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5-(Naphth-1-yl)- and 5-[(1,1'-Biphenyl)-4-yl]isoxazole-3-carbaldehyde Oximes: Synthesis, Complexes with Palladium, and Application in Catalysis

V. I. Potkin[a], N. A. Bumagin[b], V. M. Zelenkovskii[a], S. K. Petkevich[a], M. V. Livantsov[b], and N. E. Golantsov[b]

[a] *Institute of Physical Organic Chemistry, National Academy of Sciences of Belarus, ul. Surganova 13, Minsk, 220072 Belarus*
e-mail: potkin@ifoch.bas-net.by

[b] *Lomonosov Moscow State University, Chemical Department, Moscow, 119991 Russia*
e-mail: bna51@mail.ru

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Abstract—1-(Naphth-1-yl)- and 1-[(1,1'-biphenyl)-4-yl-3,4,4-trichloro-3-buten-1-ones were synthesized by acylation of naphthalene and biphenyl with 3,4,4-trichloro-3-butenoyl chloride. Further reaction with hydroxylamine led to 5-(naphth-1-yl)- and 5-[(1,1'-biphenyl)-4-yl]isoxazole-3-carbaldehyde oximes. The latter form complexes with palladium, which possess high catalytic activity in the Suzuki reaction in aqueous and aqueous-alcoholic media.

Keywords: isoxazoles, oximes, complexes with palladium, catalyst, cross-coupling, quantum-chemical calculations

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Palladium complexes are effective catalysts for the formation of the carbon–carbon and carbon–heteroatom bond in cross-coupling reactions and are widely used in organic synthesis for preparation of polyfunctional biaryls, arylated olefins, acetylenes, and their heterocyclic analogs [1–3]. Compounds of this type are structural fragments of modern drugs, liquid crystal compositions used for preparation of luminophores and dyes.

An important parameter determining the efficiency of cross-coupling reactions is the nature of the ligand in the palladium complex used as a catalyst. Taking into account modern requirements, the trend to use alternative types of ligands instead of toxic, readily oxidized by air oxygen, and expensive conventional triorganylphosphines can be easily understood. As such ligands compounds of different types were suggested, but as to the ligands of the isoxazole type, they are poorly studied. Recently, we showed that derivatives of isoxazole and isothiazole are capable to form complexes with palladium(II), which exhibited a high catalytic activity in cross-coupling reactions in aqueous media ("green chemistry") [4–6]. Encapsulation of the isoxazole and isothiazole palladium complexes into the silica matrix allowed obtaining multi-usable heterogeneous catalysts which can be reused without loss of activity after 10 recycles [7].

In continuation of the studies on elaboration of efficient catalytic systems for cross-coupling reactions [8–17], the present report concerns the design and synthesis of isoxazole ligands: oximes of 5-(naphth-1-yl)- and 5-[(1,1'-biphenyl)-4-yl]isoxazole-3-carbaldehydes **I, II** having along with the electron-acceptor azole ring the electron-donor nitrogen atom of the oxime group. According to the data of quantum-chemical calculations of ligands **I, II**, the excess electron density is localized on the oxime group whose total charge is –0.227 in (**I**) and –0.168 in (**II**), whereas heterocyclic fragments bear partial positive charge of +0.229 and +0.408, respectively (the total charge of

the naphthyl substituent is –0.002 and of the biphenyl substituent, –0.240). Calculations were performed at the HF/MIDI(3d) level of theory with full geometry optimization [18]. This level of theory allows to adequately describe the structure of palladium complexes with the ligands under consideration (*vide infra*).

It was assumed that the presence of two opposite in nature coordination centers (the oxime group and the isoxazole ring) in the ligand molecule would allow palladium stabilization in different oxidation states, avoiding the premature formation of Pd black and deactivation of the catalyst in the course of the catalytic cycle. Besides, we believe that the presence of naphthyl and biphenyl substituents in the ligand molecules should promote more strong noncovalent bonding of the 1,2-azole palladium complexes with the surface of the support upon heterogenization due to π-π stacking.

As starting compounds for the synthesis of naphthyl- and biphenyl-substituted isoxazoles 1-(naphth-1-yl)-3,4,4-trichloro-3-buten-1-one (**III**) and 1-[(1,1'-biphenyl)-4-yl]-3,4,4-trichloro-3-buten-1-one (**IV**) have been chosen, which were synthesized by acylation of naphthalene and biphenyl with 3,4,4-trichloro-3-butenoyl chloride (**V**). The latter was prepared by successive transformations of the easily accessible dimer of trichloroethylene [19]. The acylation was carried out under the conditions of Friedel–Crafts reaction in the presence of unhydrous aluminum chloride as a catalyst. We have also adopted and optimized the protocol [20] used by us earlier for the synthesis of phenyl (4-methylphenyl, 4,5-dimethylphenyl)trichloroallyl ketones differing in that the reaction of acylation of naphthalene and biphenyl with 3,4,4-trichloro-3-enoyl chloride was performed in methylene chloride rather than in the corresponding arene because both naphthalene and biphenyl are solids. The yields of ketones **III, IV** reached 80–85%.

The synthesized naphthyl(biphenyl)trichloroallyl ketones **III, IV** underwent heterocyclization by the reaction with excess hydroxylamine to afford the corresponding 5-(naphth-1-yl)- and 5-[(1,1'-biphenyl)-4-yl]isoxazole-3-carbaldehyde oximes **I, II**. In the case of naphthyltrichloroallyl ketone **III** the reaction was carried out similar to the earlier elaborated procedure for heterocyclization of phenyl(4-methylphenyl, 4,5-dimethylphenyl)trichloroallyl ketones (reflux in methanol) [21, 22], the yield of 5-naphthylisoxazole-3-carbaldehyde oxime (**I**) was 85%. Unlike naphthyltrichloroallyl ketone **III**, heterocyclization of biphenyl ketone **IV** in methanol was non-selective and led to the formation of a mixture of products containing only a minor amount of the target 5-bi-phenylisoxazole **II**. The reaction in ethanol was found to be the reaction of choice leading to 5-biphenyl-isoxazolecarbaldehyde oxime **II** in 40% yield.

Ketones **III, IV** and oximes of 5-arylisoxazole-3-carbaldehydes **I, II** were identified by elemental analysis, IR, ^{1}H, ^{13}C NMR spectroscopy. In the IR spectra of ketones **III, IV** intense absorption bands of the carbonyl group are present at 1680 cm^{-1}. In the IR spectra of the isoxazole derivatives **I, II** the O–H vibrations of the oxime fragments appear as wide absorption bands in the range 3220–3278 cm^{-1}. The ^{1}H NMR spectra of ketones **III, IV** contain singlets of the methylene groups at δ 4.37 and 4.33 ppm, respectively, and multiplets of aromatic protons. The formation of the isoxazole heterocycle is proved by the presence of singlets of the =CH protons at δ 7.07–7.11 ppm in the ^{1}H NMR spectra of compounds **I, II**.

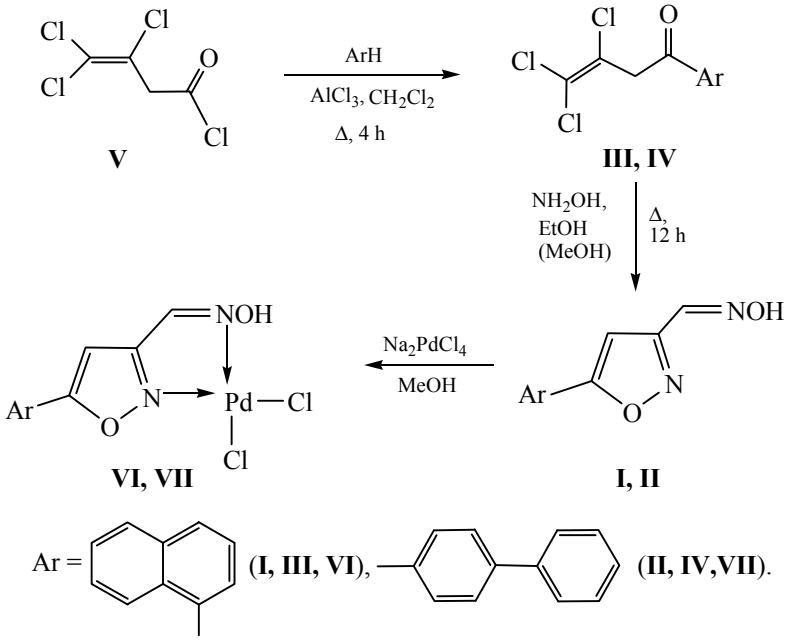
The synthesized oximes of 5-naphthyl(biphenyl)isoxazole-3-carbaldehyde **I, II** were used for preparation of complexes with palladium dichloride by the reaction with sodium tetrachloropalladate. Complexes **VI, VII** $PdCl_2$-L [L = 5-(naphth-1-yl)isoxazole-3-carbaldehyde oxime (**I**) or 5-(1,1'-biphenyl-4-yl)isoxazole-3-carbaldehyde oxime (**II**)] are formed by the reaction of equimolar amounts of sodium tetrachloropalladate and ligands **I, II** in methanol at 20°C. Specific dark-brown color of the reaction mixture caused by Na_2PdCl_4 instantly turns yellow-red upon mixing of the reagents, and a brick-red precipitate is separated. According to thin-layer chromatography, the starting isoxazole oximes **I, II** competely disappear after 5–10 min.

The synthesized palladium complexes **VI, VII** were identified by elemental analysis and IR spectroscopy, which showed the presence of characteristic vibration bands of the C=N and C=C bonds of the isoxazole heterocycles and the corresponding exocyclic fragments.

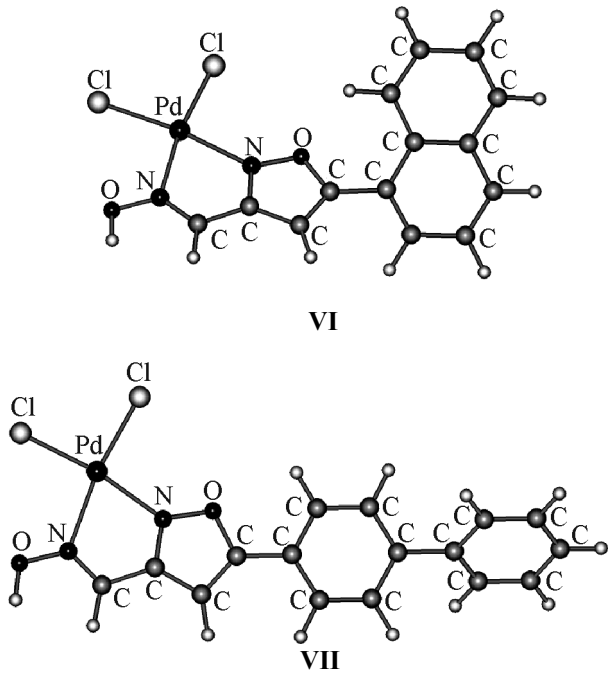
Complexes **VI, VII** are insoluble in organic solvents and water, which does not allow to register their NMR spectra and to grow single crystals for X-ray analysis. Therefore their structure was analyzed by using quantum chemical calculations of the molecular geometry and IR spectra and comparison of the calculated frequencies with the experiment (Scheme 1).

Earlier, by the example of similar palladium(II) complexes with isoxazole ligands we have shown that satisfactory results can be obtained by the use of DFT

Scheme 1.



method at the B3LYP1/MIDI(3d) level of theory [4]. However, in the case of complexes **VI, VII**, the procedure of geometry optimization cannot be completed and no minima can be found on the potential energy surface. Therefore, we have used the HF/MIDI(3d) method with full geometry optimization [18], as in the case of ligands **I, II**.



Calculated structures of complexes **VI** and **VII**.

The calculations showed that isoxazole ligands in complexes **VI, VII** coordinate to palladium atom in a bidentate cyclic type via the nitrogen atoms of the heterocycle and the exocyclic oxime group with the formation of five-membered metallacycle. In complex **VI**, the naphthyl fragment is turned by 48.1° with respect to the rest of the molecule, which is practically planar. In complex **VII**, the remote phenyl fragment is also turned by 48° with respect to the plane of the molecule, whereas in the fragment isoxazole–phenyl the deviation of the benzene ring from the plane of the molecule does not exceed 0.2°. Thus, in both cases, the effective conjugation of the aromatic fragments with the isoxazole heterocycle is violated.

The deviation of atoms from the plane in the fragment PdN_2Cl_2 does not exceed 1.7° for complex **VI** and 0.14° for complex **VII**. Structural characteristics of the heterocyclic and oxime fragments of the ligands for the two complexes are very similar and only slightly different from the corresponding parameters of the complexes of 5-(2,5-dimethylphenyl)isoxazole-3-carbaldehyde oxime with copper(II) chloride, determined by X-ray, and of the complex of 5-(4-methylphenyl)isoxazole-3-carbaldehyde with palladium(II) chloride, calculated at the B3LYP1/MIDI(3d) level of theory [4, 22]. In particular, the bond distances

Table 1. Selected bond distances *d*, Å, and bond angles ω, deg, in complexes **VI** and **VII**

Bond	*d*, Å		Angle	ω, deg	
	VI	**VII**		**VI**	**VII**
$Pd–N_{isox}$	2.126	2.123	NPdN	74.8	74.7
$Pd–N_{oxime}$	2.203	2.204	ClPdCl	93.5	93.6
Pd–Cl[a]	2.245	2.247	$PdNO_{isox}$	135.9	135.9
$C–N_{isox}$	1.286	1.287	$PdNO_{oxime}$	124.0	124.0
$C–N_{oxime}$	1.253	1.254	CNO_{isox}	108.0	107.8
$C–C_{isox}$	1.356–1.414	1.360–1.412	CNO_{oxime}	120.9	120.9
$C_{isox}–C_{oxime}$	1.476	1.475	CCN_{isox}	110.5	110.7
$C_{isox}–C_{arom}$	1.470	1.461	CON_{isox}	109.0	109.2
$C–C_{arom}$	1.356–1.432	1.378–1.393	CCN_{oxime}	116.7	116.7
$N–O_{isox}$	1.335	1.336	CCC_{isox}	102.8	102.8
$N–O_{oxime}$	1.328	1.328	CCO_{isox}	109.7	109.5

[a] Average of two values (2.444 and 2.246 Å for complex **VI**, 2.246 and 2.248 Å for complex **VII**).

in the heterocycle differ by no more than 0.05 Å. The structure of molecules **VI, VII** is shown in figure, the principal bond distances and angles are given in Table 1.

For the optimized structures of complexes **VI, VII** the main IR frequencies were calculated and assigned. The calculation of IR spectra was performed using the standard procedure of GAMESS software, with scaling factor of 0.911. The use of scaling factors in quantum chemical calculations of IR spectra was analyzed in detail in review [23]. The results of calculations were interpreted using the Facio program [24, 25]. The obtained frequencies (Tables 2, 3) are in satisfactory agreement with the experimental data, which is indicative of the validity of the calculated structures of the complexes shown in figure.

Complexes **VI, VII** were tested as catalysts of the Suzuki reaction in the form of their stable 0.005 M suspensions in methanol. Bearing in mind the goal of adaptating new catalysts to aqueous media and elaboration of the basis of ecologically safe processes we have used aqueous and aqueous-alcoholic media as solvents for the reaction. As a model Suzuki reaction, we have chosen the reaction of 4-methoxyphenylboronic acid highly prone to protodeboronation with 3-bromobenzoic acid. The experiments were carried out in 50% aqueous methanol at 20 and 75°C or in water at 100°C in the presence of 0.1 mol % of palladium complexes and potassium carbonate as a base. All reactions were performed in air, without inert atmosphere. Introducing the catalyst into the reaction mixture even at room temperature led to visible change of the original color of complexes and complete dissolution of the suspensions after 2–3 min, so that the reaction proceeded under homogeneous conditions. The results of investigation of catalytic activity of complexes **VI, VII** are presented in Table 4.

As follows from these data, complexes **VI, VII** at higher temperatures (75 or 100°C) show high catalytic activity. The reactions were completed in 1–2 min with the formation of the target 4'-methoxy[1,1'-biphenyl]-3-carboxylic acid **VIII** in 98–100% yield (runs 2, 3, 5, and 6). The formed acid **VIII** was identified by ^{1}H NMR spectroscopy, the position and multiplicity of the signals corresponded to the literature data [26].

In all experiments, no palladium black was formed till the reaction was completed. The absence of palladium black during the reaction confirms the suggestion made above that Pd(0) can be stabilized by isoxazole ligands **IV, V**. After the reaction, sizable aggregates of Pd precipitated, so, the reaction can be

Table 2. Calculated and experimental values of principal vibration frequencies in the IR spectrum of complex **VI**

Type of vibrations[a]	Frequency, cm^{-1}	
	experimental	calculated
$\nu(O–H)$	3442	3450
$\nu(C–H)_{arom}$	3053	3045
$\nu(C–H)_{isox} + \nu(C–H)_{arom}$	3016	3024
$\nu(C=C)_{arom} + \nu(C=N)_{isox}$	1623	1622
$\nu(C=N)_{isox} + \nu(C=C)_{arom}$	1600	1596
$\nu(C=N)_{oxime} + \nu(C=C)_{oxime}$	1530	1533
$\nu(C=C)_{arom} + \delta(C=C)_{isox}$	1512	1506
$\delta(C–H)_{arom}$	1470	1483
$\nu(C=C)_{arom} + \delta(C–H)_{arom} + \delta(O–H)$	1450	1442
$\delta(C–H)_{arom}$	1390	1386
$\nu(C=C)_{arom}$	1342	1315
$\delta(C–H)_{oxime} + \delta(O–H)$	1270	1268
$\nu(N–O)_{isox} + \delta(C–H)_{oxime} + \delta(C–H)_{isox}$	1126	1130
$\delta(C–H)_{isox}$	1103	1107
$\nu(C–O)_{isox} + \delta(C–H)_{arom} + \delta(O–N–C)_{isox}$	1027	1031
$\delta(C–H)_{arom}$	990	994
$\delta(C–O–N)_{isox}$	930	936
$\nu(N–O) + \delta(O–H)_{oxime}$	833	839
$\delta(C–H)_{isox} + \delta(C–H)_{arom}$	801	802
$\delta(C–H)_{isox} + \delta(C–H)_{arom}$	773	777

[a] Hereinafter the assignment is given for vibrations having largest contribution in the vibrational frequency.

Table 3. Calculated and experimental values of principal vibration frequencies in the IR spectrum of complex **VII**

Type of vibrations	Frequency, cm^{-1}	
	experimental	calculated
$\nu(O–H)$	3443	3450
$\nu(C–H)_{isox}$	3117	3109
$\nu(C–H)_{arom}$	3030	3038
$\nu(C=N)_{isox} + \nu(C=C)_{arom}$	1608	1613
$\nu(C=N)_{isox} + \nu(C=C)_{arom}$	1573	1578
$\nu(C=N)_{oxime} + \nu(C–C)_{oxime}$	1553	1543
$\delta(C–H)_{arom}$	1486	1483
$\delta(C–H)_{arom}$	1446	1454
$\delta(C–H)_{arom} + \delta(O–H)$	1409	1401
$\delta(O–H) + \delta(C–H)_{oxime}$	1287	1291
$\nu(C–O) + \delta(C–H)_{oxime} + \delta(O–H)$	1254	1246
$\delta(C–H)_{arom}$	1201	1198
$\delta(C–H)_{isox} + \delta(C–H)_{arom}$	1181	1182
$\nu(N–O)_{oxime} + \delta(C–H)_{arom}$	1150	1146
$\nu(N–O)_{isox} + \delta(C–H)_{isox} + \delta(C–H)_{oxime}$	1116	1122
$\delta(C–H)_{isox}$	1065	1057
$\nu(C–O)_{isox} + \delta(O–N–C)_{isox} + \delta(C–H)_{isox}$	1042	1039
$\delta(C–H)_{arom}$	1006	1013
$\delta(C–O–N)_{isox}$	945	953
$\delta(C–C–N)_{isox}$	843	836
$\delta(C–H)_{isox} + \delta(C–H)_{arom}$	820	816
$\delta(C–H)_{arom}$	766	762
$\delta(C–H)_{isox}$	726	730

easily monitored visually. TLC monitoring of the reaction mixtures at the moment of formation of Pd black always showed the absence of aryl halide. The solution remained practically colorless, which is an indirect indication of low concentration of colloid (nanosized) palladium in solution and in the reaction products. Palladium black is easily separated from the reaction products by filtration or centrifugation. It is noteworthy that the content of palladium in the target products, especially when they are supposed to be used as drugs, must not exceed 10 ppm.

The activity of the complexes was very high: in 50% aqueous methanol the reaction was completed at room temperature in 15–20 min with quantitative yield (runs 1 and 4). In a comparative experiment when the reaction was catalyzed with 0.1 mol % Na_2PdCl_4 the reaction mixture turned dark immediately after addition of the catalyst, and after 5 min palladium black was formed. The yield of the coupling product after 10 min was 89% (run 7). After the formation of Pd black the reaction practically stopped and after 4 h the yield increased only to 92%. At a higher temperature the product of cross-coupling was formed

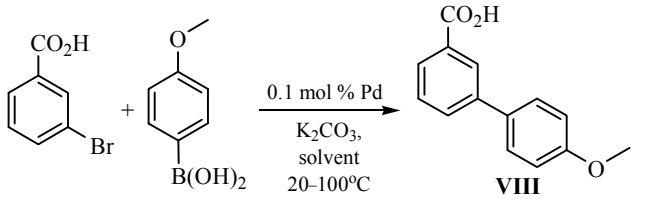
quantitatively in 5 min (run 8). Note also that in all reactions the formation of small amounts (1–2%) of the product of homocoupling of arylboronic acid, 4,4'-dimethoxy-1,1'-biphenyl, was observed. Since the reactions were not carried out in an inert atmosphere, the side product is formed, most probably, by the Pd-catalyzed oxidation of the starting arylboronic acid by air oxygen [27], but the contribution of this process is small. High yields of the product of cross-coupling observed in the model reaction with participation of arylboronic acid allowed us to avoid further optimization of the catalytic system with respect to the solvent and the base.

The results obtained on the effective catalysis of the Suzuki reaction by isoxazole palladium complexes in aqueous media were used for the synthesis of biaryls with furyl and thienyl groups, on the basis of which new drugs are now under development [28–31]. Also, polythiophene motif is often present in conducting polymers [32]. However, 2-furyl- and 2-thienylboronic acids used for their synthesis are prone to proto-deboronation, so, their use in the Suzuki reaction is extremely problematic [33].

Under the worked out conditions (0.01–0.1 mol % of Pd complex **VI** or **VII**, 2.5 equiv. of K_2CO_3, for water-insoluble aryl halides, with addition of 1 mol % of Bu_4NBr, water, 100°C), 2-furyl- and 2-thienylboronic acids react with various aryl bromides containing electron-acceptor and electron-donor groups with the formation of the corresponding heterobiaryls (**IX-XVIII**) in high yields (Scheme 2).

The activity of azole complexes **VI** and **VII** in water is so high that in the case of activated aryl bromides containing electron-withdrawing substituents, the amount of the catalyst can be reduced by an order of magnitude, to 0.01 mol %, practically without changing the yield and time of the reaction. Under these conditions, 4-bromobenzaldehyde and 5-bromothiophene-2-carbaldehyde smoothly react with 2-furyl- and 2-thienylboronic acid to afford the products of cross-coupling in 96–98% yield. For comparison, it

Table 4. Reaction of 3-bromobenzoic acid with 4-methoxyphenylboronic acid on palladium complexes **VI, VII**[a]



VIII

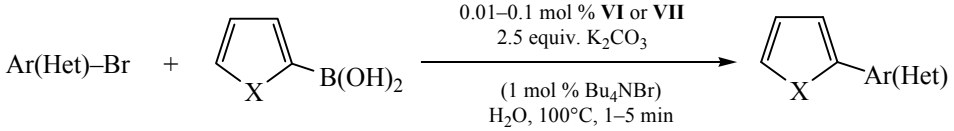
Exp. no.	Pd complex	*T*,°C [b]	Time, min	Yield of **VIII**, % [c]
1	**VI**	20	15	99
2	**VI**	75	2	100
3	**VI**	100	1	98
4	**VII**	20	20	100
5	**VII**	75	2	99
6	**VII**	100	1	100
7	Na_2PdCl_4	20	10 240	89 92
8	Na_2PdCl_4	100	5	99

[a] ArBr (0.50 mmol), Ar'B(OH)$_2$ (0.60 mmol), K_2CO_3 (1.25 mmol), H_2O + MeOH (2.5 mL each) or 5 mL H_2O. [b] 20°C and 75°C in aqueous methanol, 100°C in water. [c] Yield from ^{1}H NMR data.

should be noted that in ethanol with catalysis with 1 mol % of the phosphine complex [$Pd(OAc)_2$ + 2RuPhos] similar reactions proceed at 85°C only in an inert atmosphere and are completed in 2–24 h [RuPhos is dicyclohexyl(2',6'-diisopropylbiphen-2-yl)phosphine] [34].

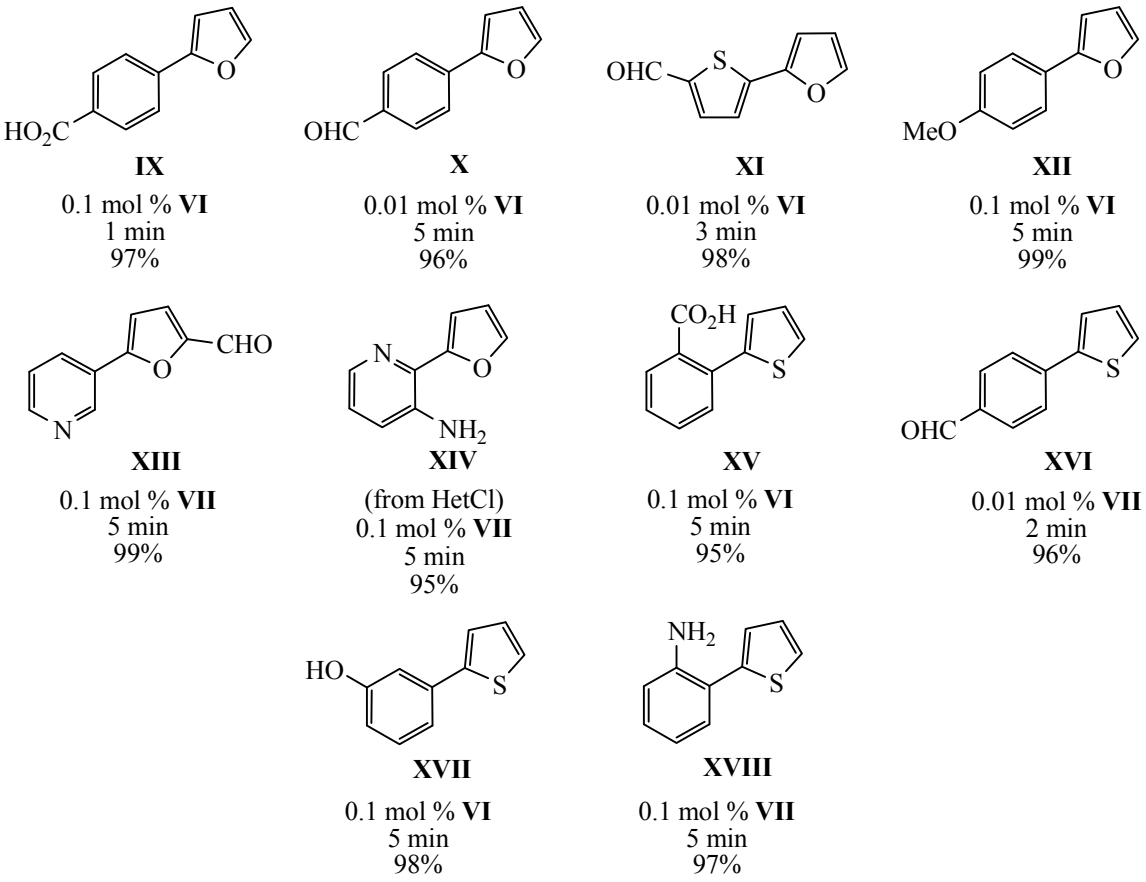
By the example of the synthesis of 2-(2-furyl)-pyridine-3-amine (**XIV**) we have shown principal possibility of using more cheap hetaryl chlorides instead of bromides. In the presence of 0.1 mol % of complex **VI** the reaction of 3-amino-2-chloropyridine with 2-furylboronic acid after 5 min gives the target product **XIV** in high yield (95%). In dry dioxane, the

Scheme 2.

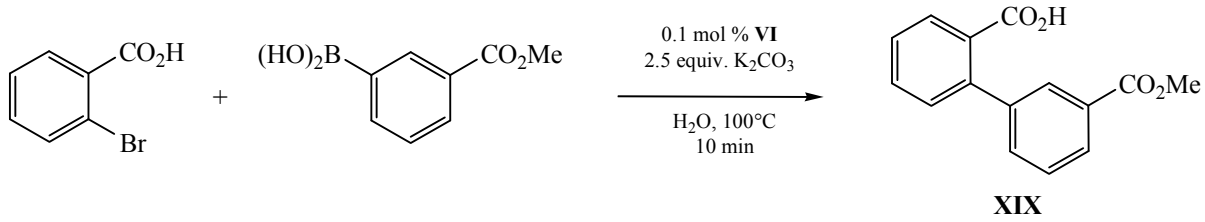


IX–XVIII

Scheme 3.



Scheme 4.



completion of the reaction requires 18 h of reflux of the reaction mixture, two-fold excess of 2-furylboronic acid, and catalysis with 3 mol % of $Pd[P(t\text{-}Bu)_3]_2$, the yield being 88% [35] (Scheme 3).

A high potential of the developed catalytic system for the synthesis of polyfunctional compounds is also proved by the preparation of 3'-(methoxycarbonyl)-biphenyl-2-carboxylic acid (**XIX**) containing the carboxyl and ester groups in one molecule, in preparative yield (97%) (Scheme 4).

Note that all of the aforementioned reactions were performed in air without an inert atmosphere. For the catalyst concentrations from 0.01 to 0.1 mol % in neither case in the cross-coupling reaction, as well as in the model reaction, palladium black was formed, and the reaction mixtures remained practically colorless until completion of the reaction. At the moment of formation of aggregates of palladium black (0.8–1.0 μm), according to TLC data, aryl(hetaryl) halide was lacking in the reaction mixture.

Therefore, it was shown on a large number of examples that oxime-isoxazole palladium complexes are stable and efficient catalysts of the Suzuki reaction in aqueous media with participation of hetarylboronic acids (TON to 9800, TOF to 288000 h^{-1}). Under the developed conditions the reactions proceed with

practically quantitative yields, which allows to significantly simplify the process of isolation of target compounds.

EXPERIMENTAL

IR spectra were taken on a Fourier spectrometer Protege-460 Nikolet in KBr. ^{1}H and ^{13}C NMR spectra were registered on a Bruker Avance-500 spectrometer in $CDCl_3$ (ketones **I, II**) and in $(CD_3)_2CO$ (isoxazoles **IV, V**). Chemical shifts are referred to the residual signals of the solvent [in $CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.2 ppm, $(CD_3)_2CO$: δ_H = 2.05 ppm, δ_C = 30.2 ppm, $(CD_3)_2SO$: δ_H = 2.50 ppm, δ_C = 40.1 ppm].

The residual content of palladium in the target products was determined by atomic absorption spectroscopy on a MGA-915 spectrometer. Melting points were measured on a Koeffler bench. TLC was performed on Silufol UV-254 plates, eluent hexane–Et_2O, 2 : 1. Commercial reagents and solvents (Aldrich, Merck) were used without further purification.

General procedure for the synthesis of α-naphthyl(*p-diphenyl*)trichloroallyl ketones (III, IV). To the solution of 2.26 g (10.9 mmol) of 3,4,4-trichloro-3-butenoyl chloride **V** in 30 mL of dry methylene chloride at 10–12°C 1.46 g (10.9 mmol) of dry $AlCl_3$ was added and the mixture was stirred for 20 min. After that, the solution of 13.06 mmol of naphthalene (or biphenyl) in 5 mL of methylene chloride was added and refluxed until evolution of HCl ceased (4 h for naphthalene and 2 h for biphenyl). After completion of the reaction, the reaction mixture was poured onto ice, organic layer was separated, washed with water, with dilute solution of potassium carbonate, water, and dried over calcium chloride. The solvent was removed in a vacuum, solid residue was crystallized from ethanol.

1-(Naphth-1-yl)-3,4,4-trichloro-3-buten-1-one (III). Yield 80%, mp 97–98°C. IR spectrum, cm^{-1}: 3064, 3067, 3046, 2962, 2923, 2854 (CH), 1681 (C=O), 1610, 1580, 1557, 1507 (C=C), 1436 (CH), 1413, 1303, 1232, 1204, 1175, 1090, 1079 (C–C, C–O), 922, 912, 805 (C–Cl). ^{1}H NMR spectrum, ($CDCl_3$), δ, ppm: 4.37 s (2H, CH_2), 7.52 t (1H$_{arom}$, ^3J 7.7 Hz), 7.56 t (1H$_{arom}$, ^3J 7.4 Hz), 7.63 t (1H$_{arom}$, ^3J 7.7 Hz), 7.89 t (2H$_{arom}$, ^3J 7.4 Hz), 8.04 d (1H$_{arom}$, ^3J 8.2 Hz), 8.69 d (1H$_{arom}$, ^3J 8.2 Hz). ^{13}C NMR spectrum, ($CDCl_3$), δ, ppm: 49.16 (1C, CH_2), 124.38, 125.78, 126.93, 128.14, 128.59, 128.67, 133.83 (7C, 7CH$_{arom}$), 121.47, 125.98, 126.14, 130.37, 134.15 (5C$_{quart}$), 196.11 (1C, C=O). Found, %: C 56.33; H 2.97; Cl 35.66. $C_{14}H_9Cl_3O$. Calculated, %: C 56.13; H 3.03; Cl 35.50.

1-[(1,1'-Biphenyl)-4-yl]-3,4,4-trichloro-3-buten-1-one (IV). Yield 85%, mp 87–89°C. IR spectrum, cm^{-1}: 3054, 3031, 2958, 2921, 2850 (CH), 1680 (C=O), 1602, 1582, 1559, 1510, 1473 (C=C), 1450 (CH), 1406, 1327, 1309, 1221, 1190, 1110, 1073, 1026 (C–C, C–O), 994, 920, 841 (C–Cl). ^{1}H NMR spectrum, ($CDCl_3$), δ, ppm: 4.33 s (2H, CH_2), 7.43 t (1H$_{arom}$, ^3J 7.5 Hz), 7.50 t (2H$_{arom}$, ^3J 7.5 Hz), 7.64 d (2H$_{arom}$, ^3J 7.5 Hz), 7.72 d (2H$_{arom}$, ^3J 8.3 Hz), 8.03 d (2H$_{arom}$, ^3J 8.3 Hz). ^{13}C NMR spectrum, ($CDCl_3$), δ, ppm: 46.31 (1C, CH_2), 127.39 (2C, 2CH$_{arom}$), 127.56 (2C, 2CH$_{arom}$), 128.60 (1C, 1CH$_{arom}$), 128.95 (2C, 2CH$_{arom}$), 129.16 (2C, 2CH$_{arom}$), 121.28, 125.92, 134.55, 139.63, 146.63 (5C$_{quart}$), 191.99 (1C, C=O). Found, %: C 58.88; H 3.49; Cl 32.44. $C_{16}H_{11}Cl_3O$. Calculated, %: C 59.02; H 3.41; Cl 32.66.

5-(Naphth-1-yl)isoxazole-3-carbaldehyde oxime (I). To the mixture of 59.6 mmol of hydroxylamine hydrochloride and 128.8 mmol of Et_3N in 50 mL of methanol 23.8 mmol of naphthyl trichloroallyl ketone **III** was added by portions, and the reaction mixture was refluxed for 12 h, then the reaction mixture was poured into water, acidified with HCl to pH 6, the light-yellow precipitate was filtered off, washed with water, and crystallized from $CHCl_3$. Yield 85%, mp 171–172°C. IR spectrum, cm^{-1}: 3250 (OH), 3049, 3014, 2925, 2851 (CH), 1640, 1603, 1582, 1565, 1512 (C=N, C=C), 1446, 1435 (CH), 1393, 1286, 1110, 1020, 987 (C–C, C–O). ^{1}H NMR spectrum, (acetone-d_6), δ, ppm: 7.06 s (1H, CH$_{isox}$), 7.64 m (3H$_{arom}$), 7.91 d (1H$_{arom}$, ^3J 7.4 Hz), 8.04 d (1H$_{arom}$, ^3J 7.4 Hz), 8.11 d (1H$_{arom}$, ^3J 8.2 Hz), 8.30 d (1H$_{arom}$, ^3J 8.2 Hz), 8.32 s (1H, CH=NOH). ^{13}C NMR spectrum, (acetone-d_6), δ, ppm: 101.76 (1C, CH$_{isox}$), 125.91 (1C, CH$_{arom}$), 126.53 (1C, CH$_{arom}$), 127.80 (1C, CH$_{arom}$), 128.85 (1C, CH$_{arom}$), 129.16 (1C, CH$_{arom}$), 130.00 (1C, CH$_{arom}$), 132.40 (1C, CH$_{arom}$), 140.81 (1C, CH=NOH), 128.29, 131.36, 135.13, 160.31, 171.23 (5C$_{quart}$). Found, %: C 70.49; H 4.52; N 11.71. $C_{14}H_{10}N_2O_2$. Calculated, %: C 70.58; H 4.23; N 11.76.

5-[(1,1'-Biphenyl)-4-yl]isoxazole-3-carbaldehyde oxime (II) was prepared similarly but the reaction was performed in ethanol. Yield 40%, mp 172–174°C. IR spectrum, cm^{-1}: 3221 (OH), 3055, 3025, 2923, 2853 (CH), 1633, 1614, 1599, 1581, 1553, 1523 (C=N, C=C), 1483, 1439 (CH), 1406, 1273, 1113, 1072, 1050, 1025, 994 (C–C, C–O). ^{1}H NMR spectrum,

(acetone-d_6), δ, ppm: 7.11 s (1H, CH_{isox}), 7.40 t (1H_{arom}, ^3J 7.4 Hz), 7.49 t (2H_{arom}, ^3J 7.4 Hz), 7.72 d (2H_{arom}, ^3J 7.4 Hz), 7.81 d (2H_{arom}, ^3J 8.5 Hz), 7.99 d (2H_{arom}, ^3J 8.5 Hz), 8.26 s (1H, CH=NOH), 11.24 br.s (1H, OH). ^{13}C NMR spectrum, (acetone-d_6), δ, ppm: 97.86 (1C, CH_{isox}), 127.53 (2C, 2CH_{arom}), 128.08 (2C, 2CH_{arom}), 128.72 (2C, 2CH_{arom}), 129.21 (1C, 1CH_{arom}), 130.20 (2C, 2CH_{arom}), 127.12, 127.49, 144.07, 160.58, 170.82 (5C_{quart}), 140.87 (1C, CH=NOH). Found, %: C 73.04; H 4.69; N 10.55. $C_{16}H_{12}N_2O_2$. Calculated, %: C 72.72; H 4.58; N 10.60.

General procedure for preparation of complexes VI, VII. To the solution of 0.2 mmol of the corresponding ligand in 10 mL of methanol at 20°C 10 mL (0.2 mmol) of 0.02 M solution of Na_2PdCl_4 in methanol was added dropwise while stirring. Upon mixing, dark-brown color of the solution of Na_2PdCl_4 instantly turned orange, and stable fine-crystalline suspension of the complex was formed. The mixture was stirred for 10 min, the solvent was removed on a rotary evaporator, solid product was washed with water (3 × 2 mL), and dried in a vacuum.

Complex VI. Yield 96%. Found, %: C 40.68; H 2.34; Cl 17.29; N 6.82; Pd 25.36 $C_{14}H_{10}Cl_2N_2O_2Pd$. Calculated, %: C 40.46; H 2.43; Cl 17.06; N 6.74; O 7.70; Pd 25.61

Complex VII. Yield 97%. Found, %: C 43.73; H 2.79; Cl 16.27; N 6.41; Pd 248.19 $C_{16}H_{12}Cl_2N_2O_2Pd$. Calculated, %: C 43.52; H 2.74; Cl 16.06; N 6.34; Pd 24.10.

Suzuki reaction catalyzed by isoxazole palladium complexes VI and VII *(general procedure).* To the mixture of 1.2 mmol of hetarylboronic acid, 1.0 mmol of aryl(hetaryl) bromide, 3.2 mg (0.01 mmol) Bu_4NBr (for water-insoluble aryl halides), and 0.35 g (2.5 mmol) of K_2CO_3 in 5 mL H_2O preheated to 80°C, 0.1 mL of suspension of complexes **VI** or **VII** (0.01–0.1 mol % Pd) in methanol (0.001–0.01 M) was added. The reaction mixture was placed in a silicone bath preheated to 150°C and was refluxed with vigorous stirring to complete conversion (amount of catalyst, reaction time and yields of the products are given in the schemes of reactions). The reaction was monitored by TLC (eluent hexane–Et_2O, 3 : 1). In the case of activated aryl bromides the reaction was very exothermic, so that in scaled syntheses an effective condenser must be used.

When the products of the reaction were aryl (hetaryl)benzoic acids, to obtain an analytically pure sample the reaction mixture was diluted with water, heated, filtered to remove small amounts (~0.01–0.1 mol %) of palladium black, 10–15 % v/v of alcohol was added, the mixture was heated to ~50°C and slowly acidified with 5% HCl to pH 2–3 at stirring. As a result, easily filtered precipitates were formed, and analytically pure samples were obtained without using chromatographic methods. In the case of water-insoluble heterobiaryls, the reaction mixture was diluted with saturated solution of NaCl, extracted with Et_2O or EtOAc, the extract was dried over Na_2SO_4 and filtered through small layer of silica gel. The solvent was removed on a rotary evaporator, the residue, as a rule, had purity of no less than 99%. Analytically pure samples were obtained by crystallization of heterobiaryls from minimal amount of aqueous alcohol (10–20% H_2O) or by transformation of amines into hydrochlorides. The characteristics of the synthesized compounds are presented below.

4-(2-Furyl)benzoic acid (IX). White crystals, mp 231–232°C (mp 230–232°C [36]). ^{1}H NMR spectrum (DMSO-d_6–$CDCl_3$, 1 : 3), δ, ppm: 6.65 d.d (1H_{furan}, ^3J 3.4 Hz, ^3J 1.8 Hz), 7.15 d (1H_{furan}, ^3J 3.4 Hz), 7.81 m (2H_{arom}, 1H_{furan}), 7.98 д (2H_{arom}, ^3J 8.5 Hz), 12.90 br.s (1H, COOH). ^{13}C NMR spectrum (DMSO-d_6–$CDCl_3$, 1 : 3), δ, ppm: 104.8 (1CH_{furan}), 108.9 (1CH_{furan}), 128.4 (2CH_{arom}), 130.2 (2CH_{arom}), 141.8 (1CH_{furan}), 125.3, 133.3, 154.6 (3C_{quart}), 171.1 (1C, COOH).

4-(2-Furyl)benzaldehyde (X). Light-yellow crystals, mp 43–44°C (mp 42–44°C [37]). IR spectrum, cm^{-1}: 3018, 2917, 2849, 1696, 1608, 1565, 1476, 1215, 1169, 1012. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.52 d.d (1H_{furan}, ^3J 3.3 Hz, ^3J 2.0 Hz), 6.83 d (1H_{furan}, ^3J 3.3 Hz), 7.54 d (1H_{furan}, ^3J 2.0 Hz), 7.79 d.d (2H_{arom}, ^3J 8.0 Hz, ^4J 2.5 Hz), 7.88 d.d (2H_{arom}, ^3J 8.0 Hz, ^4J 2.0 Hz), 9.99 s (1H, CHO). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 108.1 (1CH_{furan}), 112.2 (1CH_{furan}), 123.8 (2CH_{arom}), 130.3 (2CH_{arom}), 143.6 (1CH_{furan}), 134.8, 136.0, 152.5 (3C_{quart}), 191.5 (CHO).

5-(2-Furyl)thiophene-2-carbaldehyde (XI). Light-orange powder, mp 39–40°C (mp 38°C [38]). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.49 d.d (1H_{furan}, ^3J 3.4 Hz, ^3J 1.9 Hz), 6.77 d (1H_{furan}, ^3J 3.4 Hz), 7.32 d (1$H_{thiophene}$, ^3J 4.0 Hz), 7.50 (1H_{furan}, ^3J 1.9 Hz), 7.70 (1$H_{thiophene}$, ^3J 4.0 Hz), 9.91 s (1H, CHO). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 108.8 (1CH_{furan}), 112.4 (1CH_{furan}), 123.0 (1$CH_{thiophene}$), 137.3 (1$CH_{thiophene}$), 143.6 (1CH_{furan}), 141.6, 142.4, 148.3 (3C_{quart}), 182.7 (CHO).

2-(2-Furyl)pyridine-3-amine (XIV) [35]. Light-yelow oil. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.52 br.s (2H, NH_2), 6.56 d.d (1H$_{furan}$, ^3J 3.4 Hz, ^3J 1.8 Hz), 6.97 d (1H$_{furan}$, ^3J 3.3 Hz), 7.02 d.d (1H$_{pyridine}$, ^3J 9.4 Hz, ^4J 1.9 Hz), 7.17 d.d (1H$_{pyridine}$, ^3J 9.4 Hz, ^3J 4.2 Hz), 7.40 d (1H$_{furan}$, ^3J 1.8 Hz), 7.91 d.d (1H$_{pyridine}$, ^3J 4.2 Hz, ^4J 1.9 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 107.8 (1CH$_{furan}$), 110.5 (1CH$_{furan}$), 122.3 (1CH$_{pyridine}$), 123.6 (1CH$_{pyridine}$), 141.9 (1CH$_{furan}$), 142.7 (1CH$_{pyridine}$); 138.5, 139.7, 151.2 (3C$_{quart}$).

2-(2-Thienyl)benzoic acid (XV). Flesh-colored crystals, mp 98°C (mp 95–97°C [39]). ^{1}H NMR spectrum (DMSO-d_6–$CDCl_3$, 1 : 3), δ, ppm: 7.08 m (2H$_{thiophene}$), 7.36 d.d (1H$_{thiophene}$, ^3J 4.9 Hz, ^3J 1.3 Hz), 7.70 m (3H$_{arom}$), 7.89 d (1H$_{arom}$, ^3J 7.6 Hz). ^{13}C NMR spectrum (DMSO-d_6–$CDCl_3$, 1 : 3), δ, ppm: 126.1. (1CH$_{thiophene}$), 126.9 (1CH$_{thiophene}$), 127.3 (1CH$_{thiophene}$), 127.9 (1CH$_{arom}$), 130.6 (1CH$_{arom}$), 131.8 (1CH$_{arom}$), 132.0 (1CH$_{arom}$), 130.2, 135.3, 141.7 (3C$_{quart}$), 171.1 (COOH).

2-(2-Thienyl)aniline (XVIII). Light-brown powder, mp 37–38°C (mp 35–37°C [40]). IR spectrum, cm^{-1}: 3451, 3373, 3069, 2992, 2924, 1615, 1488, 1452, 1304, 1204, 1158, 955, 848, 751, 703. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.96 br.s (2H, NH_2), 6.79 m (2H$_{arom}$), 7.14 m (1H$_{arom}$, 1H$_{thiophene}$), 7.19 d (1H$_{thiophene}$, ^3J 3.1 Hz), 7.28 d (1H$_{arom}$, ^3J 7.6 Hz), 7.32 d (1H$_{thiophene}$, ^3J 5.3 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 115.9 (1CH$_{arom}$), 118.5 (1CH$_{arom}$), 125.2 (1CH$_{thiophene}$), 125.8 (1CH$_{thiophene}$), 127.5 (1CH$_{thiophene}$), 129.1 (1CH$_{arom}$), 131.0 (1CH$_{arom}$), 120.0, 141.5, 144.0 (3C$_{quart}$).

2-(4-Methoxyphenyl)furan (XII) [40], **5-(3-pyridyl)furan-2-carbaldehyde (XIII)** [42], **4-(2-thienyl)benzaldehyde (XVI)** [43], **3-(2-thienyl) phenol (XVII)** [44] and **2-(3'-methoxycarbonyl) biphenyl-2-carboxylic acid (XIX)** [45] are known compounds, physicochemical characteristics of the obtained products correspond to the literature data.

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