

This article was downloaded by:

On: 30 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## 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>

### ORGANYL (CHLOROETHYNYL) SULPHIDES, ORGANYL (CHLOROVINYL) SULPHIDES AND RELATED PROBLEMS

A. N. Mirskova<sup>a</sup>; M. G. Voronkov<sup>a</sup>; A. V. Martynov<sup>a</sup>; N. V. Luts kaya<sup>a</sup>

<sup>a</sup> Siberian Division of the USSR Academy of Sciences, Institute of Organic Chemistry, Irkutsk, USSR

**To cite this Article** Mirskova, A. N. , Voronkov, M. G. , Martynov, A. V. and Luts kaya, N. V.(1979) 'ORGANYL (CHLOROETHYNYL) SULPHIDES, ORGANYL (CHLOROVINYL) SULPHIDES AND RELATED PROBLEMS', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 6: 1, 211 — 212

**To link to this Article:** DOI: 10.1080/03086647908080379

**URL:** <http://dx.doi.org/10.1080/03086647908080379>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## ORGANYL(CHLOROETHYNYL)SULPHIDES, ORGANYL(CHLOROVINYL)SULPHIDES AND RELATED PROBLEMS

A.N. Mirskova, M.G. Voronkov, A.V. Martynov and N.V. Lutsкая

Institute of Organic Chemistry  
Siberian Division of the USSR Academy of Sciences  
664033 Irkutsk, USSR

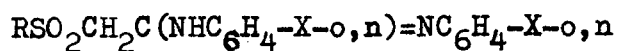
Organyl( $\beta,\beta$ -dichlorovinyl)- and organyl( $\alpha,\beta,\beta$ -trichlorovinyl)sulphides,  $\text{CCl}_2=\text{CHSR}$ ,  $\text{CCl}_2=\text{CClSR}$ ,  $(\text{CCl}_2=\text{CHS})_2\text{R}$ , have been obtained by dechlorination and dehydrochlorination of  $\alpha,\beta,\beta,\beta$ -tetrachloroethylorganylsulphides and by reactions of tri- and tetrachloroethylenes with mono- and dithiols of the aliphatic and aromatic series in the presence of radical initiators.

Depending on the reactant ratio and the reaction conditions the reactions of organyl( $\beta,\beta$ -dichlorovinyl)sulphides with mercaptides lead to cis- and trans- $\alpha,\beta$ -bis(organylthio)- $\beta$ -chloroethenes, bis(organylthio)acetylenes, tris(organylthio)ethenes. Dehydrochlorination of organyl( $\beta,\beta$ -dichlorovinyl)sulphides has permitted to prepare for the first time organyl(chloroethynyl)sulphides which react readily with trialkylphosphites, Li- and Mg-organic compounds to give organylthioethynylphosphonates,  $\text{RSC}\equiv\text{CP}(\text{O})(\text{OR})_2$ , and thioethynyl ethers,  $\text{RSC}\equiv\text{CR}$ , respectively.

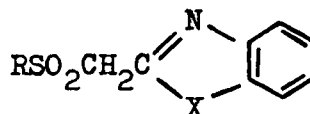
The reactions of organyl(chloroethynyl)sulphides with alcohols and mercaptans in the presence of their sodium derivatives involve the  $\text{C}\equiv\text{C}$  and  $\text{C}-\text{Cl}$  bonds depending on the reaction conditions and the nature of the reactants. Propyl alcohol and propylmercaptan regeospecifically add to the propyl(chloroethynyl)sulphide triple bond with the nucleophile attacking the carbon atom bound to sulphur in the first case and the carbon atom attached to chlorine in the second case.

The lability of chlorine atoms in the gem-dichlorovinyl group increases in going from organyl( $\beta,\beta$ -dichlorovinyl)sulphides to the corresponding sulphones. The reaction of the latter with aromatic amines  $o,n\text{-X-C}_6\text{H}_4\text{NH}_2$  ( $\text{X} = \text{H}, \text{F}, \text{Br}, \text{OCH}_3$ ) forms  $\text{N},\text{N}'$ -diarylorganylsulphonylacetamidines (I) and 2-organylsulphonylmethylbenzazols (II) when  $o$ -aminophenol and  $o$ -phenylenediamine

are the case.



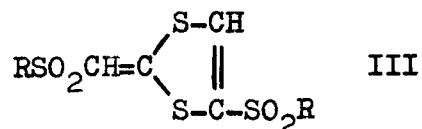
I



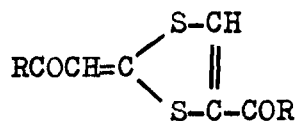
II

II: X = O, NH

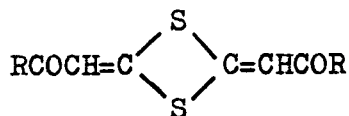
Organyl(β,β-dichlorovinyl)sulphones react with alkylxanthogenic acid salts to give previously unknown 2-organylsulphonyl-1,3-dithiols (III)



A similar reaction with organyl(β,β-dichlorovinyl)ketones leads to the formation of two types of products. These are 2-acylmethylene-4-acyl-1,3-dithiols (IV) and 2,4-bis-acylmethylene-1,3-dithioethanes (V)



IV



V