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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

THE OXIDATIVE HALOGENATION OF HYDROXY SULFIDES

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To cite this Article Derzhinskii, A. R. , Konyushkin, L. D. and Prilezhaeva, E. N.(1979) 'THE OXIDATIVE HALOGENATION OF HYDROXY SULFIDES', Phosphorus, Sulfur, and Silicon and the Related Elements, 6: 1, 75 - 76

To link to this Article: DOI: 10.1080/03086647908080311 URL: http://dx.doi.org/10.1080/03086647908080311

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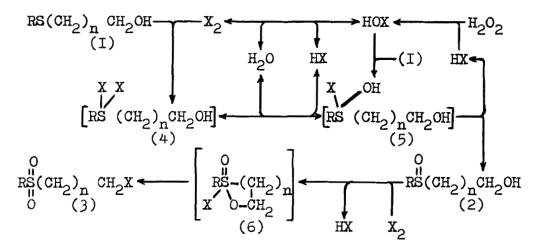
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THE OXIDATIVE HALOGENATION OF HYDROXY SULFIDES

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The oxidative halogenation of OH-containing substituted dialkyl-sulfides (1) or sulfoxides (2) by chlorine/water or hydrogen peroxide/halogen acid (HX)-mixtures allows to obtain high yields of halosubstituted sulfones (3) (R= $^{\rm C}_2{\rm H}_5$ - $^{\rm nC}_{10}{\rm H}_{21}$, $^{\rm C}_6{\rm H}_5$; X=Cl, Br; n=1-3):



We suppose the oxidation of the hydroxy sulfide (1) to the corresponding sulfoxide (2) to be the first reaction stage. At the second stage the hydroxy sulfoxide may react with halogen to give the intermediate (6) through intermolecular rearrangement of which the halosulfone (3) would be formed.

The intermediance of the sulfoxide (2), not found in reaction mixtures in standard reaction conditions, is proved by the fact that in the presence of heavy metal salts oxidative halogenation of hydroxy sulfides can be stopped at the stage of sulfoxide formation.

The mode of participation of hydroxy groups in the forma-

tion of sulfone (3) is confirmed by mass-spectral analysis of sulfones (R=C₈H₁₇, X=Cl, n=1,2) obtained by oxidative chlorination carried out in water containing $\sim 50\%$ of H₂¹⁸0 in the presence of H³⁶Cl:

presence of H^{Jo}Cl:

$$Cl_2/H_2^{16}O+H_2^{18}O+H^{36}Cl$$
 $Cl_2/H_2^{16}O+H_2^{18}O+H^{36}Cl$
 $Cl_2/H_2^{16}O+H_2^{18}O+H^{36}Cl$
 $Cl_2/H_2^{16}O+H_2^{18}O+H^{36}Cl$
 $Cl_2/H_2^{16}O+H_2^{16}O+H^{36}Cl$
 $Cl_2/H_2^{16}O+H_2^{16}O+H^{36}Cl$
 $Cl_2/H_2^{16}O+H_2^{16}O+H^{36}Cl$
 $Cl_2/H_2^{16}O+H_2^{16}O+H^{36}Cl$
 $Cl_2/H_2^{16}O+H_2^{16}O+H^{36}Cl$
 $Cl_2/H_2^{16}O+H_2^{16}O+H^{36}Cl$
 $Cl_2/H_2^{16}O+H_2^{16}O+H^{36}Cl$
 $Cl_2/H_2^{16}O+H_2^{16}O+H^{36}Cl$
 $Cl_2/H_2^{16}O+H^{36}Cl$
 Cl_2/H_2^{16

(2)
$$C1_2/H_2^{16}O+H_2^{18}O+H_2^{36}C1$$
 II $C_8H_17_5(CH_2)_nCH_2C1$ III III

The insertion of only one ¹⁸0 in the product of oxidative chlorination of the hydroxy sulfide (1), the absence of ¹⁸0 in the sulfone formed by oxidative chlorination of the sulfoxide (2) and the presence of ³⁶Cl in negligible amounts in both chlorosulfones (3) is consistent with the reaction scheme proposed.

We have also found that oxidative halogenations of various functionally substituted sulfides and sulfoxides afford convenient synthetic routes to some sulfur compounds which are rather difficult to obtain.