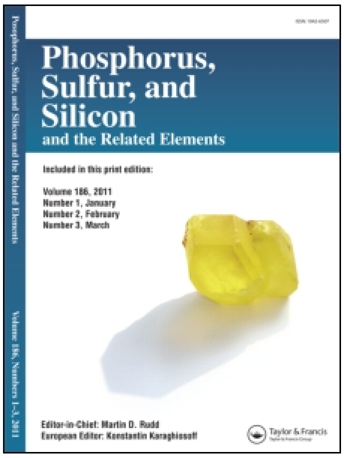

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

STUDIES ON THE SYNTHESIS OF THIOLS AND THEIR S-SUBSTITUTED DERIVATIVES

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To cite this Article Kuliyev, Ali M. and Mamedov, Fakhraddin M.(1979) 'STUDIES ON THE SYNTHESIS OF THIOLS AND THEIR S-SUBSTITUTED DERIVATIVES', Phosphorus, Sulfur, and Silicon and the Related Elements, 6: 1, 179 — 180
To link to this Article: DOI: 10.1080/03086647908080363
URL: http://dx.doi.org/10.1080/03086647908080363

Phosphorus and Sulfur
1979, Vol. 6, pp. 179–180

STUDIES ON THE SYNTHESIS OF THIOLS AND THEIR S-SUBSTITUTED DERIVATIVES

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Aromatic thiols belong to a group of not yet sufficiently explored compounds. The presence of an active hydrogen atom makes it possible to conduct various chemical conversions and to obtain new S-substituted derivatives.

The investigation has been carried out with the use of alkyl and dialkyl thiophenols, halogeno- and dihalogeno-thiophenols, tetralil and naphthalene thiols, and o-hydroxy-thiophenols.

The reactions of the above thiol compounds have been studied with the compounds containing a mobile halogen atom and active bonds.

It was found that a reaction of thiols with phosphorus trichloride, monochloroacetic acid, alkylene chlorohydrins, chloral and di- and triaryl-hydroxychlorosilanes in the presence of alkali is a single-route reaction yielding corresponding S-substituted derivatives while the reaction with epichlorohydrin proceeds in three directions to form, depending on the reactant ratio, monochlorohydrin, glycidil arylsulfide, and 1,3-arylthio propan-2-ol.

The reaction of thiols with thioepichlorohydrin is also a single-route reaction to form corresponding thioglycidil sulfides.

The analysis of the NMR spectra of arylthioglycidil sulfides indicated a strong long-range interaction through the field, which has not yet been described for this type of compounds and consists in additional magnetic screening of the methylene group protons of the tiirane cycle due to anisotropic magnetic susceptibility of the phenylglycide group. The analysis of IR and NMR spectra, dipol moments, and atomic models of thioglycidil sulfides enabled us to suggest a spatial configuration for their molecules.

Addition reactions of thiols to metacrylates, olefin hydrocarbons ,and acetylene alcohols have been studied in the presence of organic base, sulfuric acid, and chloroplatinic acid, respectively, and a number of S-substituted thiols have been obtained.

A method for obtaining monothiomethylphenols and a series of sulfur-containing hindered phenols has been developed, which is based on a decomposion of Mannich bases with thiols. The method is useful in the organic synthesis.

The reaction of o-hydroxyalkyl-thiophenols with phosphorus trichloride was found to be a multiple-route reaction. It is believed that its end product, 2-chloro-5-alkylbenzo-1-hydroxy-3-thio-2-phospholane, is formed by the conversion of intermediate o-hydroxy-alkylthiophenolphospholane and o-hydroxy--alkyl-thiophenol-bis-phospholane.

The mechanism of the antioxidizing action of monomethylphenols, 2-(2-thioheptylthio)-4-tert-butylphenol, and 2,2'--dithio-bis-(1-hydroxy-4-tert-butylphenyl)methane has been studied for cumene oxidation. It can be anticipated that a reaction of peroxide radicals with phenol hydroxyl group is involved in chain terminations while sulfide sulfur reaction is involved in hydroperoxide decomposition.

It has been shown by comparing the ratio of inhibited oxidation reaction at the end of the induction period and uninhibited oxidation reaction that phenyl sulfide conversion products also display inhibiting activity.

The products obtained have been tested as components of lubricating oils and polymeric materials. The effect of the composition and structure of the products on the properties of these materials has been investigated.