BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (8), 2341—2342 (1976)

The Photochemical Sulfenylation of Halides with Organic Disulfides

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(Received March 29, 1976)

Synopsis. The reaction of organic disulfides with aryl radicals photochemically generated from aryl halides was investigated. Diaryl sulfides were obtained from diaryl disulfides when the radiation was provided by a low-pressure mercury lamp, while dialkyl disulfides afforded alkyl aryl sulfides whether the radiation source was a low- or a high-pressure mercury lamp.

There have been several methods reported for the formation of an aryl-sulfur linkage; in those methods, organic disulfides occupy a fairly significant position as sulfenylation reagents. The disulfide linkage is known to be cleaved by a nucleophilic[1] or electrophilic[2] attack. In addition, disulfides are good radical-trapping reagents, and the formation of an aryl-sulfur linkage by this type of reaction has been demonstrated with phenylazotriphenylmethane[3] and *N*-nitrosoacetylarylamine[4] as radical sources.

The photolysis of aryl halides is known to generate aryl radicals.[5] Halobenzenes, because of their thermal stability and availability, have more advantages as free radical sources than do azo or *N*-nitroso compounds. Thus, if disulfides can be used as scavengers of photochemically generated carbon radicals from halobenzenes, the formation of aryl-sulfur linkages would be easily achieved under milder conditions. This reaction, however, presents a potential problem in that organic disulfides decompose on ultraviolet irradiation to give thiyl radicals.[6] In the present experiments the photochemical sulfenylatin of halobenzenes with organic disulfides was examined, and this problem was solved by the use of a large excess of halobenzenes in the presence of an aqueous solution of sodium thiosulfate.

When a solution of diphenyl disulfide in iodobenzene was irradiated in a Vycor tube with a low-pressur mercury lamp (50 W), phenyl radicals were generated and diphenyl sulfide was obtained in a 39% yield. Iodine was simultaneously formed and colored the solution deeply, thus strongly decreasing the efficiency of the photochemical reaction. Moreover, a significant part of the phenyl radicals were considered to be trapped by the iodine to regenerate the starting material instead of reacting with the disulfide. Accordingly, if the free iodine could be removed from the reaction system as soon as it is formed,[7] a better yield of diphenyl sulfide would be expected. Thus, sodium thiosulfate was used to consume iodine. A solution of diphenyl disulfide in an excess of iodobenzene and an aqueous solution of thiosulfate were stirred vigrously and irradiated with a low-pressure lamp. The yield of diphenyl sulfide was thus raised remarkably.

$$C_6H_5I + RSSR \longrightarrow RSC_6H_5 + RS\cdot + 1/2\, I_2$$

Table 1 shows the results of the sulfenylation of iodobenzene with various diaryl disulfides. Arylthio radicals partly recombine to form diaryl disulfide, which again undergoes the reaction with phenyl radicals and probably causes the yield of monosulfide to exceed the stoichiometric amount in some cases.

Compared with experiments using a low-pressure lamp, which afforded aryl phenyl sulfides in good yields, the use of a high-pressure mercury lamp (450W) resulted in a negligible yield of monosulfides, although the consumption of diaryl disulfide was large. This observation is attributable to the rapid photodecomposition of diaryl disulfide to thiyl radicals, which leads to side reactions.[8]

Dialkyl disulfides also reacted with iodobenzene to

Table 1. Reaction of iodobenzene with disulfides

R in disulfide	Low-pressure lamp: Conversion of disulfide (%)	Low-pressure lamp: Yield of sulfide[a] (%)	High-pressure lamp: Conversion of disulfide (%)	High-pressure lamp: Yield of sulfide[a] (%)
C_6H_5	59	102	84	3
p-$CH_3C_6H_4$	72	84	73	5
p-ClC_6H_4	80	73	53	4
p-$CH_3OC_6H_4$	100	101	26	0
Me	61	117	63	90
Et	53	95	67	82
n-Pr	51	126	63	67
i-Pr	44	60	57	28
t-Bu	20	0	13	0
$PhCH_2$[b]	59	51	58	42
allyl[c]	73	34	94	31

a) Based on consumed disulfide. b) In addition to benzyl phenyl sulfide, dibenzyl sulfide was formed in a yield of 21% (low-pressuse lamp) or 13% (high-pressure lamp). c) In addition to allyl phenyl sulfide, diallyl sulfide was formed in a yield of 11% (low-pressure lamp) or 7% (high-pressure lamp).

TABLE 2. REACTION OF ARYL HALIDES WITH DISULFIDES[a)]

Ar-X (mmol)		R_2S_2 (mmol)		Solvent (ml)	Conversion of disulfide (%)	Yield of RSAr[b)] (%)
p-$CH_3C_6H_4I$	15.8	Ph_2S_2	1.77	C_6H_6 1	46	32
p-$CH_3C_6H_4I$	20.2	Et_2S_2	2.01	C_6H_6 1	44	33
C_6H_5Br	47.8	Et_2S_2	2.92	—	49	29
p-HOC_6H_4Br	23.2	p-$CH_3C_6H_4S$-)-$_2$	1.53	C_6H_6 6	100	62
p-$CH_3OC_6H_4Br$	39.8	p-ClC_6H_4S-)-$_2$	2.51	—	44	39
p-$CH_3OC_6H_4Br$	39.8	Me_2S_2	3.51	—	72	125

a) Irradiated by a low-pressure lamp (50 W). b) Based on consumed disulfide.

give alkyl phenyl sulfides on irradiation. Both low- and high-pressure lamps were effective in the formation of sulfides. An attack by a phenyl radical on the disulfide linkage rather than α-hydrogen abstruction occurred mainly, much as in the cases of thermal reactions.[3)] The yields of alkyl phenyl sulfides were influenced by steric factors. In the case of di-*t*-butyl disulfide, the consumption of the disulfide was very small and neither *t*-butyl phenyl sulfide nor *t*-butyl phenyl disulfide was obtained.

The photochemical sulfenylation by the use of disulfide was also studied with various aryl halides. The results are summarized in Table 2. The reaction effected with a low-pressure lamp afforded good yields of the expected monosulfides. *p*-Bromophenol gave diaryl sulfides by the reaction with diaryl disulfides, but the expected monosulfides could not be obtained from dialkyl disulfides.

Experimental

Reaction of Disulfides with Iodobenzene: General Procedure. Into a reaction tube (Vycor for a low-pressure lamp; Pyrex for a high-pressure lamp) were placed a disulfide (2.5 mmol), iodobenzene (5 ml), and a 1 M aqueous solution of sodium thiosulfate (5 ml). The reaction tube was degassed and sealed *in vacuo*. Irradiation was carried out with an external helical low-pressure mercury lamp (50 W) or a high-pressure mercury lamp (450 W) for 48 h with vigorous stirring. The organic layer was separated from the reaction mixture, and the aqueous layer was washed with dichloromethane. After being dried over anhydrous sodium sulfate, the combined organic layer was concentrated to exactly 10 ml. Phenyl monosulfide and recovered disulfide were identified and determined by GLPC using a standard solution of each authentic sample.

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