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BOND SWITCH AT π-HYPERVALENT SULFUR CONTAINED IN CYCLIC SULFURANES

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Concerning the role and nature of π-sulfuranes, the following three examples are described, in which bond switch at π-hypervalent sulfur is the common subject. These phenomena cannot be observed in the chemistry of σ-sulfuranes.

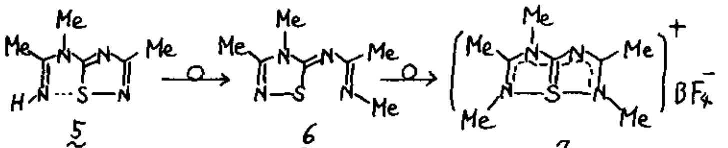
I) Reaction of 4-aryl-2-benzoyl-5-imino-Δ^2-1,3,4-thiadiazoline with dimethyl acetylenedicarboxylate gave 2-arylamino-4,5-dimethoxycarbonylthiazole (1) and usual adducts, i.e., cis-(2) and trans vinyl compounds (3) and N-benzoyl compound which is a byproduct. The yields of these products were determined in various aprotic solvents and alcohols. Plots of log (1/2+3) against E_T gave a straight line including all the solvents (r=0.980) and the substituent effect on the aryl group was also examined (ρ= 0.353 against σ_p^-).

It was shown that the reaction proceeded by competition to π-sulfurane by 1,3-dipolar cycloaddition to give 1 and to zwitter ion to give vinyl compounds (2+3).

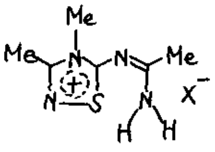
II) Heating 3,4-dimethyl-5-imino-1,2,4-thiadiazoline with acetimidate gave 5-(1-iminoethylmethylamino)-3-methyl-1,2,4-thiadiazole (5). Alkylation of 5 with Meerwein reagents gave mono-alkylated product (6) and 6 was again alkylated with the same reagent under reflux in dichloromethane to afford 1,2,3,5,6-pentamethyl-1,3,4,6-tetraaza-6a-thia(^{IV}S)pentalenium salt (7). In each step, bond switch at π-hypervalent sulfur took place to give the product.

Even by protonation of 5, bond switch to 8 was observed, and moreover, rapid equilibration between 5 and 8 was established by NMR.

III) A series of 1,2,5,6-tetrasubstituted 1,3,4,6-tetraaza-6a-thia(^{IV}S)pentalenes (9) were prepared, where 1,6-dimethyl derivatives are especially useful for NMR study to see the nature of this π-sulfurane.



5 6 7



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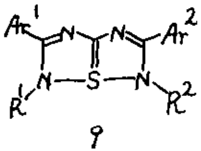

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