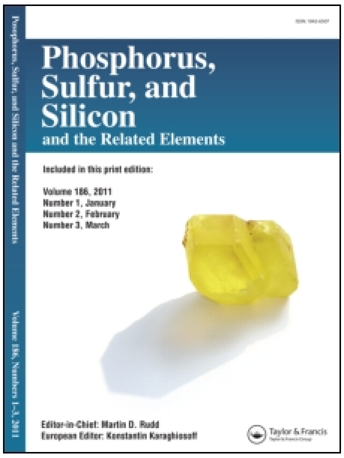

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# Alkoxysulfanes AlkylO-S-Y as Building Blocks and Ligands

Mathias Kersten[a]; Eberhard Wenschuh[a]
[a] Institut für Chemie der Humboldt-Universität zu Berlin, Berlin, Germany

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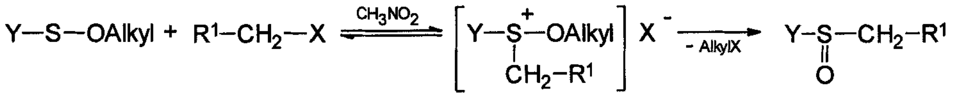
# ALKOXYSULFANES AlkylO-S-Y AS BUILDING BLOCKS AND LIGANDS

MATHIAS KERSTEN and EBERHARD WENSCHUH
Institut für Chemie der Humboldt-Universität zu Berlin, Hessische Straße 1-2,
D-10115 Berlin, Germany

Abstract The Thio-ARBUZOV-Reaction has proved to be a facile synthetic route for the conversion of alkoxysulfanes into sulfinyl derivatives. Scope and limitations of the reaction are discussed. Because of their donor properties the alkoxysulfanes are suitable ligands which has been confirmed by the preparation of palladium(II) complexes.

Alkoxysulfanes of the type AlkylO-S-Y are shown to represent valuable building blocks in sulfinate, sulfinamide and unsymmetric sulfoxide synthesis[1,2]. The mentioned $\lambda^2$-sulfanes possess donor properties and can be alkylated at the sulfur atom. The quasi-sulfonium intermediate formed in the first step stabilizes by dealkylation and S=O bond formation (see Equation 1).



$$Y{-}S{-}OAlkyl + R^1{-}CH_2{-}X \xrightleftharpoons{CH_3NO_2} \left[\begin{array}{c} Y{-}\overset{+}{S}{-}OAlkyl \\ | \\ CH_2{-}R^1 \end{array}\right] X^- \xrightarrow[-\,AlkylX]{} \begin{array}{c} Y{-}S{-}CH_2{-}R^1 \\ \| \\ O \end{array}$$

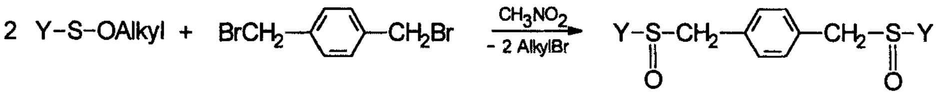
(1)

Y = OAlkyl, Ph, >N R$^1$ = H, Alkyl, Ph, Allyl etc. X = Cl, Br, I

The reactivity of a large number of halogen components towards Thio-ARBUZOV-Reactions has been investigated[3] and some general conclusions can be drawn concerning structural demands on the electrophile. It appears that the number of suitable organic halides for Thio-ARBUZOV transformations is limited only on those compounds containing a sp$^2$- or sp-hybridized carbon or nitrogen atom neighbouring the -CH$_2$-X group. Besides that successful Thio-ARBUZOV-Reactions require strong acceptor solvents like nitromethane or acetonitrile which are capable to enhance the polarity of the carbon halogen bond and can stabilize the ionic sulfonium intermediate due to their polar characteristics.

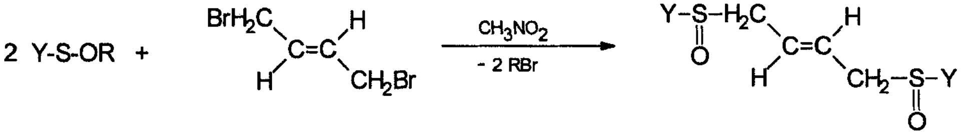
A variety of new sulfinates and sulfoxides prepared via Thio-ARBUZOV transformations of dialkoxysulfanes and methyl benzenesulfenate, respectively, can be presented and both the synthetic potential and the limitations of the reaction will be discussed.

Interestingly interactions of alkoxysulfanes with dielectrophiles like α,α′ dibromoxylenes (see Equation 2a),



Y = OAlkyl, Ph Alkyl = ⁿPr, ⁱPr, Me (2a)

2,2′ dibromomethylbiphenyl or 1,4 dibromo-2-butene (see Equation 2b) yield the corresponding bis-sulfinyl derivatives according to a "double" Thio-ARBUZOV-Reaction [3].



Y = OAlkyl, Ph Alkyl = ⁿPr, ⁱPr, Me (2b)

Due to the donor properties of their HOMO (3p lone pair at the sulfur atom) alkoxysulfanes can also be used as ligands in transition metal complexes with soft metal centers like Palladium(II) or Platinum(II) (see Equation 3).

$$[PdCl_2(NCPh)_2] + 2\ AlkylO\text{-}S\text{-}Y \xrightarrow{toluene} [PdCl_2\{S(Y)OAlkyl\}_2] + 2\ PhCN \qquad (3)$$

Y = OAlkyl,

Alkyl = ⁱPr, ⁿPr, Me

A crystal structure of $[PdCl_2\{S(O^iPr)_2\}]$ is presented and bond lengths and angels of the coordinated di-n-propoxysulfane are compared with those of the free ligand[4].

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