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A MILD REDUCTION OF ARENESULFONIC ACID AND ITS DERIVATIVES WITH DIPHOSPHORUS TETRAIODIDE

Hitomi SUZUKI,* Hiroyuki TANI, and Atsuhiro OSUKA

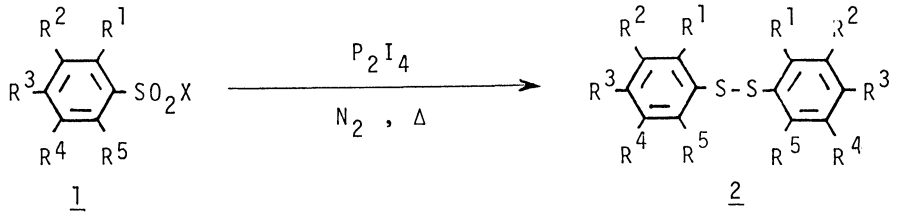
Department of Chemistry, Faculty of Science,

Ehime University, Bunkyo-cho, Matsuyama 790

When treated with diphosphorus tetraiodide in boiling acetonitrile or under neat conditions, arenesulfonic acids, their salts, chlorides, esters, and amides are reduced to aryl disulfides in good to moderate yields.

Diphosphorus tetraiodide (P_2I_4) exhibits a high affinity for oxygen and acts as a unique reagent for deoxygenation and dehydration.[1] It is highly efficient for the deoxygenation of epoxides,[2] sulfoxides,[3,4] selenoxides,[4] amine N-oxides,[5] and benzyl alcohols.[6] It can dehydrate aldoximes[2,7] amides,[8] and nitroalkanes[4] to nitriles, convert alcohols to olefins and iodides,[7,9,10] cleave acetals and ketals,[11] and combine carboxylic acids and amines into amides[12] under mild conditions. In the present letter, we wish to report a further application of this reagent to the deoxygenation of arenesulfonic acid and its derivatives. Sulfonic acid, an organosulfur compound of the highest oxidation state, is known to be quite resistant to the conversion into compounds of lower oxidation state.

On treatment with P_2I_4 in boiling acetonitrile for several hours, arenesulfonic acids, their salts, chlorides, and esters all undergo reductive dimerization to give the corresponding aryl disulfides in good to moderate isolated yields. The reaction is clean and mild with only slight amounts of by-products. When benzene is used as solvent instead of acetonitrile, sulfonic acids are reduced, but sulfonic acid salts are unaffected. Direct reduction of sulfonic acid to thiol or disulfide is a difficult process to effect,[13,14] and this transformation is usually performed in a two-step manner which involves an initial conversion to sulfonyl chloride, followed by treatment with appropriate reducing agent.[15]



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Arenesulfonamides are stable towards P_2I_4 in boiling acetonitrile, but they

Table 1. Reduction of arenesulfonic acid and its derivatives with P_2I_4

Substrate[a]						Reaction	Disulfide	
R^1	R^2	R^3	R^4	R^5	X	time/h	Mp θ_m/°C	Yield/%[b]
H	H	H	H	H	OH	3	58-60	43
H	H	Me	H	H	OH	6	43-45	77
H	H	H	H	H	O^-Na^+	5	58-60	50
H	H	Me	H	H	O^-Na^+	6	43-45	63
Me	H	H	H	H	O^-Na^+	3	38-39	52
Me	H	H	H	Me	O^-Na^+	2	102-104	62
H	Me	H	Me	H	O^-K^+	3	oil	48
Me	H	Me	H	H	O^-K^+	6	oil	57
Me	H	Me	H	H	Cl	3	oil	54
H	Me	H	Me	H	OMe	6	oil	42
Me	H	H	Me	H	OMe	8	46-48	59
Me	H	H	H	H	NH_2	6[c]	38-39	61
H	Me	H	H	H	NH_2	6[c]	oil	65
H	H	Me	H	H	NH_2	5[c]	43-46	90

a) Arenesulfonic acid and salt were dehydrated prior to reduction by azeotropic distillation with benzene.

b) No attempts were made to optimize the results. Yield is based on the isolated compound and would be higher if allowance is made for unchanged substrate, the amount of which was not determined, however. Products are all known,[16] and identified by IR, NMR, and MS spectra as well as by direct comparison with authentic specimens.

c) Reaction was carried out at 120-125 °C under neat condition.

are successfully reduced under neat conditions to give aryl disulfides as the sole product. To our knowledge, such smooth conversion of sulfonamide to disulfide has not been described so far; major reduction products reported of arenesulfonamide are arenesulfinate and its degradation products.[17] Many other attempts to reduce sulfonamide have led to the fission of the aryl-sulfur bond, giving parent arene rather than thiol or disulfide.[18] Arenesulfones are inert to P_2I_4 and remain unchanged even after prolonged heating under neat conditions. The representative results of the reduction are summarized in Table 1.

Recently, a mild reduction of arenesulfonic acid to arenethiol has been performed by using iodotriphenylphosphonium iodide.[14] In that case triphenylphosphine oxide is formed as by-product and needs to be removed from the product mixture by some appropriate way. In our case the oxygen-containing phosphorus compounds are water-soluble and easily removed from the organic phase on aqueous work-up.

The experimental procedure is exemplified by the reduction of sodium arenesulfonate in acetonitrile and of arenesulfonamide under neat conditions.

1) To a magnetically stirred suspension of sodium arenesulfonate (1; 1.0 mmol) in dry acetonitrile (20 mL) under nitrogen, freshly prepared P_2I_4 (1.7 mmol) is added in one portion and the mixture is heated to gentle reflux. The bright color of the solution gradually changes to dark brown. After several hours the reaction mixture is diluted with water and the organic phase is extracted with ether. The extract is washed with 5%-aqueous sodium sulfite, dried over sodium sulfate, and evaporated. The residue is chromatographed on a short column of alumina using hexane as the solvent to give aryl disulfide 2, which is further recrystallized from hexane.

2) A mixture of arenesulfonamide (1.0 mmol) and P_2I_4 (1.2 mmol) is heated in a sealed tube at 120-125 °C for 5-6 h. The resulting dark brown mixture is then worked up as described above.

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