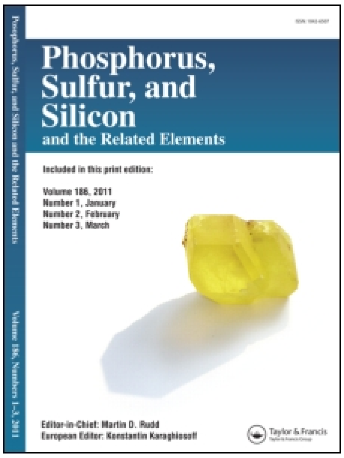

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Neil Burford[a]; Jack Passmore[a]; Xiaoping Sun[a]
[a] Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada

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PHOTOLYSIS OF 1,3,2,4-DITHIADIAZOLYL $R\overline{CNSNS}^{\bullet}$ RADICALS AND THEIR CONCERTED PHOTOCHEMICALLY SYMMETRY ALLOWED REARRANGEMENT TO 1,2,3,5-DITHIADIAZOLYL $R\overline{CNSSN}^{\bullet}$ BY THE NET EXCHANGE OF ADJACENT S AND N ATOMS

NEIL BURFORD, JACK PASSMORE, AND XIAOPING SUN
Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada, E3B 6E2.

Abstract 1,3,2,4-dithiadiazolyl $R\overline{CNSNS}^{\bullet}$ radicals undergo two photochemical processes, i.e. the unimolecular dissociation to RCN and $SNS^{\bullet}$; and dimeric rearrangement to 1,2,3,5-dithiadiazolyl $R\overline{CNSSN}^{\bullet}$.

INTRODUCTION

SNS^+ undergoes cycloadditions with various nitriles to give 6π 1,3,2,4-dithiadiazolium $R\overline{CNSNS}^{+}$, which on reduction give 7π 1,3,2,4-dithiadiazolyl $R\overline{CNSNS}^{\bullet}$ radicals. Several pure $R\overline{CNSNS}^{\bullet}$ ($R=CH_3$, Bu^t, Ph, $p\text{-}O_2NC_6H_4$) have been isolated[1-3]. However, we have found that for a variety of R, the radical $R\overline{CNSNS}^{\bullet}$ undergo unprecedented rearrangement to the thermodynamically more stable 1,2,3,5-dithiadiazolyl $R\overline{CNSSN}^{\bullet}$ by the net exchange of two adjacent S and N atoms. Several $R\overline{CNSSN}^{\bullet}$ ($R=Bu^t$, CF_3, Ph, $3,5\text{-}(O_2N)_2C_6H_3$) were prepared in essentially quantitative yield by the facile rearrangement. In solution, this rearrangement proceeds in the dark for electronegative derivatives (eg. for $R=CF_3$, $3,5\text{-}(O_2N)_2C_6H_3$), and only in the light for electropositive derivatives (eg. for $R=Bu^t$, Ph). In addition, we have discovered a unimolecular photochemical dissociation of $R\overline{CNSNS}^{\bullet}$ to RCN and $SNS^{\bullet}$.

PHOTOLYSIS OF $Bu^t\overline{CNSNS}^{\bullet}$ to Bu^tCN and $SNS^{\bullet}$

On irradiation at 254 nm, $Bu^t\overline{CNSNS}^{\bullet}$ underwent photolysis to give Bu^tCN (^1H and ^{13}C NMR) and S_8 (FT-Raman). The ESR kinetic study showed that on photolysis at this wavelength, the concentration of $Bu^t\overline{CNSNS}^{\bullet}$ (represented by the peak height (h) of the ESR spectra) decayed as the function of time (a linear relationship between lgh and t), showing the photolysis to be a first order process with respect to $Bu^t\overline{CNSNS}^{\bullet}$ concentration. This is consistent with a dissociation occurring via a concerted unimolecular pathway (Eqn.1)

$$Bu^t\overline{CNSNS}^{\bullet} \text{ -----> } RCN + SNS^{\bullet} \qquad (1)$$

This photolysis likely proceeds via a high energy dissociative state of $(Bu^t\overline{CNSNS}^{\bullet})^{*}$ (STO-3G), and is photochemically symmetry allowed.

UV-VIS SPECTROSCOPIC STUDIES OF RCNSNS• AND ITS REARRANGEMENT TO RCNSNS•

The UV-Vis spectrum of PhCNSNS• exhibited several bands at 250, 280, 360, 376, and 480 nm. The absorbances at 280, 360, 376, and 480 nm are proportional to the square of the radical concentration $[\mathrm{PhCNSNS^\bullet}]^2$, unambiguously showing the dimerization of PhCNSNS• in solution (Eqn.2)

$$2\ \mathrm{PhCNSNS^\bullet} \rightarrow (\mathrm{PhCNSNS^\bullet})2 \qquad (2)$$

Thus all the four bands at 280, 360, 376, and 480 nm originate from the radical dimer absorptions. The dimerization enthalpy and entropy were determined (ΔH_d=-19 kJ/mol, ΔS_d=-66.5 J/mol) by a variable temperature ESR study, based on which the dimerization of PhCNSNS• (0.02 M) at room temperature is ca. 3%. The photolytic study showed that direct irradiation at $(\mathrm{PhCNSNS^\bullet})_2$ dimer absorption (376 nm) effected fast rearrangement of PhCNSNS• to the disulfide isomer PhCNSSN•, supporting that this rearrangement proceeds via the excitation of an intermediate radical dimer (Eqn.3)

$$(\mathrm{PhCNSNS^\bullet})_2 \dashrightarrow (\mathrm{PhCNSNS^\bullet})_2^* \dashrightarrow (\mathrm{PhCNSSN^\bullet})_2 \qquad (3)$$

The unrearranged radical dimer $(\mathrm{PhCNSNS^\bullet})_2$ most likely possesses a head-to-tail configuration (see 5 in ref.1), which allows the rearrangement to proceed in a concerted pathway with minimal movement of all the atoms, leading to another head-to-tail dimer $(\mathrm{PhCNSSN^\bullet})_2$ (see 6 in ref.1). This rearrangement was shown (CNDO) to be photochemically symmetry allowed. The UV-Vis spectroscopic studies also showed that the absorbances of $(\mathrm{RCNSNS^\bullet})_2$ dimer (R=Ph, p-$O_2NC_6H_4$, 3,5-$(O_2N)_2C_6H_3$, and CF_3) at 376 nm at 0.02 M RCNSNS• solutions are directly proportional to the ionization energy of the corresponding RCN which reflect the electronegativity of R. It appears that the extent of RCNSNS• dimerization was greater the higher the electronegativity of R, consistent with the observed qualitatively faster rearrangement[3] of radicals with electronegative R.

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