SYNTHESIS OF NEW VERDAZYL BUILDING BLOCKS

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СИНТЕЗ НОВЫХ BUILDING BLOCKS НА ОСНОВЕ ВЕРДАЗИЛЬНЫХ РАДИКАЛОВ

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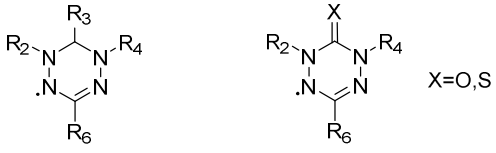
Аннотация. *Метод модификации органических каркасов спин-содержащими строительными блоками предлагается перспективной альтернативой классическому многостадийному синтезу радикальных фрагментов непосредственно на органическом каркасе. Одной из наиболее удобных реакций для модификации молекул может выступать палладий-катализируемые реакции кросс-сочетания.*
Полученные вердазильные радикалы, имеющие галогенированные заместители, благодаря своей высокой стабильности являются оптимальными для одностадийной модификации. Стабильные радикалы с объёмными сопряженными заместителями в положениях 2 и 4 были синтезированы из 1,3,5-замещённых формазанов, полученных по реакции гидразонов с арендиазоний тозилатами – новым классом стабильных диазониевых солей.

The study of different types of stable organic radicals is one of the important trends in modern organic chemistry. Stability of the resulting radical can be achieved using two approaches: 1) appending bulky substituents into the molecule to prevent radical recombination; 2) delocalization of an unpaired electron through the conjugated π-system. Combining these factors, extreme kinetic and thermodynamic stability can be achieved, giving possibility for various practical appliances of organic radicals. Many organic molecules with unpaired electrons have found appliance as ligands for complexes of transition metals [1], magnetic materials [2], spin labels [3], catalysts for living-radical polymerization [4].

Verdazyl (tetrahydro-s-tetrazin-1-(2H)-yl) radicals **1,2** are a class of stable organic radicals that has some important advantages: usually they do not dimerize in solution and are resistant to exposure of air and moisture [5]. Their general structures are shown in Figure 1. There are two types of verdazyl radicals: "Kuhn verdazyls" **1** (3-alkyl/aryl-2,4,6-substituted) [6] and 3-oxo- and 3-thioxo-2,4,6-substituted verdazyls **2 [7].**



1 **2**

Fig. 1. General structures of verdazyl radicals

Kuhn verdazyls are easily synthesized from suitable formazans, whereas obtaining of oxo- and thioxo-verdazyls involves usage of phosgene/thiophosgene [8], making these syntheses dangerous and, therefore, inconvenient.

Nowadays molecules containing conjugated spin systems with ferromagnetic or antiferromagnetic properties are of the utmost interest [9]. Typical syntheses include multi-step reactions to construct fragments with an unpaired electron on scaffold, but it is more convenient to modify molecules with radical-containing building blocks in one step [10]. One of the methods for these purposes is to use Pd-catalysed cross-coupling reactions. Therefore radicals that are used for modification should contain arylhalide fragments vital for all of the cross-coupling reactions. Despite those facts, there were no previous reports about successful high-yield syntheses of verdazyl radicals with bromo- or iodophenylene substituents in 2, 4 or 6 positions.

Moreover, there are still no examples of verdazyls with bulky conjugated substituents in 2 and 4 positions, and this option may be used for increasing general stability of radicals both through additional delocalization of an unpaired electron though π-conjugation and appending bulky substituents.

For further appliances 6-(4-bromophenyl) and 6-(3-iodophehyl) substituted verdazyl radicals **4a,b**, additionally stabilized with conjugated biphenyl groups at 2 and 4 positions, were synthesized in high yields (Figure 2).

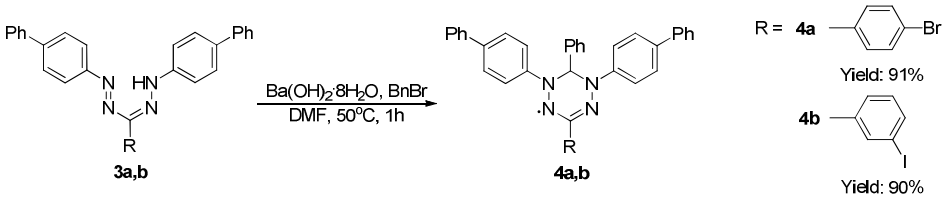


*Fig. 2. Synthesis of 2,3,4,6-subsituted verdazyl radicals **4a,b** from formazans*

Solid-state structures of verdazyls **4a,b** were determined by single X-Ray diffractions. The molecular structure of compound **4b** is shown in Figure 3. Structural parameters of verdazyls **4a,b** in solid states are similar to the parameters of previously reported 6-(4-azidophenyl)-2,4-diphenylverdazyl [11].

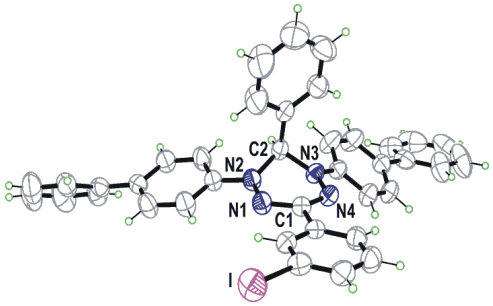


*Fig. 3. Molecular structure of compound **4b** with numbered atom in heterocycle (50% probability chosen for the ellipsoids)*

ESR spectra of **4a,b** were obtained in deoxygenated toluene solution, showing the nine-line hyperfine patterns, which are typical for verdazyls [12] with an average spacing a_N = 5.5 G (4N) for both radicals (Figure 4). Simulations of ESR spectra display that all nitrogen atoms in verdazyl ring are equivalent.

Radical-containing building blocks for further one-step modification of organic molecules were synthesized. These compounds were characterized by ESR, UV-vis spectra, CVA and X-Ray data. High stability of obtained

verdazyl radicals makes them suitable for appliance in modification of molecules with palladium-catalyzed cross-coupling reactions.

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