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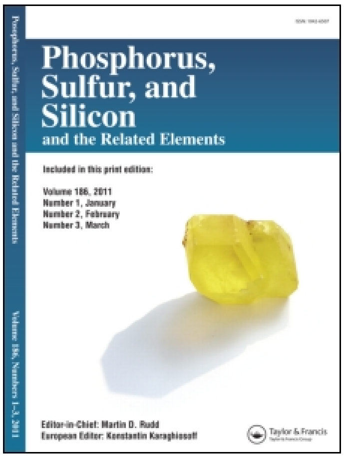

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OXIDATION OF ORGANIC SULFUR COMPOUNDS WITH DINITROGEN TETROXIDE

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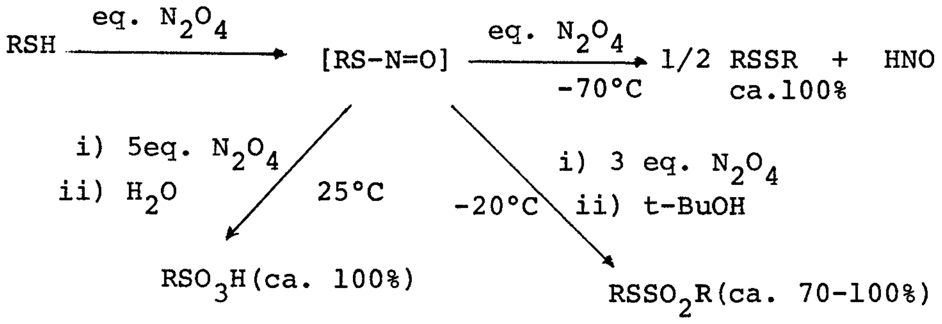
Symmetrical disulfides were known to be oxidized with excess N_2O_4 to the corresponding sulfonic anhydride in good yields. We have found that the oxidation of methyl phenyl disufide or an intermediate, phenyl methanethiolsulfinate undergoes via forming the unstable intermediate, i,e. the thionitrite, which are derived by the cleavage of sulfur-sulfur bond of the subsrates. The oxidation products were symmetrical disulfides, thiolsulfonates , and sulfonic acids which were undoubtedly derived from the scission of sulfur-sulfur bond.

While, both aromatic and alkyl thiols reacted readily with excess N_2O_4 at low temperature(ca. -20°C) to afford the corresponding thiolsulfonate in good yields.



The corresponding thiolsulfonates, disulfides or sulfonic acids can be prepared selectively by the simple and selective oxidation of the thiol with N_2O_4 when the reation temperature and concentration of N_2O_4 were carefully controlled.