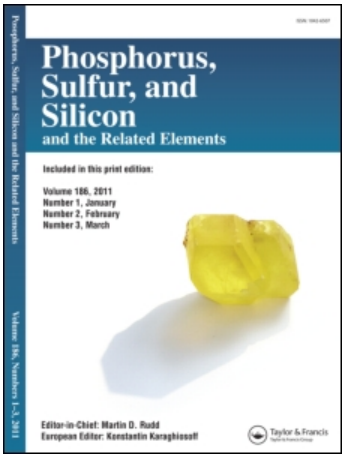

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ORGANYL (CHLOROETHYNYL) SULPHIDES, ORGANYL (CHLOROVINYL) SULPHIDES AND RELATED PROBLEMS

A. N. Mirskova[a]; M. G. Voronkov[a]; A. V. Martynov[a]; N. V. Lutskaya[a]
[a] Siberian Division of the USSR Academy of Sciences, Institute of Organic Chemistry, Irkutsk, USSR

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

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

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

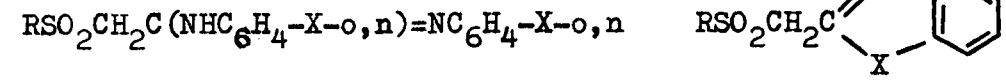
Organyl(ß,ß-dichlorovinyl)- and organyl(α,ß,ß-trichlorovinyl)sulphides, CCl_2=CHSR, CCl_2=CClSR, $(CCl_2=CHS)_2R$, have been obtained by dechlorination and dehydrochlorination of α,ß,ß,ß-tetrachloroethylorganylsulphides and by reactions of tri- and tetrachloroethylenes with mono- and dithiols of the aliphatic and aromatic series in the presence of radical initiators.

Depending on the reactant ratio and the reaction conditions the reactions of organyl(ß,ß-dichlorovinyl)sulphides with mercaptides lead to cis- and trans-α,ß-bis(organylthio)-ß-chloroethenes, bis(organylthio)acetylenes, tris(organylthio)ethenes. Dehydrochlorination of organyl(ß,ß-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, RSC≡CP(O)$(OR)_2$, and thioethynyl ethers, RSC≡CR, respectively.

The reactions of organyl(chloroethynyl)sulphides with alcohols and mercaptans in the presence of their sodium derivatives involve the C≡C and C–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(ß,ß-dichlorovinyl)sulphides to the corresponding sulphones. The reaction of the latters with aromatic amines o,n-X-$C_6H_4NH_2$ (X = H,F, Br, OCH_3) forms N,N'-diarylorganylsulphonylacetamidines (I) and 2-organylsulphonylmethylbenzazols (II) when o-aminophenol and o-phenylenediamine

are the case.

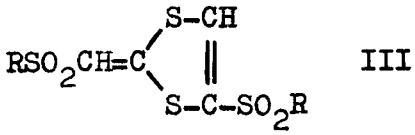


I

II

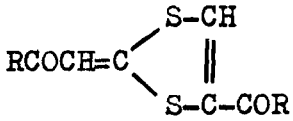
II: X = O, NH

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

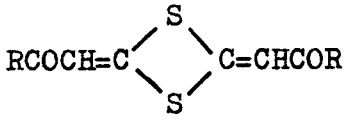


III

A similar reaction with organyl(ß,ß-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