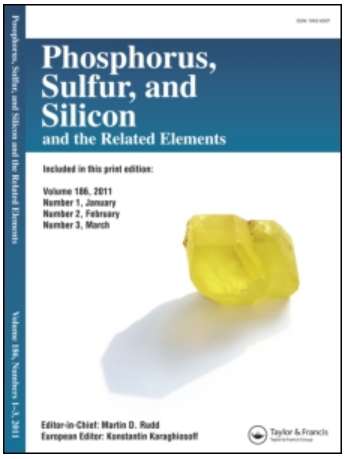

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THE OXIDATIVE HALOGENATION OF HYDROXY SULFIDES

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THE OXIDATIVE HALOGENATION OF HYDROXY SULFIDES

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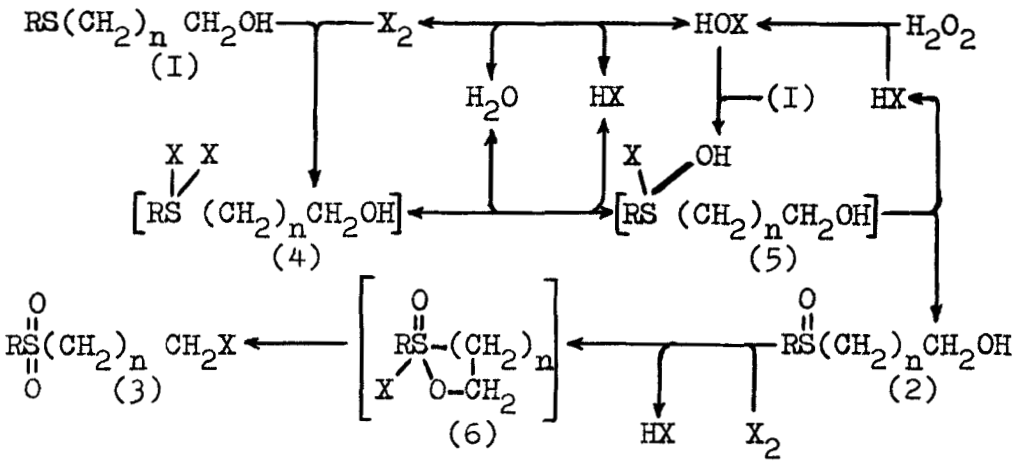
The oxidative halogenation of OH-containing substituted dialkylsulfides (1) or sulfoxides (2) by chlorine/water or hydrogen peroxide/halogen acid (HX)-mixtures allows to obtain high yields of halosubstituted sulfones (3) (R=C_2H_5 - $nC_{10}H_{21}$, C_6H_5; X=Cl, Br; n=1-3):

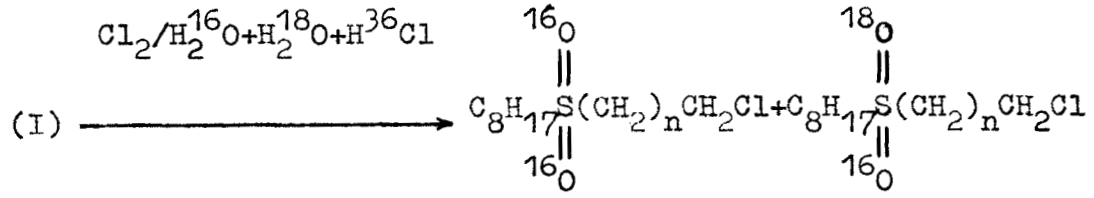


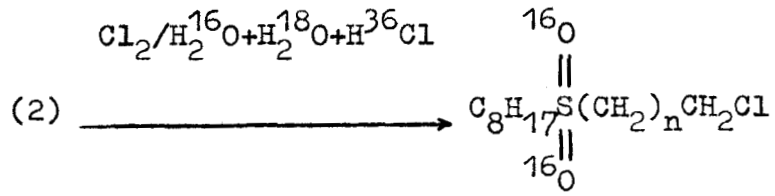
We suppose the oxidation of the hydroxy sulfide (1) to the corresponding sulfoxide (2) to be the first reaction stage. At the second stage the hydroxy sulfoxide may react with halogen to give the intermediate (6) through intermolecular rearrangement of which the halosulfone (3) would be formed.

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 ($R=C_8H_{17}$, X=Cl, n=1,2) obtained by oxidative chlorination carried out in water containing ~50% of $H_2^{18}O$ in the presence of $H^{36}Cl$:





The insertion of only one ^{18}O in the product of oxidative chlorination of the hydroxy sulfide (1), the absence of ^{18}O in the sulfone formed by oxidative chlorination of the sulfoxide (2) and the presence of ^{36}Cl 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.