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New polysulfur–nitrogen heterocycles as precursors of thiazyl radicals

Konstantin V. Shuvaev,[a] **Victor A. Bagryansky,***[a,b] **Nina P. Gritsan,***[b,c] **Alexander Yu. Makarov,**[d] **Yuri N. Molin**[b,c] **and Andrey V. Zibarev***[d]

[a] *Department of Natural Sciences, Novosibirsk State University, 630090 Novosibirsk, Russian Federation*
[b] *Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. Fax: + 7 3832 34 2350; e-mail: vbag@ns.kinetics.nsc.ru, gritsan@ns.kinetics.nsc.ru*
[c] *Department of Physics, Novosibirsk State University, 630090 Novosibirsk, Russian Federation*
[d] *N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. Fax: + 7 3832 34 4752; e-mail: zibarev@nioch.nsc.ru*

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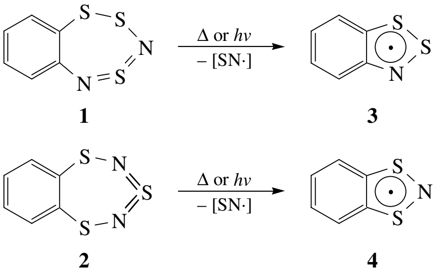
Both thermolysis and photolysis of 1,2,4$\lambda^4\delta^2$,3,5- and 1,3$\lambda^4\delta^2$,5,2,4-benzotrithiadiazepines in hydrocarbon solvents yielded stable 1,2,3- and 1,3,2-benzodithiazolyls, which can be considered as a particular case of a previously unmentioned trend of neutral polysulfur–nitrogen heterocycles to form thiazyl π-radicals.

Much progress towards organic molecular magnets based on aryl-substituted thiazyl π-radicals, such as 4-aryl-1,2,3,5-dithiadiazolyls, 1,2,3- and 1,3,2-benzodithiazolyls,[1] stimulates the design and synthesis of novel radical derivatives. In this context, new precursors to thiazyl radicals are especially desirable.

Recently, it was found by EPR spectroscopy that the thermolysis and photolysis of 1,3$\lambda^4\delta^2$,2,4-benzodithiadiazines represent a quantitative approach to 1,2,3-benzodithiazolyls, including previously unknown derivatives.[2,3] The key intermediates are R–S–N: $\longleftrightarrow$ R–S≡N nitrenoids (R–S = 1,2,3-benzodithiazol-2-yl), which were identified under matrix isolation conditions.[4] Based on these findings, it would be expected that other polysulfur–nitrogen heterocycles can also serve as the sources of thiazyl radicals.

Indeed, we found that the thermolysis and photolysis of dilute (10^{-3} M) solutions of isomeric 1,2,4$\lambda^4\delta^2$,3,5- and 1,3$\lambda^4\delta^2$,5,2,4-benzotrithiadiazepines (**1** and **2**, respectively)[5,6] in hydrocarbons afforded 1,2,3- and 1,3,2-benzodithiazolyls (**3** and **4**, respectively)[†] (Scheme 1), which were unambiguously identified by a comparison of their EPR spectral parameters (hfc constants and *g*-factors) with published data.[2,3]



Scheme 1

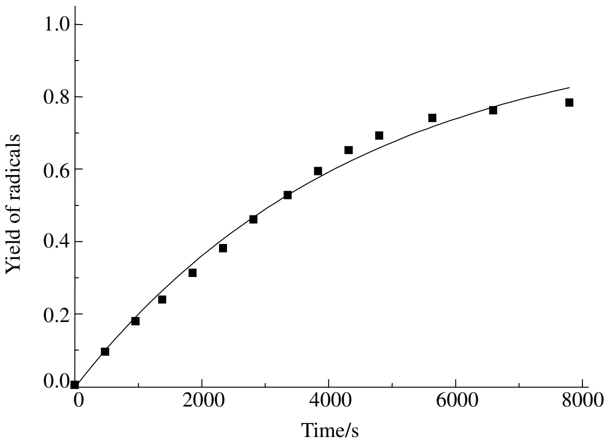


Figure 1 Kinetics of the formation of radical **3** upon thermolysis of a solution of **1** in squalane at $T = 150$ °C (initial concentration of **1** was 10^{-3} M).

The yields of the thermal transformation of **1** and **2** into **3** and **4** are 85±15% in both cases; however, the reaction rate in the case of **1** (Figure 1) is higher than that in the case of **2** (Figure 2).

The kinetic build-up curve for radical **3** in the thermolysis of **1** in squalane (Figure 1) was adequately approximated by the first-order equation $A(t) = A(\infty)(1 - e^{-kt})$, where $A(\infty)$ is the concentration of **3** at $t = \infty$, and k is the reaction rate constant. The latter was found to be $(2.3\pm0.2)\times10^{-4}$ s^{-1} at $T = 150$ °C.

In contrast to **3**, the kinetic build-up curve for isomeric radical **4** in the thermolysis of **2** in squalane (Figure 2) featured a lag, and it cannot be described by an ordinary exponential equation. This type of kinetic curves is known, in particular, for self-catalytic and branching chain reactions. One can also

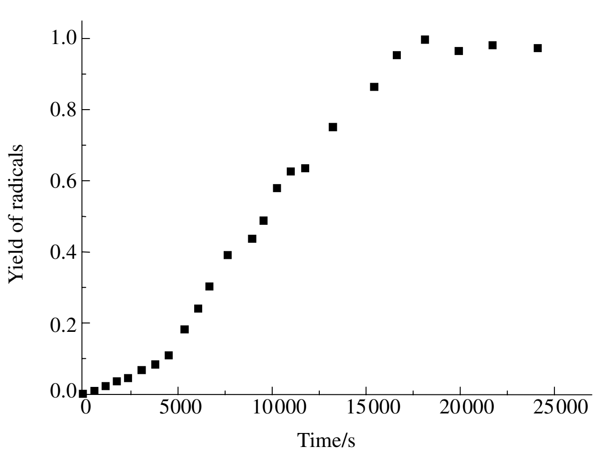


Figure 2 Kinetics of the formation of radical **4** upon thermolysis of a solution of **2** in squalane at $T = 140$ °C (initial concentration of **2** was 10^{-3} M).

[†] *The thermolysis* of 10^{-3} M solutions of **1**[6] or **2**[5] in absolute squalane (2,6,10,15,19,25-hexamethyltetracosane) was performed in an EPR Teflon valve-equipped quartz tube degassed by three freeze–pump–thaw cycles and thermostatted to within ±0.5 °C.

The photolysis of 10^{-3} M solutions of **1** or **2** in absolute dodecane or hexane, respectively, degassed as described above, was performed at ambient temperature in the same type of EPR tubes using selected lines of a DRSh-500 high-pressure mercury lamp equipped with a water filter. Glass filters were used to isolate individual lines (313, 365, 436 nm).

The EPR spectra of radicals **3** and **4** were recorded on a Bruker EMX spectrometer (MW power of 0.64 mW, modulation frequency of 100 kHz and modulation amplitude of 0.01 mT), and they were identical to those previously published.[2,3] Spectral integrations and simulations were performed with the WIN-EPR Simfonia and WinSim software programs. The *g*-factors of radicals were measured using DPPH as a standard ($g = 2.0036$). The yields of radicals were determined using a single crystal of $CuCl_2\cdot2H_2O$ as a standard sample with a known amount of paramagnetic species.

The *thermolysis* of **5**[6] and **6**[11] into radicals **1** and **7**, respectively, will be described elsewhere. The observed EPR spectra of **1**[2,3] and **7**[10] were consistent with published data.

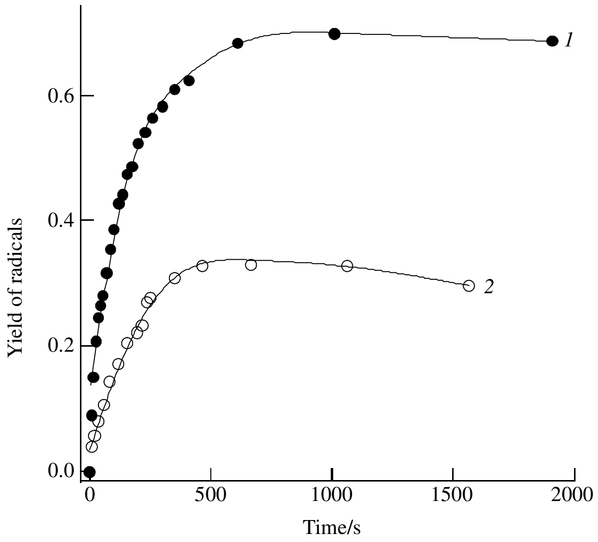


Figure 3 (*1*) Kinetics of the formation of radical **3** under irradiation of **1** in dodecane at 436 nm and (*2*) kinetics of the formation of radical **4** under irradiation of **2** in hexane at 313 nm. Initial concentrations of **1** and **2** were 10^{-3} M.

speculate that the discussed reaction includes the transformation of initial **2** into a long-lived intermediate followed by its transformation into final **4**.

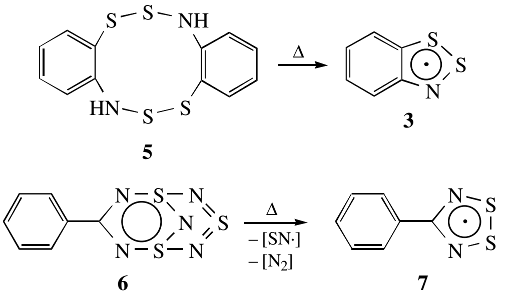
The yields of the photochemical transformation of **1** and **2** into **3** and **4** are 65±10 and 25±5%, respectively (Figure 3), probably, due to other reaction pathways, which do not lead to radicals and, to some extent, photodegradation of target radicals.[3,4]

Compound **1** with $\lambda_{max} = 457$ nm in the UV-VIS spectrum[6] readily provided radicals **3** under the irradiation of its solution in dodecane with light at 436 nm (Figure 3). In contrast to **1**, isomer **2** with $\lambda_{max} = 379$ nm in the UV-VIS spectrum[5] is stable towards irradiation at $\lambda = 436$ nm, but it can be decomposed under exposure to light with shorter wavelengths. The kinetic build-up curve for **4** in the photolysis of **2** in hexane at 313 nm is shown in Figure 3. Previously, only elemental sulfur and unidentified products were obtained in the photolysis of **2** performed on a preparative scale; no intermediates were detected.[7]

Formally, the transformation of **1** and **2** into **3** and **4** requires a ring contraction with the loss of the SN· radical, although the latter was not observed. Previously, SN· was only detected by gas-phase EPR spectroscopy,[8,9] and its properties are poorly known. One can think that SN·, if really formed, decomposes rapidly under the experimental conditions (or, ultimately, is undetectable in a condensed phase due to strong g-anisotropy).

Therefore, in addition to the previously discovered conversion of 1,3$\lambda^4\delta^2$,2,4-benzodithiadiazines into stable thiazyl radicals,[2–4] we found a new reaction of this type, namely, the formation of stable benzodithiazolyls **3** and **4** upon the thermolysis and photolysis of isomeric benzotrithiadiazepines **1** and **2**.

As follows from our preliminary EPR data, other related compounds, such as 7*H*,14*H*-dibenzo[*d*,*i*][1,2,6,7,3,8]tetrathiadiazecine **5** and 7-phenyl-1λ^4,3$\lambda^4\delta^2$,5λ^4-trithia-2,4,6,8,9-pentaazabicyclo[3.3.1]nona-1(9),2,3,5,7-pentaene **6**, also give stable thiazyl radicals **1** and 4-phenyl-1,2,3,5-dithidiazolyl **7**,[10] respectively, under conditions of thermolysis (Scheme 2).[†]



Scheme 2 Note that a circle in the dithiatriazine ring of compound **6** does not mean a 6π-electron aromatic system (it illustrates typical problems, which sulfur–nitrogen compounds of unusual structures pose in terms of the simple bonding theory).

Thus, the results allowed us to recognise a previously unmentioned propensity of neutral polysulfur–nitrogen heterocycles to form stable thiazyl radicals under relatively mild conditions. Beyond the context of molecular magnets, these findings are important for the understanding of the heteroatom reactivity of this class of compounds.

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