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EXCHANGE AND REDOX REACTIONS OF DIARYL SULFIDES WITH AROMATIC HYDROCARBONS

Chung Hwa Han and William E. McEwen

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01002

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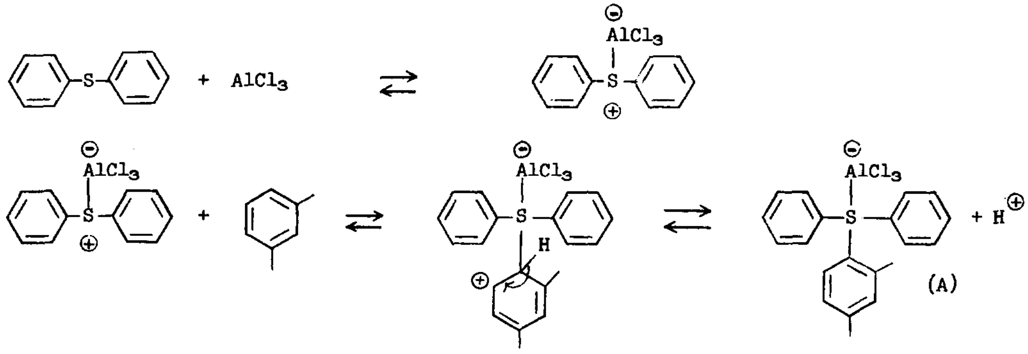
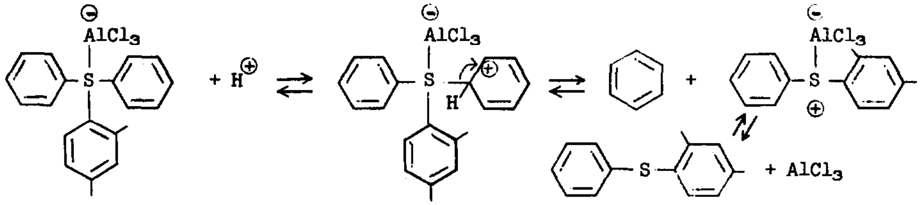
When an aromatic hydrocarbon is caused to react with a diaryl sulfide in the presence of aluminum chloride, a complex mixture of products results. For example, the reaction of diphenyl sulfide with o-xylene has been found to produce phenyl 3,4-dimethylphenyl sulfide (40.3%), phenyl 2,3-dimethylphenyl sulfide (7.3%), 2,3-dimethylphenyl 3,4-dimethylphenyl sulfide (3.0%) bis-(2,3-dimethylphenyl) sulfide (5.2%), bis-(3,4-dimethylphenyl) sulfide (11.1%), benzene (57.5%), a diphenyl-3,4-dimethylphenylsulfonium salt (isolated as the iodide in 5.5% yield), and, after exposure of the reaction mixture to water, hydrolysis products of triarylsulfonium salts (0.30% of 3,4-dimethylphenol and 0.08% of 2,3-dimethylphenol). Obviously, the exchange products (amounting to a total yield of 67%) are of greater importance than the products of the redox reaction. Similar products are obtained when m-xylene is used in place of o-xylene, the major ones being phenyl 2,4-dimethylphenyl sulfide (34.0%) and diphenyl-2,4-dimethylphenylsulfonium iodide (13.3%). We suggest that the mechanism of a typical exchange reaction is that shown in Scheme 1.

Scheme 1

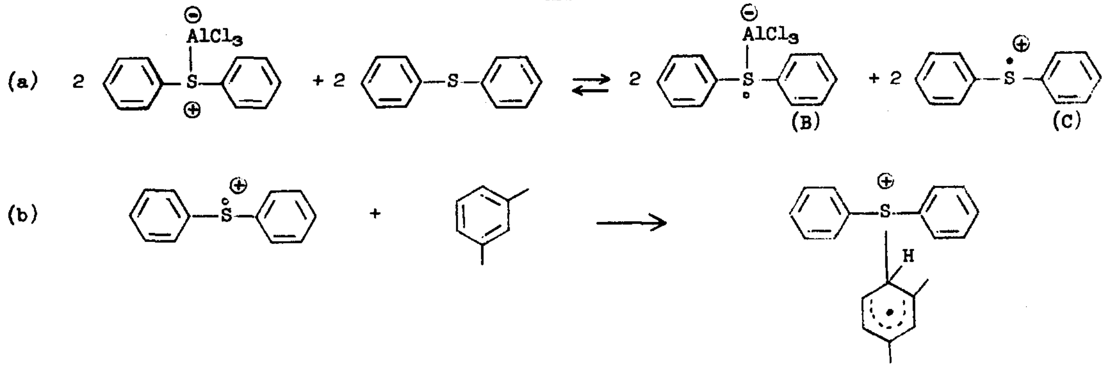


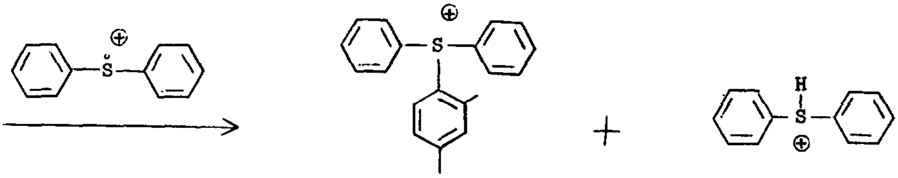


The proposed intermediate (A) is a tetracovalent sulfur compound, and the existence of such compounds has been discussed by other workers (1). Of course, protonation of the m-xylyl group of (A) would be expected to occur more rapidly than protonation of a phenyl group, but such a process would lead only to regeneration of the reagents; undoubtedly, the reaction is a reversible one. It is significant that the amount of benzene produced in each reaction is roughly comparable to the total of the molar amounts of substituted diphenyl sulfides formed.

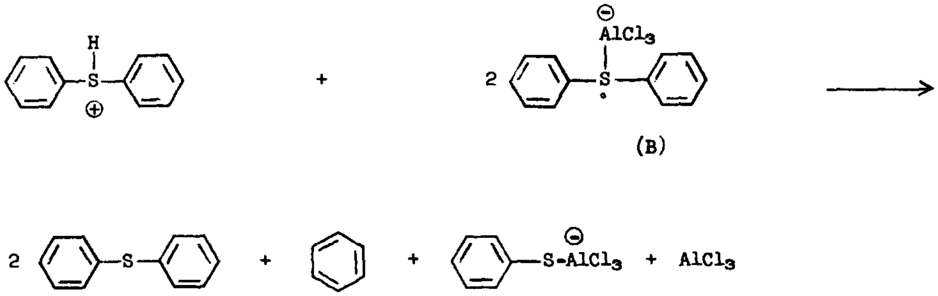
With regard to the formation of triarylsulfonium salts in these reactions, the oxidizing power of aluminum chloride, especially in apparent one electron oxidations, has been observed by various workers (2). Of particular interest with respect to this communication is the report that a thianthrene cation radical is formed when thianthrene is treated with aluminum chloride (3). Furthermore, benzyl phenyl sulfide is known (4) to form a complex with aluminum chloride, one which undergoes reaction with water to give thiophenol and benzyl chloride. These facts and analogy with the mechanism which has been proposed for the generation of diarylsulfinium cation radicals by the action of concentrated sulfuric acid on diaryl sulfides (5), provide the basis for the typical mechanism, shown in Scheme 2, which we suggest for the formation of triarylsulfonium salts in the reactions of diaryl sulfides with aromatic hydrocarbons.

Scheme 2



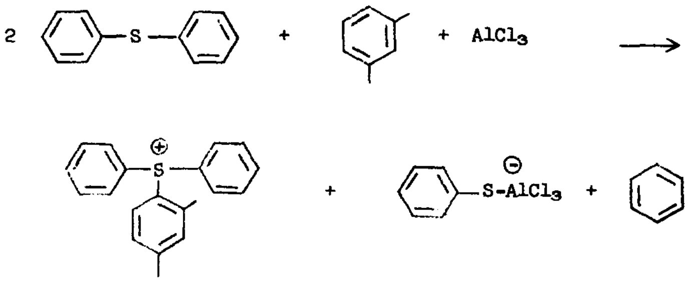


Owing to the positive charge of the diphenylsulfinium ion radical (C), the substitution reaction has some of the character (e.g., orientation and activating effects of substituents) of an electrophilic substitution reaction, although it is actually an aromatic radical substitution reaction. Although the details of the subsequent reactions are not entirely clear, it is thought that the conjugate acid of diphenyl sulfide undergoes reaction with the radical ion (B) (6) to form diphenyl sulfide, benzene and a complex of the conjugate base of thiophenol with aluminum chloride. As indicated below for the reaction carried out in chlorobenzene as solvent, thiophenol has been found to be a product in a situation which resulted in the formation of relatively large amounts of triarylsulfonium salts.



(B)

The stoichiometry of a typical redox reaction is thought to be as follows:



When a relatively unreactive aromatic compound, such as chlorobenzene, is mixed with diphenyl sulfide and treated with aluminum chloride, an exchange product, phenyl *p*-chlorophenyl sulfide, is obtained in only 0.14% yield. The remaining products are the result of self-condensation reactions of diphenyl sulfide and include thianthrene (1.7%), diphenyl-p-thiophenoxyphenylsulfonium iodide (22.4%), bis-(p-diphenylsulfoniophenyl) sulfide diiodide (10.3%), thiophenol (1.3%), benzene (3.5%) and diphenyl disulfide (0.65%).

The structures of the triarylsulfonium salts were proved by pyrolysis and subsequent vpc analyses of the pyrolysates (7). The diaryl sulfides were isolated by use of preparative scale vpc and both their ir and nmr spectra compared with authentic samples.

References and Footnotes

(1) K. Mislow, T. Simmons, J. T. Melillo and A. L. Ternay, Jr. have suggested that a tetracovalent sulfur compound is formed as an intermediate in the hydrochloric acid-catalyzed racemization of optically active sulfoxides: J. Amer. Chem. Soc., 86, 1452 (1964). V. Franzen and C. Mertz provided evidence for the formation of a tetracovalent sulfur intermediate in the exchange reactions of triarylsulfonium salts with organolithium reagents: Ann., 643, 24 (1961). This list is not intended to be exhaustive.

(2) J. J. Rooney and R. C. Pink, for example, have reported the occurrence of one electron oxidations of aromatic hydrocarbons, such as anthracene, chrysene and perylene, to the corresponding cation radicals by the action of aluminum chloride: Proc. Chem. Soc., 142 (1961). See also H. M. Buck, W. Bloemhoff and L. J. Oosterhoff, Tetrahedron Letters, 5 (1960); R. E. Banks, L. F. Farnell, R. N. Haszeldine, P. N. Preston and L. H. Sutcliffe, Proc. Chem. Soc., 396 (1964).

(3) H. J. Shine and J. L. Piette, J. Amer. Chem. Soc., 84, 4798 (1962).

(4) D. P. Harnish and D. S. Tarbell, J. Amer. Chem. Soc., 70, 4123 (1948).

(5) H. J. Shine, "The Formation of Cations and Cation Radicals from Aromatic Sulfides and Sulfoxides," ch. 6 in M. J. Janssen, ed., Organosulfur Chemistry, Interscience Publishers, New York, N. Y., 1967. See also U. Schmidt, K. H. Kabitze, K. Markan and A. Muller, Angew. Chem., 72, 708 (1960); Ann. Chem., 672, 78 (1964); Angew. Chem. Internat. Ed., 3, 602 (1964). The thianthrene radical ion produced by the action of concentrated sulfuric acid on thianthrene is the same as that produced by the action of aluminum chloride (3) on the same substrate, as shown by the epr spectra of the two samples.

(6) Evidence for the formation of a radical intermediate analogous to (B), one in which the sulfur atom accommodates nine electrons in its valence shell, has been reported by R. J. Gritter and D. J. Carey, J. Org. Chem., 29, 1160 (1964). Also, evidence for the formation of triarylsulfur intermediates in various reactions has been reported by M. Finkelstein, R. C. Peterson and S. D. Ross, J. Electrochem. Soc., 110, 422 (1967) and by J. W. Knapczyk and W. E. McEwen, J. Amer. Chem. Soc., 91, 145 (1969).

(7) G. H. Wiegand and W. E. McEwen, J. Org. Chem., 33, 2671 (1968).