

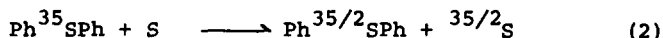
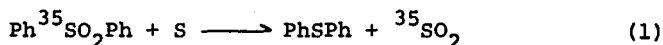
The Reaction of Elemental Sulfur with Organic Compounds. III.¹⁾
A New Type of Aromatic Displacement Reaction by Elemental Sulfur ;
Reaction with Halo Aromatics

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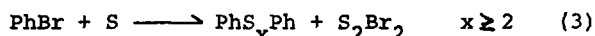
Earlier Glass and Reid²⁾ reported that elemental sulfur reacts with benzene at 350°C to yield PhSPh, PhSH and H₂S. It was shown by us that diphenyl sulfone and diphenyl sulfide react with sulfur at a somewhat lower temperature and interesting aromatic displacement reactions take place as shown below.³⁾ In these reactions both sulfonyl and sulfide groups are



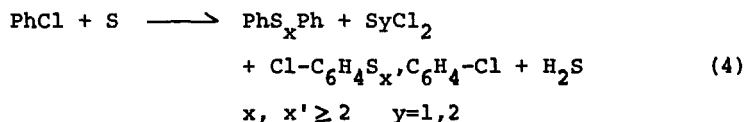
replaced by sulfur atom of elemental sulfur and no hydrogen atom of aromatic rings is replaced. We have been interested in these reactions and expected that other aromatic compounds with suitable substituents would also undergo this type of displacement reaction with elemental sulfur. In fact, we have found some of the halogenated aromatic compounds do undergo such a reaction. This letter will describe a brief account of this reaction.

When a mixture of one atom equivalent of sulfur and one mole equivalent of bromobenzene, which is also used as solvent, was heated at 230-250°C for 2 to 3 hours in a sealed tube, a dark red colored solution was

obtained. Upon exposing to moisture the mixture was decolorized with evolution of HBr and sulfur. Apparently S_2Br_2 was formed in the reaction, although it was not isolated in pure form. The principal product was a mixture of diphenyl polysulfides which were identified from gas-liquid and thin-layer chromatography. These polysulfides were readily reduced to thiophenol by treatment with $LiAlH_4$ in ether or Zn and HCl in water. The following equation summarizes the over all reaction.



Under the same condition the reaction of chlorobenzene with sulfur is sluggish and requires prolonged heating, while reduction of the reaction product with $LiAlH_4$ resulted in the formation of a mixture of thiophenol and a small amount of chlorothiophenol. Apparently the reaction of chlorobenzene takes place at two reaction sites, leading to replacements of both chlorine and hydrogen atoms. (Eq.4)



Fluorobenzene did not react with sulfur under the same condition and was recovered nearly quantitatively.

These results clearly indicate that the reactivity of halobenzene decreases with the increase of the bond strength of carbon-halogen bond.

The results of the reactions of a few bromine substituted aromatic compounds with elemental sulfur are shown in the Table 1, in which the yield of product was calculated based on bromobenzene used.

Table 1. Reaction of Elemental Sulfur with Halo Aromatics^{a)}

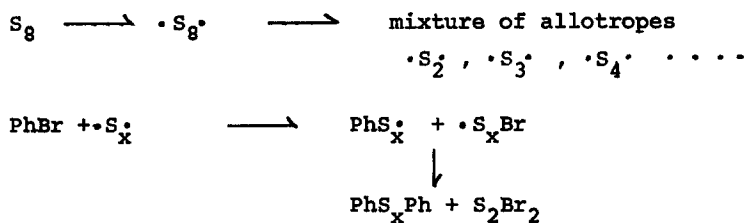
Haloaromatics	Condition		Yield of Mercaptan (Recovered Haloaromatics)		Reducing Agent
PhBr	243°C	2.5hr	29%	(53%)	LiAlH ₄
PhBr	243°C	2.5hr	29%	(57%)	Zn + HCl
p-FC ₆ H ₄ Br	243°C	2.5hr	25%	(67%)	LiAlH ₄
p-ClC ₆ H ₄ Br	243°C	2.5hr	24%	(59%) ^{b)}	LiAlH ₄
p-PhOC ₆ H ₄ Br	240°C	50min	30%		LiAlH ₄
p-PhC ₆ H ₄ Br	240°C	3hr	31%		LiAlH ₄
α-naphthyl bromide	220°C	1hr	30%		LiAlH ₄
PhCl	235°C	6hr	<1%	^{c)}	LiAlH ₄

a) In each reaction 0.01 mol of halo aromatic compound was reacted with 0.01 g atom of sulfur.

b) Small amount of p-BrC₆H₄SH was also detected.

c) Small amount of Cl-C₆H₄SH was also detected.

At an elevated temperature (above 159°C) elemental sulfur is known to undergo homolytic cleavage of S-S bond of S₈ ring⁴⁾ forming a complex mixture of many allotropes, S₂, S₃, S₄ etc.⁵⁾ In the reaction of sulfur with haloaromatics, some of these reactive allotropes of sulfur, which are expected to behave as electrophilic radical species, would interact with aromatic ring. The preliminary study indicates that bromobenzenes bearing electron-releasing substituents undergo replacement reaction more readily than those bearing electron withdrawing groups and unsubstituted one. Thus the most likely pathway is shown below.



Detailed study of kinetics, mechanism and synthetic utilities of the reaction will be reported soon from these laboratories.

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