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1,2,3,5-DITHIADIAZOLYLES, A NEW TYPE OF PERSISTENT SULFURNITROGENCONTAINING RADICALS

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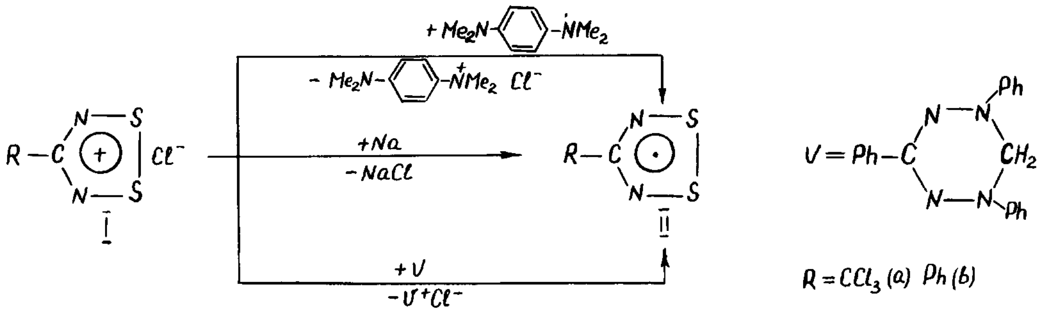
Summary: The obtaining of 5-membered sulfurnitrogencontaining cyclic free radicals of a new type starting from the 1,2,3,5-dithiadiazolium chlorides is reported. The EPR spectra and stability of these radicals are discussed.

A few types of persistent sulfurnitrogencontaining free radicals are known up to date. First of all these are acyclic arylthioaminyls which are today the object of intensive studies[1-5] and cyclic 1,2-thiazet-2-yles obtained by R.Mayer and coworkers[6-8].

We found that synthesized previously and independently by one of us[9] and by B.Banister with coworkers[10] 1,2,3,5-dithiadiazolium chlorides (Ia,b) can be easily reduced by dusty sodium in benzene or tetrahydrofuran (THF) with the formation of persistent free radicals of a new type - 1,2,3,5-dithiadiazolyles (IIa,b). Triphenylverdazyl radical or tetramethylparaphenylenediamine can be used as reducing agents as well.



The EPR measurement of radical (IIa,b) concentration using benzene solution of N,N-diphenyl-N'-picrylhydrazyl (DPPH) as a standard showed that one hour reaction between 1,2,3,5-dithiadiazolium chlorides (Ia,b) and sodium results practically in complete conversion of salt into radical (IIa,b) (at the concentration of about $1\text{-}5\cdot10^{-3}$ mol/l).

Radicals (IIa,b) remain persistent in benzene or THF solution during ~24 hours. The atmospheric oxygen does not exert essential influence on stability of (IIa,b). A typical EPR spectrum of radical (IIa,b) represent a simple 1:2:3::2:1 quintet with a small line-width. This splitting is due to the interaction of unpaired electron with two equivalent nitrogen nuclei.

Hyperfine structure splitting constants and g-values of radicals (IIa,b) have been defined by comparing them with a(N) of triphenylverdazyl and g-value of DPPH as a standard. The a(N) value in benzene and in THF for radicals (IIa, b) are equal (0.49 mT). The splitting of unpaired electron on the protons of phenyl ring for radical (IIb) as in the case of unsubstituted N,N-bis(phenylthio)aminyls[2,3] is not found. g-Value of radicals (IIa,b) is greater than that of an aromatic nitrogen-centered free radicals (2.003-2.004)[11] or N,N-bis(arylthio)aminyls (2.006-2.008) and is equal approximately 2.0104.

The low values of a(N) constant for radicals (IIa,b) as compared with N-(alkoxy)arylaminyls (~ 1.1 mT) and N-(alkylthio)arylaminyls (0.9-1.0 mT)[5] are in agreement with significant delocalization of spin density on sulfur atoms[5].

The data obtained confirms the fact that radicals (IIa,b) are the radicals of π-electronic type and their gain in stability is due to a great extent of unpaired electron localization on two sulfur atoms.

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