Research Article

Palladium Complexes Catalysed Telomerisation of Arylamines with Butadiene and Their Cyclisation into Quinoline Derivatives

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Abstract

Since alkynyl-arylamines are widely used in the chemical industry as pre products, a method of catalytic synthesis of problematic substituted quinolines from aromatic amines containing octadienal substituents has been developed. For this purpose, the processes of N-2,7-octa-dienyl anilines cyclisation under the action of transition metal complexes and telomerisation of arylamines with butadiene in the presence of palladium complexes were studied. Suppose N-2,7-octa-dienyl anilines are synthesised by telomerisation of arylamines with butadiene in the presence of palladium complexes. In that case, the cyclisation process is carried out in the presence of catalytic amounts of Pd(II) complex with dimethyl sulfoxide or nitrobenzene. The conducted research made it possible to study the opportunity of obtaining in one stage aromatic amines substituted in the nucleus by the reaction of butadiene with arylamines in the presence of palladium complexes. The research proved the principal possibility of obtaining *ortho*-substituted naphthylamines from butadiene and corresponding naphthylamines in one stage. A catalytic method for the synthesis of problematic substituted quinolines in the presence of palladium complexes has been developed. It has been established that the cyclisation of N-octadienyl-arylamines into quinolines proceeds through the stage of Kleisen amino rearrangement. N-2,7-octa-dienyl anilines and their derivatives can be widely used in the paint, pharmaceutical and chemical industries. Quinoline alkenylene derivatives can be used to produce unique polymer materials, hardeners, stabilisers, extractants, sorbing agents, catalysts for the synthesis of polyurethanes, biologically active substances and their analogues. They are pre-products in synthesising alkaloids, medicines and products used in agriculture.

1. Introduction

Nitrogen-containing heterocyclic compounds are unique organic compounds due to their extreme diversity and exceptional importance for human life [1]. Some contain one nitrogen atom and quinolines and show a wide range of biological and pharmacological activity [2,3]. Quinoline derivatives protect from tumours, inflammatory processes and infections. They have antidiabetic, antifungal and antioxidant effects and have

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low toxicity. The literature also shows that the "Quinoline" fragment is present in the molecules of many compounds of natural origin [4]. The review Kadela-Tomanek *et al.* [5] summarises the latest information on the pharmacological activity of synthetic derivatives of 5,8-quinoline-dione containing different groups in positions C-6 and (or) C-7, and on the study of the activity–mode of action relationship.

Studies on the synthesis of quinolines and their derivatives have been carried out since the XIX century, attracting researchers' attention with its theoretical and practical significance [6,7]. Currently, there are a lot of works describing methods for quinolines synthesis. The main quinolines synthesis approaches are based on developing methods for synthesising the quinolines basic structure and its further functionalisation to obtain compounds exhibiting a wide range of biological and pharmacological activity.

Weyesa and Mulugeta [8] describe methods of quinoline derivatives synthesis during transition metal catalysis and ultrasonic irradiation in an ionic liquid medium without the presence of metals. It also presents methods of further quinolines functionalisation. Besides, the work studies the synthesis conditions and describes measures to reduce side effects on the environment. Farooq *et al.* [9] carried out multicomponent synthesis in one reactor, which showed promising results. They studied the biological activity of thirteen tetrahydroquinoline derivatives. The research results proved the synthesized compounds' antioxidant, antiproliferative, and anti-inflammatory effects. According to the research results, the synthesised compounds can be the amylase enzyme inhibitors.

The copper-catalysed (I) functionalisation of 8-hydroxyquinolines in the 8-OH position with carbohydrates was carried out. The cytotoxic effect of synthesized compounds on cancer cells was studied. The study of the metals complexing properties confirmed the ability of the obtained glycoconjugates to chelate copper ions, thus increasing their anti-cancer potential [10]. Khoshimov *et al.* [11] describe methods for obtaining heterocycles and the quinoline synthesis from aniline, acetaldehyde and formaldehyde in the vapour phase. The paper presents optimal catalysts and temperature parameters volumetric velocities increasing the yield of quinoline. The effect of the catalyst layer height on the yield of 2- and 4-methylquinolines and the initial reagents conversion was studied. When using the methods presented in the paper, the purity of 2- and 4-methylquinolines is 97.0–98.0%.

The paper also describes the synthesis of some new styryl-quinolines with a benzylidenimine group. Their applicability in cell staining has been spectroscopically characterised [12]. The use of quinidine and quinine as a catalyst in the presence of acid contributed to developing a new enantioselective synthesis of quinolines to isolate enantiomers in pure form. The obtained enantiomers exhibit cytoprotective activity through the HIF1 system by stabilising the HIF1A protein [13]. Monographs [14] and papers [15] cover the issues of obtaining quinoline derivatives based on metal complexes catalysis.

The literature analysis indicates that the success in the quinolines synthesis is mainly provided by the interaction of derivatives of free amines with electrophilic reagents. However, methods for the quinolines synthesis based on N-2,7-octadienyl anilines are practically not described. Alkenylarylamines are widely used in the pharmaceutical industry. Thus, the introduction of dienes as substituents into the structure of quinolines can lead to other significant changes in the quinolines chemical properties, including the production of compounds with pronounced biological activity. Thus, a catalytic method for synthesising problematic substituted quinolines from N-2,7-octa-dienyl anilines has been developed. The research purpose. The research aims at developing catalytic methods for the synthesis of problematic substituted quinolines based on N-2,7-octa-dienyl anilines. The tasks include: (a) to study the cyclisation process of N-2,7-octa-dienyl anilines under the action of transition metal complexes; (b) telomerisation of arylamines with butadiene in the presence of palladium complexes.

2. Materials and Methods

NMR spectra ^{1}H images were taken with a Tesla-480 B device at a frequency of 100 MHz according to the internal flexible MD standard. IR spectra were measured using the UR-20 device. The mass spectrum results are recorded using the MX − 1320 (70 eV) device. The elemental analysis was performed using the C-H-N-Analyzer M-1856 device. Control for the reaction and the purity of the products was carried out using a chromatograph Crom-5 (a flame ionisation detector; columns l = 1.2 m, d = 3 mm, 5% SE-30 using Chromatone N-AW). The initial N-2,7-octa-dienyl anilines 1,4-6 were obtained using a well-known technique. The physico-chemical characteristics correspond to the literary values [16].

Method of telomerisation of arylamines **1, 4-6** with butadiene in the presence of palladium complexes included 0.14 g of AlEt$_3$ were poured into a mixture of 0.1 g Pd(acac)$_2$, 0.2 g Ph$_3$P and 2 ml of butadiene in argon flow at −5° and then stirred for 20 minutes. The catalyst solution was transferred in argon flow to a steel autoclave (V = 17 cm^3). Before that, 3 g of the corresponding arylamine and the required amount of butadiene were placed into the autoclave. The autoclave was thermostated for 6 h at 100 °C. The reaction mass was then cooled, diluted with an equal volume of benzene and passed through Al$_2$O$_3$. The solvent was boiled out, and the residue was analysed by GLC (gas-liquid chromatography).

Method of cyclisation of N-2,7-octa-dienyl anilines **1,4-6** under the action of transition metal complexes included 1.5 mmol PdSl$_2$ was added to 10 ml of nitrobenzene or DMSO and stirred for 20 min in argon flow at 40–50 °C. The catalyst solution was transferred to a steel autoclave (V = 17 ml). Before that, 5.0 ml of the corresponding substrate was placed into the autoclave and thermostated for 2 h at 160 °C. The reaction mass was then cooled, dissolved in benzene and passed through a column filled with Al$_2$O$_3$. The solvent was released by evaporation and vacuum distillation.

Method of rearrangement of N-2,7-octadienyl derivatives of condensed aromatic amines into products **13-19** reported 2.0 mmol of the corresponding amine and the required amount of CF$_3$CO$_2$H in 5.0 ml of water were placed in a glass ampoule V = 12 cm^3, blown out with argon, and then were thermostated for an hour at 160 or 180 °C [17]. The reaction mass was cooled and processed according to the method described above. Unsaturated amines were isolated using column chromatography on Al$_2$O$_3$. An eluent was a mixture of hexane-tetrahydrofuran solvents in a ratio of 10:1.

Since the synthesis of alkenyl-arylamines is carried out in the presence of transition metal complexes [18,19], the transformations of N-2,7-octa-dienyl anilines and *ortho*-N-2,7-octa-dienyl anilines were also studied in the presence of transition metal complexes. Equimolar amounts of transition metal complexes are usu-

ally necessary for this. In particular, equimolar amounts of the PdCl$_2$-C$_6$H$_5$CN complex were used to obtain quinoline and indoline derivatives from alkenyl-substituted anilines [20,21]. The behaviour of aromatic amines containing N-2,7-octadienyl substituents was studied during catalysis by transition metal complexes based on Pd(II) and Rh(III) salts to develop original catalytic methods for obtaining problematic substituted quinolines.

Even though these methods of quinoline synthesis are effective, they have some limitations. Firstly, cyclization reactions do not proceed in the absence of catalysts. Secondly, they are selective only at a close temperature range. Besides, when naphthylamine derivatives are used as a reagent instead of N-2,7-octa-dienyl anilines, naphthylamine rearrangement can occur.

3. Results and Discussions

The trial experiments revealed that solutions of palladium and rhodium halides in dimethylsulfoxide (DMSO) and PhNO$_2$ catalyse in one stage the conversion of N-2,7-octadecadienal in quinoline derivatives. Besides, in contrast to the PdCl$_2$-C$_6$H$_5$CN, the reaction proceeds under the action of catalytic amounts PdCl$_2$ and RhCl$_3$. PdSl$_2$(RhCl$_3$) and DMSO or PhNO$_2$ form intermediate active salts of the composition PdCl$_2$(DMSO)$_n$, PdCl$_2$(PhNO$_2$)$_n$ or RhCl$_3$(DMSO)$_n$, RhCl$_3$(PhNO$_2$)$_n$, which are involved in the reaction of intramolecular cyclisation of N-2,7-octa-dienyl anilines. An excess of DMSO(PhNO$_2$) is necessary to maintain the catalyst in the active state. The optimal conditions for cyclization of N-2,7-octa-dienyl aniline (**1**) into quinoline with unsaturated radical **2** are given in Table 1.

The cyclisation **1** was supposed to go through the stage of Kleisen amino rearrangement with the formation of *ortho*-(1,7-octadiene-3-yl) aniline (**3**) [14]. Indeed, intermediate quinoline **3** is formed under similar conditions (Figure 1). Besides, as in the case of N-substituted aniline **1**, a high yield of quinoline *2* was obtained from ortho-(octadiene-3-yl)aniline (**3**) (Figure 2).

Table 1. Optimal conditions for the formation of products **1, 2**.

Compound number	Ratio of reagents	Reaction temperature, °C	Reaction time, h.	Product output, %
1	PdCl$_2$:DMSO (PhNO$_2$) is 1:1.25 mol	160	1–2	80
2	**1**: PdSl$_2$ is 1:0.3 mol	160	2	53

Spectral methods and elemental analysis established the structure of the obtained quinoline **2** (Table 2). The complex two-component catalyst $PdSl_2(DMSO)_n$ proved to be the second effective and active after the complex with nitrobenzene. The optimal conditions for the cyclization of N-2,7-octa-dienyl aniline (**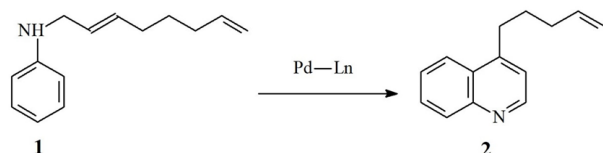1**) into quinoline **2** are given in Table 1. At lower temperatures, complete conversion **1** requires more time. Besides, a temperature increase leads to a yield decrease **2** due to side processes. Under the optimal conditions, the cyclisation products of N-2,7-octa-dienyl anilines substituted into the nucleus (**4-6**) were isolated and identified (Figure 3).

The yield of quinolines (**7-9**) depends almost not on the structure of the studied anilines and averages 49% (Figure 4). The reaction is accompanied by dehydration. A part of the resulting hydrogen is released from the reaction mass; its other part is consumed for hydrogenation of nitrobenzene into aniline, which is proved by gas-liquid chromatography. Similar rhodium complexes also catalyse the cyclisation of amine **1** into quinoline **2** but with less selectivity.

A difficulty separable mixture of isomers is formed in experiments using $RhCl_3(DMSO)_n$ and $RhCl_3(PhNO_2)_n$ complexes. The content of **2** in isomers is 23%. Therefore, under mild conditions and in the presence of $PdSl_2(DMSO)_n$ and $PdCl_2(PhNO_2)_n$ various N-2,7-octa-dienyl

Figure 1. N-2,7-octa-dienyl aniline (1) cyclised forming quinoline with unsaturated radical 2.

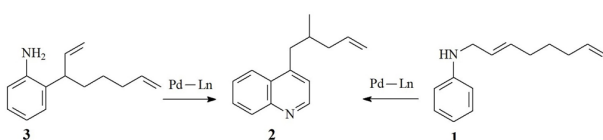
Figure 2. Quinoline 2 was obtained from ortho-(octadiene-3-yl)aniline (3).

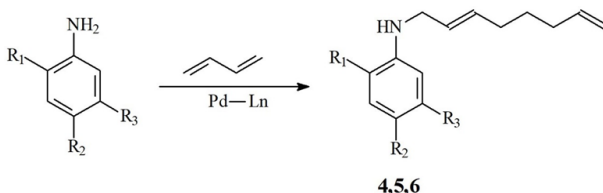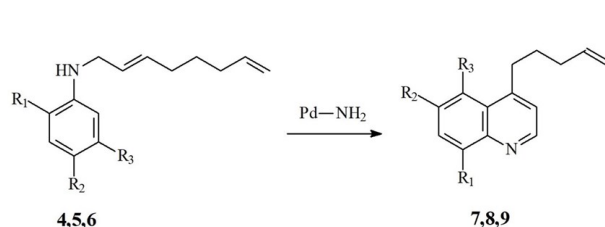Figure 3. The cyclisation products of N-2,7-octa-dienyl anilines substituted into the nucleus (4-6).
R_1 = Me, R_2 = R_3 = H (**4**); R_1 = R_2 = Me, R_3 = H (**5**); R_1 = R_3 = Me, R_2 = H (**6**)

Figure 4. The yield of quinolines (7-9) from anilines (4-6).
R_1 = Me, R_2 = R_3 = H (**4,7**); R_1 = R_2 = Me, R_3 = H (**5,8**); R_1 = R_3 = Me, R_2 = H (**6,9**)

Table 2. IR spectrum and ^1H NMR results for the obtained compound.

Compound number	Molar mass, g/mol	IR spectrum, cm^{-1}	NMR ^1H, md.
2	197	890, 920, 1000, 1605, 3075	1.45 corresponds to the methylene proton 2.85 corresponds to methylene protons at the aromatic nucleus 8.03 – allylic protons 4.25, 5.53, 7.45 - a group of olefin and aromatic protons
14	255	920, 975, 1000, 3030, 3070, 3380, 3460	1.5 corresponds to methylene protons, 1.9 to allyl protons, 3.52 to methylone protons in the aromatic nucleus, 4.83, 5.33, 7.3 correspond to the group of olefin and aromatic protons
16	251	920, 1000, 3070, 3400, 3470	1.4 corresponds to methylene protons, 1.9 allyl protons, 3.3 to the methylene proton located between the aromatic core and the vinyl group, 4.83, 5.33, 7.3 correspond to the group of olefin and aromatic protons

anilines selectively transform into the corresponding quinolines **7, 8**. The initial N-2,7-octadienyl aniline (**11**) is obtained from the corresponding arylamine and butadiene under the action of palladium-containing catalysts. Besides, *ortho*-(1,7-octadiene-3-yl)aniline (**12**) is formed as a result of rearrangement of N-2,7-octa-dienyl aniline in the presence of a catalyst (Figure 5).

The interaction between butadiene and arylamines catalysed by low-valent palladium complexes was studied for combining telomerisation and cyclisation. Naphthylamines are amines with condensed aromatic rings. They are characterised by easy Kleisen amino rearrangement and used as the initial aromatic amines. The interaction between butadiene and β-naphthylamine in the presence of transition metal complexes Pd(acac)$_2$-Ph$_3$P-AlEt$_3$, PdCI$_2$-DMSO at a temperature of 100 °C definitely leads to the production of β-naphthylamine with an octadienyl radical in the aromatic ring with a 67% yield.

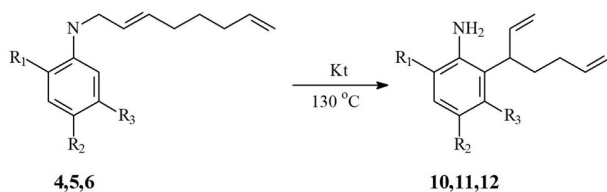
Figure 5. Ortho-(1,7-octadiene-3-yl)aniline (12) is formed as a result of rearrangement of N-2,7-octa-dienyl aniline (11) in the presence of a catalyst.
R$_1$ = Me, R$_2$ = R$_3$ = H (**4,10**); R$_1$ = R$_2$ = Me, R$_3$ = H (**5,11**); R$_1$ = R$_3$ = Me, R$_2$ = H (**6,12**)

The results of the IR spectrum prove the presence of an ethylenic bond and the NH$_2$ group (Table 2). Hydrogenation of alkenylated β-naphthylamine using palladium catalyst proceeds with the absorption of two moles of hydrogen. It leads to the formation of two isomers separated by gas-liquid chromatography in a ratio of 1:1 with a molar mass of 255 g/mol. The resulting compound is supposed to be a mixture of *ortho*-octadiene-β-naphthylamines (Figure 6). It was assumed that the N-2,7-octadienyl derivative of β-naphthylamine is formed first. After that, there is a rearrangement in the presence of palladium complexes with the formation of *ortho*-substituted products [22]. This is confirmed by the telomerisation of β-naphthylamine with butadiene under milder conditions (Table 3).

In contrast to β-naphthylamine, amination of butadiene with α-naphthylamine in the presence of a three-component Pd(acac)$_2$ catalyst-Ph$_3$P-AlEt$_3$ does not lead to the production of an aromatic amine substituted into the nucleus. Besides, N-2,7-octadienal-α-naphthylamine **17** is formed with a good but selective yield (71%). A bis-N-2,7-octadienal derivative is not formed (Figure 7). Telomerization of α-naphthylamine with butadiene in the presence of a three-component catalyst with the addition of CF$_3$CO$_2$H leads to the formation of an amino-Kleisen rearrangement product **16** along with **15** (Table 3, Figure 8).

Spectral methods confirm the structure of the rearrangement product **16** (Table 2). Analysis of nuclear magnetic-resonance spectra ^{1}H and ^{13}C showed that the rearrangement pro-

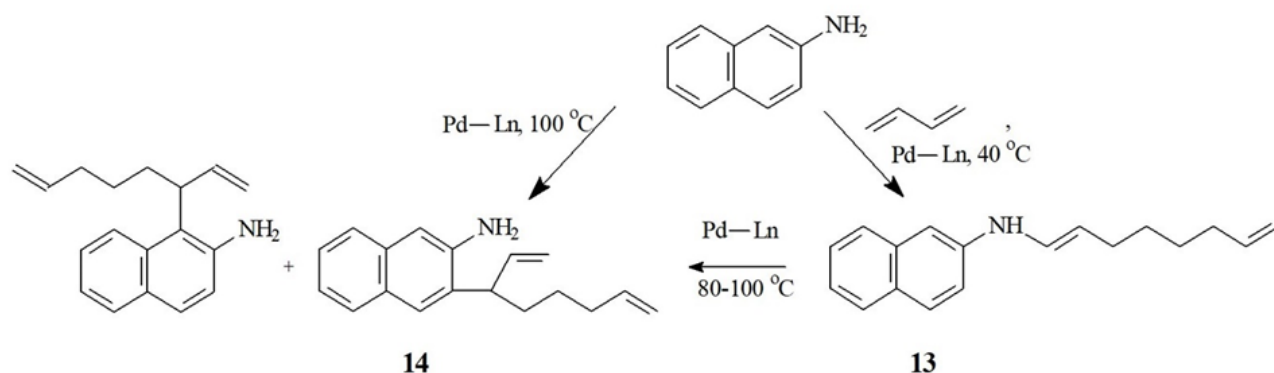Figure 6. The formation of N-2,7-octadienal-β-naphthylamine 13 and 14.

Table 3. Optimal conditions for the formation of products **1, 2**.

Compound number	Catalyst	Reaction temperature, °C	Product output, %
14	Pd-Ln	800–100	65
15	Pd(acac)$_2$-Ph$_3$P-AlEt$_3$	100	6
12	CF$_3$CO$_2$H	160	62

ceeds in the β-position of the aromatic nucleus and does not affect the adjacent aromatic ring. Rearrangement of N-2.7-octadienyl-α-naphthylamine proceeds most fully in the presence of catalytic amounts of CF_3CO_2 (Table 3). It should be noted that N-2,7-octadienyl derivatives of α-naphthylamine and β-naphthylamine in the presence of complexes $PdCl_2(DMSO)_n$, $PdCl_2(PhNO_2)_n$ are not cyclised. They are rearranged into the corresponding ortho-substituted naphthylamines. In contrast to α-naphthylamine, the interaction between 6-aminoquinoline or condensed aromatic amine with a heteroatom in the nucleus and butadiene in the presence of a catalytic system $Pd(acac)_2$-Ph_3P-$AlEt_3$-CF_3CO_2H at 100 °C does not result in a rearrangement product. In this case, there is the formation of mono- and Bis-N-2,7−octadienyl derivatives of 6-aminoquinolines **17,18** (Figure 9). Rearrangement of N-2,7-octadienyl-6-aminoquinoline occurs only at 180 °C in the presence of CF_3CO_2H (Figure 10). The most significant yield of the
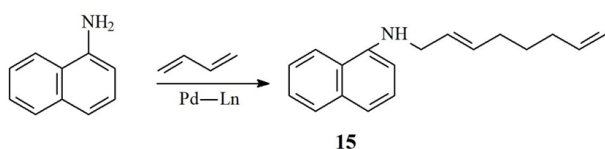

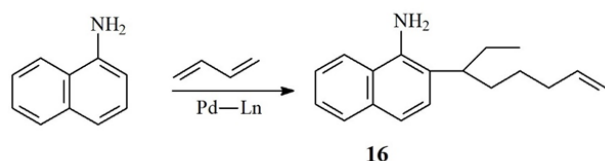Figure 7. The formation of N-2,7-octadienyl-α-naphthylamine (15).

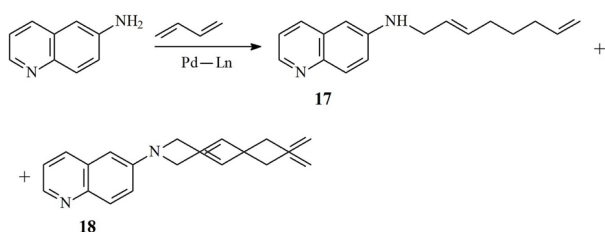Figure 8. The formation of a product resulting from the Kleisen amino rearrangement (16).

Figure 9. The formation of mono- and Bis-N-2,7−octadienyl derivatives of 6-aminoquinolines 17,18.
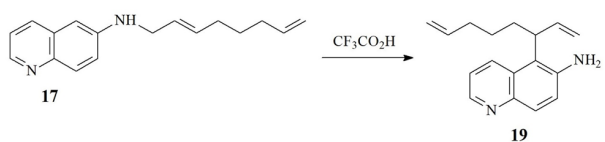

Figure 10. The rearrangement of N-2,7-octadienyl-6-aminoquinoline.

rearrangement product is observed in the presence of an equimolar amount of CF_3CO_2H (Table 4). Spectral methods confirm the structure of the rearrangement product **19**. Analysis of infra-red and nuclear magnetic-resonance spectra ^{1}H and ^{13}C showed that the rearrangement proceeds in the 5th position of the aromatic nucleus.

The experiment results prove the identification of the structures of the synthesised derivatives of N-2,7-octa-dienyl anilines and quinolines (Appendix). Therefore, the proposed method allows the cyclisation of 2,7-octa-dienyl anilines in the presence of palladium complexes selectively and in one stage.

The methods for the synthesis of quinoline derivatives described in the literature involve mainly acid-catalysed reactions of N-alkenyl anilines photochemical cyclisation of ortho-alkenylanilines under the action of metal-complex catalysts [20,23–26]. However, these reactions proceed through the formation of intermediate compounds and are not always selective.

For example, in work [8], cyclization reactions into quinoline derivatives proceed through intermediate stages and the formation of by-products like water and hydrogen gas. In another case [11], the authors managed to achieve the formation of target products with a good yield. However, these reactions proceed effectively at 400 °C and higher temperatures leading in some cases to the occurrence of side reactions - tarring, polymerization, decomposition, *etc.*

4. Conclusions

The conducted research made it possible to study the opportunity of obtaining in one stage aromatic amines substituted in the nucleus by the reaction of butadiene with arylamines in the presence of palladium complexes. The research proved the principal possibility of obtaining *ortho*-substituted naphthylamines from butadiene and corresponding naphthylamines in one stage. A catalytic method for the synthesis of problematic substituted quinolines in the presence of palladium complexes has been developed. It has been established that the cy-

Table 4. Yield **19** depending on the ratio **17**:CF_3CO_2H.

No.	Ratio 17:CF_3CO_2H	Yield19, %
1	1:0.5	16
2	1:0.75	43
3	1:1.0	78

clisation of N-2,7-octa-dienyl anilines into quinolines proceeds through the stage of Kleisen amino rearrangement. New data on the synthesis of N-2,7-octa-dienyl anilines and the possibility of their further chemical modification into problematic substituted quinolines have been obtained. The synthesis of 11 new compounds, which are not described in the literature, was carried out. Scientists studying the synthesis of heterocyclic compounds and chemical industry enterprises can find the results of the paper useful.

Acknowledgement

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Appendix (Supporting Information Data)

4-(4-pentenyl)quinoline (**2**), boiling point 120 °C (2 mm Hg, $n_d^{20} = 1.5820$. Infra-red spectrum (v, cm^{-1}): 920, 1,000, 3,075 (CH = CH 2); 835, 1,605 (C9H 5 N) Nuclear magnetic-resonance spectrum ^{1}N (δ, ppm): 1.52 m (2H, CH$_2$), 2.03 m (2H, CH$_2$ = C - C), 2.83 t (2H, Ar - CH$_2$, J = 6 Hz), 4.95 m (2H, CH$_2$ = C), 5.53 m (1H, CH = C), 7.45 m (6H, C9H$_6$ N). M$^+$ = 197 g/mol. It was found, %: C 85.20; H 7.63; N 7.00. C14 H15N. It was calculated, %: C 85.28; H 7.61; N 7.11.

8-methyl-(4-pentenyl)quinoline (**7**), boiling point 135 °C (3 mmHg, $n_d^{20} = 1.5460$. Infra-red spectrum (v, cm^{-1}): 925, 1,050, 3,090 (CH = CH 2); 845, 1,610 (C 9H 5 N). Nuclear magnetic-resonance spectrum ^{1}H (δ, ppm): 1.57 m (2H, CH$_2$), 2.05 m (2H, CH$_2$ = C – C), 2.73 s (3H, Ar – CH$_3$), 2.83 t (Ar – CH$_2$, J = 6Гц); 4.90 m (2H, CH$_2$ = C), 5.43 m (1H, CH = C), 7.25 m (5H, C $_9$H $_5$ N). M$^+$ = 211 g/mol. It was found, %: C 85.25; H 7.99; N 6.70. C15H17N. It was calculated, %: C 85.31; H8.06; N 6.63.

6,8-dimethyl-(4-pentenyl)quinoline (**8**), boiling point 152 °C (2 mm Hg, $n_d^{20} = 1.5670$. Infra-red spectrum (v, cm^{-1}): 915, 1,000, 3,080 (CH = CH 2); 845, 1,615 (FROM 9H 4 N). Nuclear magnetic-resonance spectrum ^{1}N (δ, M. D.): 1.53 m (2H, CH$_2$), 2.10 m (2H, CH$_2$ - C = C), 2.55 s (3H, Ar-CH$_3$); with 2.73 (3H, Ar-CH$_3$); 2.90 m (2H, Ar-CH$_2$, J = 6Гц); 4.95 m (1H, CH=C); 5.55 m (CH $_2$=C); 7.7 m (From $_9$H $_4$ N). M$^+$ = 225 g/mol. It was found, %: C 85.20; H 8.41; N 6.19. C16H19N. It was calculated, %: C 85.33; H8.45; N 6.22.

5,8-dimethyl-(4-pentenyl)quinoline (**9**), boiling point 150 °C (2 mm Hg, $n_d^{20} = 1.5730$. Infra-red spectrum (v, cm^{-1}): 920, 1,000, 3,070 (CH = CH 2); 840, 1,610 (C9H 4 N). Nuclear magnetic-resonance spectrum ^{1}N (δ, ppm): 1.63 m (2H, CH$_2$), 2.23 m (2H, CH$_2$ - C = C), 2.60 s (3H, Ar-CH$_3$); 2.80 s (3H, Ar-CH$_3$); 2.88 t (2H, Ar-CH$_2$, J = 6 Hz); 5.0 m (1H, CH=C); 5.60 m (CH $_2$=C); 7.8 m (C $_9$H $_4$ N). M$^+$ = 225 g/mol. It was found, %: C 85.23; H 8.40; N 6.20.

C16H19N. It was calculated, %: C 85.33; H8.45; N 6.22.

Individual compounds had the following constants:

2-(N-2,7-octadienyl)naphthylamine (**13**), n_d^{20} = 1.6020. IR spectrum (v, cm⁻¹); 765, 1,530, 1,630, 3,040 (CH in $C_{10}H_7$); 925, 1,010, 3,075 (CH=CH 2), 3,380, 3,450 (NH). NMR spectrum ^1N (δ, ppm): 1.45 m (4H, CH_2), 1.98 m (4H, CH_2 - C = C), 3.45 m (2H, $N - CH_2$); 4.87 m (4H, CH_2= C): 5.53 m (2H, CH = C); 7.30 m (6H $C_{10}H_7$); M^+ = 251 g/mol. It was found, %: C 85.87 ; H 8.30; N 5.48. C18H21N. It was calculated, %: C 86.06; H 8.37; N 5.57.

A mixture of isomers of (1,7-octadiene-3-yl)-2-naphthylamine (**14**), n_d^{20} = 1.6160. IR spectrum (v, cm⁻¹): 750, 1,525, 1,630, 3,030 (CH in $C_{10}H6$); 920, 1,000, 3,070 (CH = CH 2), 3,380, 3,460 (NH₂). NMR spectrum ^1N (δ, ppm): 1.41 m (4H, CH_2), 1.90 m (2H, $CH_2 – C = C$), 3.16 m (3H, Ar-CH); 3.6 (2H, NH₂); 4.83 m (4H, CH_2 = C): 5.33 m (2H, CH = C); 7.27 m (6H $C_{10}H_6$); M^+ = 251 g/mol. It was found, %: C 85.90; H 8.25; N 5.45. C18H21N. It is calculated, %: C 86.06; H 8.37; N 5.57.

1-(N-2,7-octadienyl)naphthylamine (**15**), n_d^{20} = 1.5990. IR spectrum (v, cm⁻¹); 775, 1,535, 1,630, 3,020 (CH in $C_{10}H_7$); 915, 1,000, 3,070 (CH=CH 2), 975, 3,020 (trans CH = CH); 3,430 (NH). NMR spectrum ^1N (δ, ppm): 1.36 m (4H, CH_2), 1.95 m (4H, $CH_2 – C = C$), 3.54 m (2H, $N – CH_2$ -- C = C); 3.98 m (1H, N – H); 4.92 m (2H, CH_2= C): 5.45 m (3H, CH = C); 7.16 – 7.57 m (7N, $C_{10}H_7$); M^+ = 251 g/mol. It was found, %: C 86.00; H 8.25; N 5.53. C18H21N. It was calculated, %: C 86.06; H 8.37; N 5.57.

2-(1,7-octadiene-3-yl)-1-naphthylamine (**16**). n_d^{20} = 1,3670. IR spectrum (v, cm⁻¹); 750, 1,520, 1,630, 3,020 (CH in $C_{10}H6$); 920, 1,000, 3,070 (CH = CH 2), 3,400, 3,475 (NH 2). NMR spectrum ^1N (δ, ppm): 1.4 m (4H, CH_2), 1.90 m (2H, $CH_2 – C = C$), 3.3 m (3H, Ar – CH – C = S); 3.9 (2H, NH₂); 4.9 m (4H, CH_2= C): 5.6 m (2H, CH = C); 7.3 m (6H $C_{10}H_6$); M^+ = 251 g/mol. It was found, %: C 85.96; H 8.30; N 5.45. C18H21N. It was calculated, %: C 86.06; H 8.37; N 5.57.

6-((N-2,7-octadienal)aminoquinoline (**17**)), n_d^{20} = 1.6095. IR spectrum (v, cm⁻¹); 920, 1,000, 3,080 (CH = CH 2), 980, 3,035 (trans CH = CH); 3,380 (NH). NMR spectrum ^1N (δ, ppm): 1.57 m (2H, CH_2), 2.06. m (4H, $CH_2 – C = C$), 3.7 m (2H, $N – CH_2 – C = C$); 4.8 m (1H, N – H);5.03 m (2H, CH_2= C): 5.63 m (3H, CH = C); 6.67-8.63 m (6H, $C_9H_6 N$); M^+ = 252 g/mol. It was found, %: C 80.52; H 7.90; N 11.03. C17H20N₂. It was calculated, %: C 80.94; H 7.95; N 11.11.

6-(bis-N - 2,7-octadienal)aminoquinoline (**18**)), n_d^{20} = 1.5800. IR spectrum (v, cm⁻¹): 920, 1,000, 3,085 (CH = CH 2), 975, 3,015 (trans CH = CH); 830, 1,515 (C $_9H_6 N$). NMR spectrum^1N (δ, ppm): 1.47 m (2H, CH_2), 2.03. m (8H, $CH_2 – C = C$), 3.87 d (4H, $N – CH_2 – C = C$, J = 2 Hz); 4,93 m (2H, CH_2= C): 5.53 m (6H, CH = C); 6.83 – 8.60 m (6H, C_9H_6N); M^+ = 360 g/mol. It was found, %: C 83.30; H 8.81; N 7.70. C25H32N₂. It was calculated, %: C 83.33; H 8.83; N 7.78.

5-(N-1,7-octadiene-3-yl)-6-aminoquinoline (**19**)), n_d^{20} = 1.5870. IR spectrum (v, cm⁻¹); 715, 1,515, 1,635, 3010 (CH in C_9H_5N); 920, 1,000, 3,085 (CH = CH 2), 840, 1,635 (C $_9H_5N$); 3,225, 3,360 (NH₂). NMR spectrum ^1N (δ, ppm): 1.25 m (4H, CH_2), 1.88 m (4H, CH_2 - C = C), 2.05 m (1H, Ar - CH_2 - C = C); 4.1 s (1H, N H_2); 5.0 m (4H, CH_2 = C): 5.95 m (3H, CH = C); 7.15 - 8.68 m (5H, C $_9H_5 N$); M^+ = 252 g/mol. It was found, %: C 80.60; H 7.85; N 11.05. C17H20N₂. It was calculated, %: C 80.94; H 7.95; N 11.11.