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Benzo-15-Crown-5 Based Nitronyl-Nitroxide and Imino-Nitroxide Radicals

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New Benzo-15-Crown-5 based nitronyl-nitroxide and the corresponding imino-nitroxide radicals have been synthesized and characterized. 4'-Formyl-benzo-15-crown-5 reacts with N,N'-dihydroxy-2,3-diamino-2,3-dimethylbutane to yield the N,N'-dihydroxyimidazolidine and the dehydration product N-hydroxyimidazolidine. Mild oxidation of these two species leads to the corresponding stable nitronyl-nitroxide and imino-nitroxide radicals respectively.

Keywords: Crown ether; Benzo-15-crown-5; Nitronyl-nitroxide radicals; Esr

INTRODUCTION

One of the emerging goals of crown ether chemistry is the conception of species capable to detect or recognize cations, molecules or supermolecules.[1-7] In this context crown ethers, bearing a stable radical, appear as a potential tool for an esr-based detection or recognition. This is rendered possible owing to the different coupling constants observed after complexation as well as the possibility of superhyperfine splitting. This feature reflects the strength of the complexation and accounts for the effect of the guest species upon the spin density distribution of the host.[8,9] As a matter of fact, while the chemistry of the first cyclic polyethers was being developed,[1,2] the first

stable aliphatic and aryl nitronyl nitroxides (4,5-dihydro-4,4,5,5-tetramethylimidazole-1-oxyl-3-oxide) were synthesized.[10,11] Since then a special interest was given to these species as building blocks for the design of magnetic molecular assemblies. [12-18] In order to explore the wide prospect offered by host molecules bearing stable radicals, we have initiated a program devoted to the synthesis of different crown ethers and cryptands bearing nitronyl nitroxide radicals. Such species could find application in all fields associated to host-guest chemistry as well as molecular magnetic materials.

We present herein the synthesis and characterization of the two new Benzo-15-Crown-5 based Nitronyl-Nitroxide (**1**) and Imino-Nitroxide radicals (**2**).

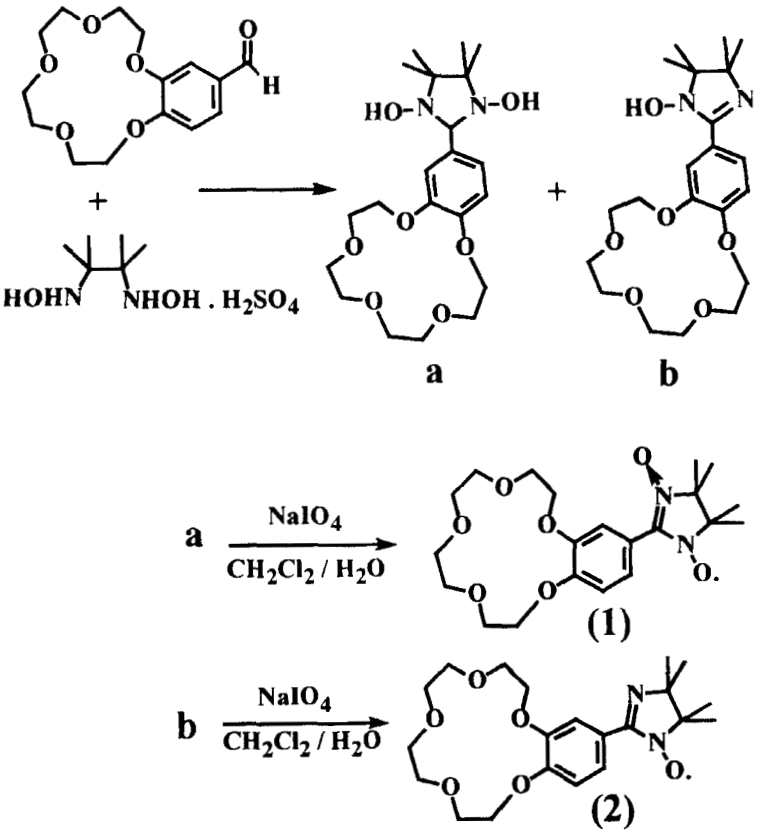
RESULTS

Synthesis

The reaction of the monosulfate salt of N,N'-dihydroxy-2,3-diamino-2,3-dimethylbutane with 4'-Formyl-benzo-15-crown-5 in dry methanol at reflux temperature yields N,N'-dihydroxyimidazolidine and the dehydration product N-hydroxyimidazolidine. Mild oxidation using sodium periodate in phase transfer conditions (CH_2Cl_2/H_2O) affords the corresponding blue nitronyl-nitroxide (**1**) and orange imino-nitroxide (**2**) (scheme 1).

Esr Spectra

The esr spectra of compounds **1** and **2**, recorded in dichloromethane, are shown in figure 1. For the nitronyl-nitroxide (**1**), the five-line pattern with a ratio 1:2:3:2:1 is observed as expected for coupling with two identical nitrogen nuclei (I=1).[11] The hyperfine coupling constant is a_N = 7.5 G. The imino-nitroxide (**2**) shows a seven line pattern consistent with two nonequivalent nitrogen atoms with the following coupling constants $a_{N(1)}$ = 9.3 G and $a_{N(2)}$ = 4.2 G respectively.



SCHEME 1

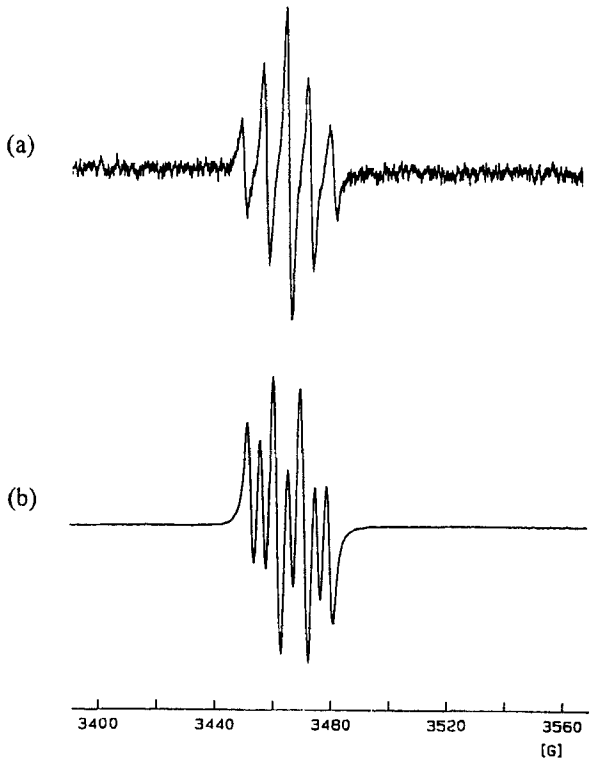


FIGURE 1. Room temperature esr spectra in dichloromethane. (a) **1**, (b) **2**.

CONCLUSION

These results represent a first example of crown ethers bearing stable nitronyl nitroxide and imino nitroxide radicals. These species could give considerable information about the guest ions or molecules by means of esr spectroscopy. They could therefore play an important role in host-guest chemistry regarding the molecular detection and recognition. One of our present objectives is to synthesize a variety of crown ethers and cryptands bearing such radicals. Besides, the complexation of open shell metal ions will give birth to a new route for the design of magnetic molecular materials.

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