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*S.A. Varenichenko, O.K. Farat, K.V. Yanova, V.I. Markov***REACTION OF 2-METHYL-2,3,5,6,7,8-HEXAHYDRO-4H-1,3-BENZOXAZIN-4-ONE WITH DIAZONIUM SALTS****Ukrainian State University of Chemical Technology, Dnipro, Ukraine**

We found that the interaction of 2-methyl-2,3,5,6,7,8-hexahydro-4H-1,3-benzoxazin-4-one with various activated and non-activated diazonium salts in hydrochloric and acetic acids leads to the formation of corresponding previously unknown arylhydrazones with high yields, independent of the structure of the diazo component. The azo coupling reaction proceeds at the non-activated  $sp^3$ -hybrid C-8 atom due to the activating action of the acid medium with the formation of 2-methyl-6,7-dihydro-2H-1,3-benzoxazine-4,8(3H,5H)-dione 8-arylhydrazone. This reaction proceeds regioselectively at the C-8 atom due to steric hindrances, namely the large size of the diazonium salts. The structures of the synthesized arylhydrazones were confirmed by modern physicochemical methods of analysis including  $^1H$  NMR spectroscopy and mass spectrometry. The discovered reaction allows synthesizing arylhydrazones, which are difficult to access by other methods in one step. Isolation of the reaction products is not difficult and can be achieved by simple filtration after neutralization. The resulting arylhydrazones can be used as building blocks in organic synthesis and as ligands for binding metal ions.

**Keywords:** 1,3-benzoxazin-4-one, diazonium salt, azo coupling reaction, arylhydrazone, CH-activation.

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**Introduction**

Aromatic azo compounds are widely used in organic chemistry. With the help of the azo coupling reaction, many practically significant substances are prepared, such as dyes [1], indicators [2], biologically active substances [3], etc. [4]. Carrying out the azo coupling reaction with active methylene compounds leads to the synthesis of the corresponding arylhydrazones, which are also widely used, for example, as dyes [5,6], biologically active substances [7–9], etc. The reaction of diazonium salts with methine-active compounds leads to the formation of mixed azo compounds if there is no possibility of eliminating one of the activating groups [10], as occurs in the Japp-Klingemann reaction [11]. Active methine and methylene compounds also react with other electrophilic agents to form structurally complex molecules [12,13]. Examples are known when non-activated methylene compounds react with various electrophilic agents. For instance, the reaction of 5',6',7',8'-tetrahydro-1'H-spiro[cyclohexane-1,2'-

quinazolin]-4'(3'H)-one [14] with 4-methylbenzene-diazonium chloride results in arylhydrazone 1 (there is a typo in the structural formula in the original article) [15], and the reaction with the Mannich reagent leads to spiran 2 [16]. Formylation of 5,6,7,8-tetrahydrospiro[1,3-benzoxazine-2,1'-cyclohexan]-4(3H)-one under Vilsmeier-Haack reaction conditions gives compound 3 (Scheme 1) [17].

The purpose of this work is to study the interaction of 2-methyl-2,3,5,6,7,8-hexahydro-4H-1,3-benzoxazin-4-one 4 containing an unactivated methylene group with various diazonium salts.

**Experimental**

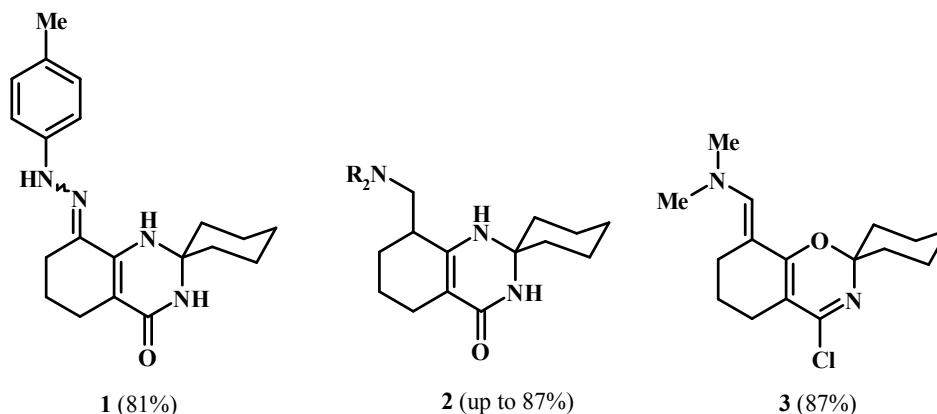
The  $^1H$  NMR spectra were obtained by using a Bruker Avance II 400 instrument (400.13 MHz) in  $DMSO-d_6$  using residual solvent peak as a reference. The mass spectra were recorded by means of a MX1321 instrument with direct injection of the sample at an ionization chamber temperature of 200°C and with 70 eV ionizing electrons. Elemental analysis was performed by means of a LECO CHN-

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*S.A. Varenichenko, O.K. Farat, K.V. Yanova, V.I. Markov*



Scheme 1

900 instrument. The reactions and the purity of the obtained compounds were monitored by TLC on Merck Silicagel 60 F-254 plates with 10:1  $\text{CHCl}_3$ –*i*-PrOH as eluent. Melting points were carried out using an Electrothermal 9100 Digital Melting Point apparatus and were uncorrected.

*Synthesis of compounds 5–8 (general method)*

Concentrated HCl (5 ml) was mechanically stirred and cooled with ice, then anhydrous sodium nitrite (0.17 g, 2.5 mmol) was added, followed corresponding aniline (2.5 mmol) in glacial acetic acid (7 ml). The mixture was stirred for 10 min, the obtained diazonium salt solution was cooled with ice and treated by slow addition of compound 4 (0.42 g, 2.5 mmol) solution in AcOH (5 ml) from a dropping funnel. The mixture was stirred for 15 min, diluted with water (10 ml), and adjusted with 25%  $\text{NH}_3$  solution to pH 8–9.

*2-Methyl-6,7-dihydro-2H-1,3-benzoxazine-4,8(3H,5H)-dione 8-[(4-nitrophenyl)hydrazone] (5)*

Brown powder, mp: 131–133°C, yield 86%.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{DMSO-d}_6$ ),  $\delta$ , ppm: 1.35 (3H, d,  $^3J=5.4$ ,  $\text{CH}_3$ ), 1.41–1.48 (2H, m,  $\text{CH}_2$ ), 1.61–1.72 (2H, m,  $\text{CH}_2$ ), 2.04–2.21 (2H, m,  $\text{CH}_2$ ), 5.05–5.14 (1H, m, CH), 7.27 (1H, br.s., NH), 7.64 (2H, d,  $^3J=8.3$ , H-Ar), 7.91 (1H, br.s., NH), 8.25 (2H, d,  $^3J=8.3$ , H-Ar). MS (EI),  $m/z$  ( $I_{\text{rel}}$ , %): 316  $[\text{M}]^+$  (70). Calculated  $\text{C}_{15}\text{H}_{16}\text{N}_4\text{O}_4$ : C 59.96; H 5.10; N 17.71. Found: C 60.16; H 5.17; N 17.83.

*2-Methyl-6,7-dihydro-2H-1,3-benzoxazine-4,8(3H,5H)-dione 8-[(4-methyl-2-nitrophenyl)hydrazone] (6)*

Red powder, mp: 87–89°C, yield 83%.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{DMSO-d}_6$ ),  $\delta$ , ppm: 1.35 (3H, d,  $^3J=5.4$ ,  $\text{CH}_3$ ), 1.41–1.48 (2H, m,  $\text{CH}_2$ ), 1.61–1.72 (2H, m,  $\text{CH}_2$ ), 2.04–2.21 (2H, m,  $\text{CH}_2$ ), 2.17 (3H, s,  $\text{CH}_3$ ), 5.05–5.14 (1H, m, CH), 6.92 (1H, d,  $^3J=8.8$ , H-Ar), 7.22 (1H, d,  $^3J=8.8$ , H-Ar), 7.29 (1H, br.s., NH), 7.73 (1H, s, H-Ar), 7.92

(1H, br.s., NH). MS (EI),  $m/z$  ( $I_{\text{rel}}$ , %): 330  $[\text{M}]^+$  (71). Calculated  $\text{C}_{16}\text{H}_{18}\text{N}_4\text{O}_4$ : C 58.17; H 5.49; N 16.96. Found: C 58.25; H 5.59; N 17.03.

*2-Methyl-6,7-dihydro-2H-1,3-benzoxazine-4,8(3H,5H)-dione 8-[(4-methoxyphenyl)hydrazone] (7)*

Yellowish powder, mp: 100–103°C, yield 75%.

$^1\text{H}$  NMR spectrum (400 MHz,  $\text{DMSO-d}_6$ ),  $\delta$ , ppm: 1.34 (3H, d,  $^3J=5.4$ ,  $\text{CH}_3$ ), 1.41–1.48 (2H, m,  $\text{CH}_2$ ), 1.61–1.72 (2H, m,  $\text{CH}_2$ ), 2.04–2.21 (2H, m,  $\text{CH}_2$ ), 3.58 (3H, s,  $\text{CH}_3$ ), 5.05–5.14 (1H, m, CH), 6.93 (2H, d,  $^3J=8.1$ , H-Ar), 7.27 (1H, br.s., NH), 7.33 (2H, d,  $^3J=8.1$ , H-Ar), 7.84 (1H, br.s., NH). MS (EI),  $m/z$  ( $I_{\text{rel}}$ , %): 301  $[\text{M}]^+$  (64). Calculated  $\text{C}_{16}\text{H}_{19}\text{N}_3\text{O}_3$ : C 63.77; H 6.36; N 13.94. Found: C 63.85; H 6.49; N 14.07.

*2-Methyl-6,7-dihydro-2H-1,3-benzoxazine-4,8(3H,5H)-dione 8-[(4-iodophenyl)hydrazone] (8)*

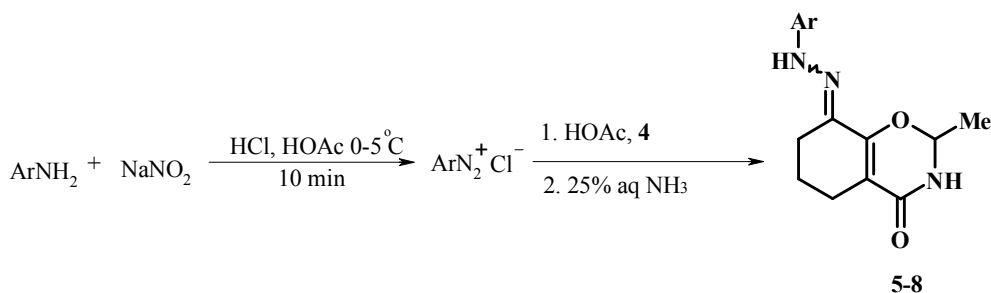
Yellowish powder, mp: 124–126°C, yield 78%.

$^1\text{H}$  NMR spectrum (400 MHz,  $\text{DMSO-d}_6$ ),  $\delta$ , ppm: 1.34 (3H, d,  $^3J=5.4$ ,  $\text{CH}_3$ ), 1.42–1.48 (2H, m,  $\text{CH}_2$ ), 1.60–1.72 (2H, m,  $\text{CH}_2$ ), 2.04–2.21 (2H, m,  $\text{CH}_2$ ), 5.05–5.12 (1H, m, CH), 7.24 (1H, br.s., NH), 7.51 (2H, d,  $^3J=8.3$ , H-Ar), 7.71 (2H, d,  $^3J=8.3$ , H-Ar), 7.93 (1H, br.s., NH). MS (EI),  $m/z$  ( $I_{\text{rel}}$ , %): 397  $[\text{M}]^+$  (82). Calculated  $\text{C}_{15}\text{H}_{16}\text{IN}_3\text{O}_2$ : C 45.36; H 4.06; N 10.58. Found: C 45.51; H 4.18; N 10.70.

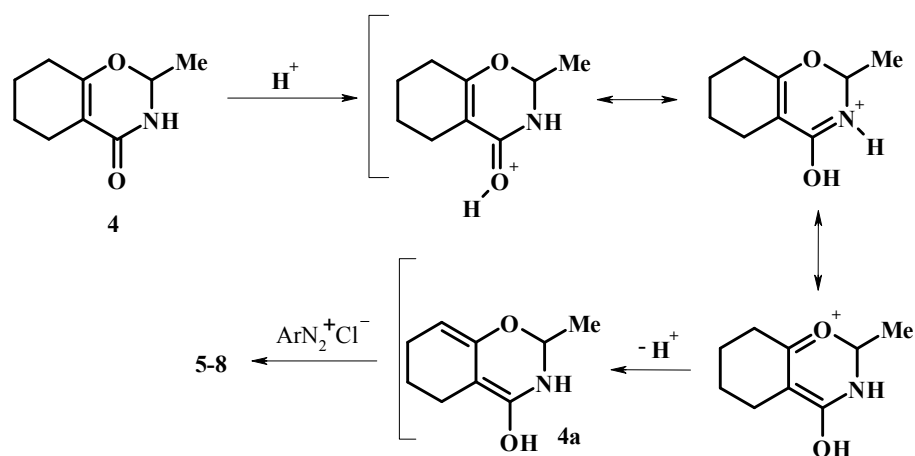
**Results and discussion**

The reaction of 2-methyl-2,3,5,6,7,8-hexahydro-4H-1,3-benzoxazin-4-one 4 with various diazonium salts yielded previously unknown arylhydrazones with high yields (Scheme 2). The reaction proceeds at the non-activated position C-8 in an acid medium through the intermediate formation of azo compounds. The structure of the reaction products was established based on the  $^1\text{H}$  NMR and mass spectra.

This reaction becomes possible probably due to the protonation of one of the active positions of



Scheme 2. 5 Ar – 4-nitrobenzene (86%), 6 Ar – 2-nitro-4-methylbenzene (83%), 7 Ar – 4-methoxybenzene (75%), 8 Ar – 4-iodobenzene (78%)



Scheme 3

compound 4 (Scheme 3). Protonation can occur at the oxygen atom of the amide group or at the carbon atom C-4' (endocyclic vinyl ether). When this intermediate is deprotonated, an isomeric vinyl ester is formed with the participation of the C-8 atom, which activates this position for attack by an electrophile. The protonation of the oxygen atom is preferable, since a thermodynamically more stable intermediate with charge delocalization is formed.

Despite the fact that the putative intermediate 4a is less stable than compound 4, it is still likely to be formed, albeit in small amounts, since the reaction with diazonium salts proceeds rapidly at the C-8 position, which can be explained by the activating effect of three heteroatoms in the intermediate 4a. The reaction proceeds with both activated and non-activated diazonium salts.

### Conclusions

Thus, it has been shown that 2-methyl-2,3,5,6,7,8-hexahydro-4H-1,3-benzoxazin-4-one reacts with activated and non-activated diazonium salts at the C-8 position to form the corresponding arylhydrazones. The reaction proceeds due to the protonation of 1,3-benzoxazin-4-one, which leads

to the activation of the C-8 position in its structure. The resulting arylhydrazones can be used as building blocks in organic synthesis and as ligands for binding metal ions.

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## РЕАКЦІЯ 2-МЕТИЛ-2,3,5,6,7,8-ГЕКСАГІДРО-4Н-1,3-БЕНЗОКСАЗИН-4-ОНУ З СОЛЯМИ ДІАЗОНІЮ

*С.А. Варениченко, О.К. Фарат, К.В. Янова, В.І. Марков*

Знайдено, що при взаємодії 2-метил-2,3,5,6,7,8-гексагідро-4Н-1,3-бензоксазин-4-ону з різними активованими та неактивованими солями діazonію в соляній та оцтовій кислотах утворюються раніше невідомі арилгідрозони з високими виходами незалежно від структури діазокомпоненти. Реакція азосполучення перебігає за неактивним  $sp^3$ -гібридним атомом С-8 за рахунок активуючої дії кислотного середовища з утворенням 2-метил-6,7-дигідро-2Н-1,3-бензоксазин-4,8(3Н,5Н)-діон 8-арилгідрозонів. Ця реакція перебігає регіоселективно за атомом С-8 за рахунок стеричних перешкод між реагентом на прекурсором. Структури синтезованих арилгідрозонів підтверджено сучасними фізико-хімічними методами аналізу, включаючи спектроскопію ЯМР  $^1H$  та мас-спектрометрію. Винайдена реакція дозволяє в одну стадію одержати важкодоступні іншими методами арилгідрозони. Виділення продуктів реакції не становить складнощів і досягається простою фільтрацією після нейтралізації. Одержані арилгідрозони можуть бути використані як будівельні блоки в органічному синтезі та як ліганди для зв'язування іонів металів.

**Ключові слова:** 1,3-бензоксазин-4-он, соль діazonію, азосполучення, арилгідрозон, СН-активація.

## REACTION OF 2-METHYL-2,3,5,6,7,8-HEXAHYDRO-4H-1,3-BENZOXAZIN-4-ONE WITH DIAZONIUM SALTS

*S.A. Varenichenko\*, O.K. Farat, K.V. Yanova, V.I. Markov*  
Ukrainian State University of Chemical Technology, Dnipro, Ukraine

\* e-mail: svetlanavarenichenko@gmail.com

We found that the interaction of 2-methyl-2,3,5,6,7,8-hexahydro-4H-1,3-benzoxazin-4-one with various activated and non-activated diazonium salts in hydrochloric and acetic acids leads to the formation of corresponding previously unknown arylhydrazones with high yields, independent of the structure of the diazo component. The azo coupling reaction proceeds at the non-activated  $sp^3$ -hybrid C-8 atom due to the activating action of the acid medium with the formation of 2-methyl-6,7-dihydro-2H-1,3-benzoxazine-4,8(3H,5H)-dione 8-arylhydrazone. This reaction proceeds regioselectively at the C-8 atom due to steric hindrances, namely the large size of the diazonium salts. The structures of the synthesized arylhydrazones were confirmed by modern physicochemical methods of analysis including  $^1H$  NMR spectroscopy and mass spectrometry. The discovered reaction allows synthesizing arylhydrazones, which are difficult to access by other methods in one step. Isolation of the reaction products is not difficult and can be achieved by simple filtration after neutralization. The resulting arylhydrazones can be used as building blocks in organic synthesis and as ligands for binding metal ions.

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