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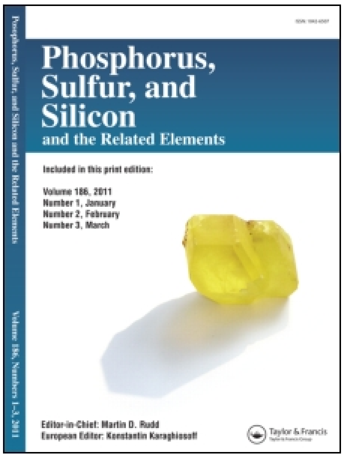

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Montmorillonite K10/$ZnCl_2$ Catalyzed Alkyl Disulfide Substitution Reactions: Preparation of Thiomethyl Derivatives for the Synthesis of Organic Conducting Materials

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Experiments are described detailing a method for the direct introduction of thiomethyl groups into activated benzenes, thiophene and benzo[*b*]thiophene using an activated mesoporous clay to promote thiomethyl substitution. Elaboration of 2,3-dithiomethylbenzo[*b*]thiophene, a product of the clay-catalyzed reaction of benzo[*b*]thiophene with dimethyl disulfide, to a tetrathiafulvalene derivative is described.

KEY WORDS: Thiomethyl substitution, montmorillonite clay, $ZnCl_2$, tetrathiafulvalene

INTRODUCTION

Only one method exists for the direct substitution of aromatic compounds by sulfur substituents with S in the (-II) oxidation state. This method utilizes S_2Cl_2 and iron catalysts and is not generally applicable to aromatic systems[1]. Other methods of preparing aromatic sulfides or thiols involve more than one reaction and, in many cases, require extreme conditions to achieve one or more of the steps. For example, thiomethylbenzenes may be prepared by chlorination of the aromatic followed by high temperature nucleophilic substitution by thiomethylate[2] or by chlorosulfonylation, reduction and methylation of the resultant thiol[3]. In this communication, we describe the preparation of some thiomethylated aromatics using a one-step procedure in which the thiomethyl group is introduced by reaction with alkyl disulfides over modified montmorillonite clay catalysts.

Commercially available K10 montmorillonite clay has been acid treated to produce a high surface area material with a large mesopore volume. When activated by addition of a Lewis acid ($ZnCl_2$ or $CuCl_2$) or a Bronsted acid, this clay is able to coordinate to a primary disulfide making the adjacent sulfur atom electrophilic. The mesopores within the clay are of sufficient size to accommodate the transition state of the thiomethylation reaction, but seem to be small enough to prevent gross polymerization of sensitive substrates such as thiophene. Thus, 2,5-dithiomethyl, tri-substituted and per-thiomethylated thiophenes may be obtained in good yield.

RESULTS

Preparation of Thiomethylated Aromatics

Table 1 gives examples of the thiomethylation of some benzenes, thiophene and benzo[*b*]thiophene. The thiomethylation of *o*-xylene is of particular significance since, although the yield of the product, 4,5-dithiomethylxylene is low (23%), this reaction results in a one-step synthesis of a material that can be elaborated directly to tetrathiafulvalene (TTF) derivatives. The per-thiomethylation of thiophene is also significant as this product could be converted to a range of TTF-thiophene polymers.

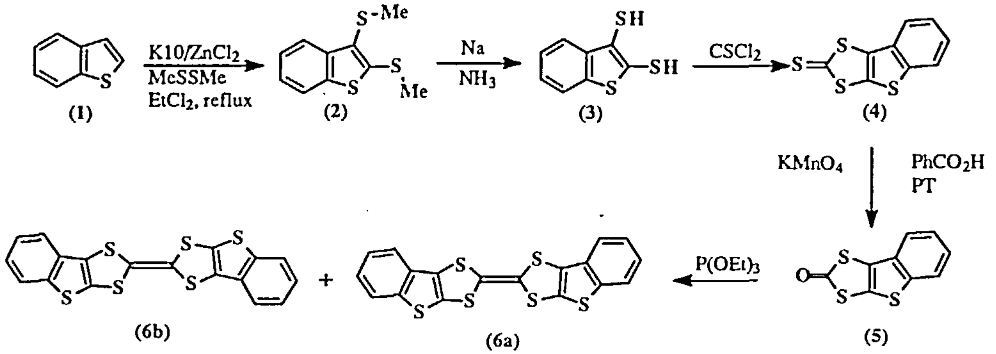
TABLE 1
Examples of Thiomethylation of Aromatics

Substrate	Product (%)	Conditions
1,3,5 trimethylbenzene	2,4,6-tri SMe (90%)	K10 / $ZnCl_2$
o-xylene	4,5-di SMe (23%)	K10 / H_2SO_4
thiophene	2,3,4,5-tetra SMe (50%)	K10 / $ZnCl_2$
benzo[*b*]thiophene	2, 3-di SMe (75%)	K10 / $ZnCl_2$

Preparation of benzo[*b*]thiophene-TTF Derivatives

Synthesis of 2,3-dithiomethylbenzo[*b*]thiophene allows the preparation of an interesting TTF analogue (6). Thus, removal of the methyl groups with Na/NH_3 and reaction of the resultant dithiol with thiophosgene gave the thione (4). Although this thione could not be coupled to the TTF derivative, oxidation and coupling of the ketone (5) with triethyl phosphite afforded (6) as a mixture of E- and Z-isomers. (6) readily formed charge transfer complexes with I_2, TCNQ and other materials. These complexes are now the subject of further characterization and investigation.

SCHEME 1



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