiimide (8,4 g, 41 mmol) in dichloromethane (300 ml) at 0°C and then letting them react at room temperature for 44 hr; yield, 30-40 mol%. N,N-Dimethyl-p-toluenesulfinamide (**2**) was synthesized from p-toluenesulfinyl chloride and dimethylamine, since the yield in the above DCC method was low with this amine.

p-Toluenesulfinamides have an absorption maximum near 240 nm. When a dilute solution ($\sim 10^{-4}$ M) of **1** or **2** in methanol, benzene, hexane, or acetonitrile was irradiated with a 35-W low pressure mercury lamp, the strong absorption near 240 nm completely disappeared within 5 to 10 minutes. This shows that the rates of photolysis of sulfinamides are very much greater than those of sulfinates, and the $-S(\rightarrow O)-N$ bond is much more readily cleaved than the $-S(\rightarrow O)-O$ bond by irradiation.

When an anhydrous methanol solution (700 ml) of **1** (3.5 g) (λ_{max} 238 nm, ε = 14,000) was irradiated in a quartz vessel surrounding a 35-W low pressure mercury lamp for 3.5 hr under nitrogen, methyl p-toluenesulfinate was formed in 30-40 % yield. No decomposition of **1** was observed when a similar mixture was allowed to stand in dark. It is known that some nucleophilic reactions proceed much faster at photo-excited states; the nucleophilic attack of the methanolic oxygen atom on the sulfinyl sulfur atom of **1** must be much faster in the photo-excited state than in the ground state. Another product isolated was p-aminophenyl p'-tolyl sulfoxide (2 mol%); no products indicative of the occurrence of homolysis were found.

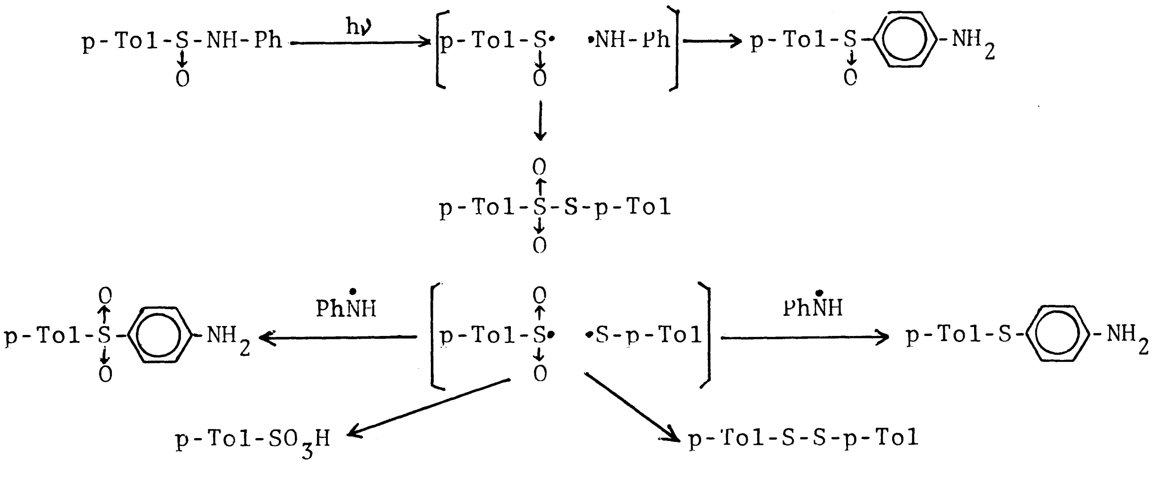
When **1** was irradiated in such aprotic solvents as benzene and acetonitrile with a low-pressure mercury lamp at room temperature, it yielded the products shown in Table 1.

Table 1. The Products of Photolysis of **1** in Benzene and Acetonitrile

Products	4.1 mmol **1** in 80 ml MeCN irradiated for 19.5 hr	4.3 mmol **1** in 130 ml C_6H_6 irradiated for 149 hr
	Yield (mol%)	
	2.5 mol%	3.7 mol%
	2.5	2.6
	-	3.2
	5.4	7.7
	-	2.6
	33	55
	7.9	-

The yield of p-aminophenyl p'-tolyl sulfoxide is several times that in the photolysis in methanol. Since it is reported that this sulfoxide is formed by heating **1** in the presence of acid,[3] an equimolar solution of **1** and p-toluenesulfonic acid in acetonitrile was allowed to stand for 23 hr in dark. However, no rearrangement was observed. These findings show that the sulfoxide is the product of a photo-rearrangement. No rearrangement to the ortho position was observed. This rearrangement appears to be analogous to the photo-rearrangement of N-phenyl-p-toluenesulfonamide to p-aminophenyl p'-tolyl sulfone;[4] the yield in this case was also only a few percent.

The products shown in Table 1 suggest that the photolysis of **1** in aprotic solvents proceeds according to the scheme shown below.



The irradiation causes the cleavage of the S-N bond, and part of the radical pairs produced recombine in cage, yielding the p-aminophenyl sulfoxide. p-Toluenesulfinyl radicals are probably fairly stable,[5] and they may dimerize to p-toluenethiol p-toluenesulfonate (p-Tol-SO$_2$-S-p-Tol), which may be cleaved by irradiation to p-TolSO$_2$• and p-Tol-S• radicals. It is also possible that two sulfinyl radicals directly yield p-Tol-SO$_2$• and p-Tol-S• radicals by disproportionation. It is known that disulfides and sulfonic acids are the products of recombination and disproportionation of ArSO$_2$• radicals.[6]

In order to determine whether or not the photolysis of **1** involves an excited triplet, a methylcyclohexane or methanol solution of **1** ($\sim 10^{-4}$ M) containing 1,3-pentadiene (piperylene, a triplet quencher; E_T = 58.8 kcal) (1-10 mol/mol **1**) was irradiated at 253 nm. The rate of disappearance of **1** was not different from that in the absence of the triplet quencher.

When **1** was irradiated in an E. P. A. matrix (ether:isopentane:ethanol) (10^{-4}M) at 77K, new absorption maxima were observed near 270, 280, and 300 nm. Since anilino radical absorbs near 300 nm,[7] it is possible that the absorptions at 270 and 280 nm are due to p-toluenesulfinyl radical.

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