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INFLUENCE OF METAL-OXIDE CATALYTIC SYSTEMS ON THE PROCESS OF OBTAINING VINYL COMPOUNDS OF TETRASENE ISOLATED FROM PYROLYSIS RESIN

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Abstract. In this work, the process of obtaining mono- and divinyl compounds was studied through the step-by-step bromination of tetracen isolated from pyrolysis resin followed by catalytic vinylation. The resulting intermediate products were vinylated in the presence of vinyl boric acid after the bromination of tetracen with N-bromo succinimide. The influence of temperature, reaction time, solvent, base content, and metal-oxide catalytic systems on the process was evaluated. In the Pd-Co_3O_4/K_2CO_3 system, increasing the temperature from 40 to 70 °C and the reaction time from 2 to 8 hours increased the product yield from 37.7 to 83.8 %. At 70 °C and 8 hours, conversion was 96.0 %, selectivity was 95.9 %, and yield was 83.8 %. Among the solvents, 2-MeTHF yielded the best results, reaching 98 % in 48 hours. When comparing the metal-oxide systems at 80 °C and 6 hours, Pd-Co_3O_4 showed the highest activity, ensuring 100 % conversion, 100 % selectivity, and a 90 % GC yield. The results showed the importance of selecting the appropriate catalyst composition, solvent, base, temperature, and reaction time when producing mono- and divinyl compounds of tetracen.

Key words: pyrolysis resin, tetracene, 5-bromine tetracene, vinyl tetracene, vinyl boric acid, metal-oxide catalyst.

Annotatsiya. Ushbu ishda piroliz qatronidan ajratilgan tetratsenni bosqichma-bosqich bromlash va keyingi katalitik vinillash orqali mono- va divinil birikmalarini olish jarayoni tadqiq qilingan. Tetratsen N-bromsuksinimid bilan bromlanib, hosil bo‘lgan oraliq mahsulotlar vinilbor kislotasi ishtirokida vinillash jarayoni olib borildi. Jarayonga harorat, reaksiya vaqti, erituvchi, asos miqdori va metall-oksidli katalitik sistemalarning ta’siri tahlil qilingan. Pd-Co_3O_4/K_2CO_3 sistemasida harorat 40 dan 70 °C gacha va reaksiya vaqti 2 dan 8 soatgacha oshirilganda mahsulot unumi 37,7 dan 83,8% gacha ortdi. 70 °C va 8 soatda konversiya 96,0 %, selektivlik 95,9 % va unum 83,8 % ni tashkil qildi. Erituvchilar orasida 2-MeTHF eng yaxshi natija berib, 48 soatda mahsulot unumi 98 % ga yetdi. Metall-oksidli sistemalar 80 °C va 6 soatda qiyoslanganda Pd-Co_3O_4 eng yuqori faollikni ko‘rsatib, 100 %

konversiya, 100 % selektivlik va 90 % GC unumga erishilgan. Natijalar tetratsenning mono- va divinil birikmalarini olishda katalizator tarkibi, erituvchi, asos, harorat va reaksiya vaqtini muvofiq tanlash muhimligini ko‘rsatdi.

Kalit so‘zlar: piroliz qatroni, tetratsen, 5-bromtetratsen, viniltetratsen, vinilbor kislotasi, metall-oksid katalizator.

Аннотация. В данной работе исследован процесс получения моно- и дивинильных производных тетрацена, выделенного из пиролизной смолы, путем последовательного бромирования и последующего каталитического винилирования. Тетрацен бромировали N-бромсукцинимидом, а образовавшиеся промежуточные продукты подвергали винилированию с использованием винилбороновой кислоты. Оценено влияние температуры, продолжительности реакции, растворителя, количества основания и металл-оксидных каталитических систем на протекание процесса. В системе Pd-Co_3O_4/K_2CO_3 при повышении температуры от 40 до 70 °C и увеличении продолжительности реакции от 2 до 8 ч выход продукта возрастал с 37,7 до 83,8 %. При 70 °C и продолжительности реакции 8 ч конверсия составила 96,0%, селективность - 95,9 %, а выход продукта -83,8 %. Среди исследованных растворителей наилучший результат показал 2-MeTHF, в среде которого за 48 ч выход продукта достиг 98 %. При сравнении металл-оксидных систем в одинаковых условиях - 80 °C и 6 ч - система Pd-Co_3O_4 проявила наибольшую активность, обеспечив 100 % конверсию, 100 % селективность и 90 % выход по данным GC. Полученные результаты показали, что эффективность получения моно- и дивинильных производных тетрацена в значительной степени определяется составом каталитической системы, природой растворителя, количеством основания, температурой и продолжительностью реакции.

Ключевые слова: пиролизная смола, тетрацен, 5-бромтетрацен, винилтетрацен, винилбороновая кислота, металл-оксидный катализатор.

INTRODUCTION: The functionalization of tetracene and closely related condensed aromatic systems is one of the important directions of organic synthesis, allowing for the targeted control of the electronic and physicochemical properties of the aromatic nucleus [1]. The use of halogenated intermediates is effective in the selective functionalization of aromatic substrates [2]. Modern mechanical research has shown that the efficiency of this process depends not only on Pd, but also on the compatibility of the stages of catalytically active Pd (0) formation [3]. In studies based on kinetic isotope effects, it is substantiated that the oxidative addition of aryl bromide occurs in the presence of a poorly coordinated Pd complex [4]. The formation of intermediate particles and their subsequent transformations are also important in the formation of alkenyl fragments in the presence of palladium [5]. It has been shown that the efficiency of producing the active Pd (0) type from the Pd (II) precatalyst is directly related to the ligand, base, solvent, and temperature [6]. It has been shown that the Pd/ZnO nanocatalyst works effectively in the Suzuki-Miyaura reaction under ligand-free conditions [7-8], while the Pd system based on MIL-101 (Cr) and fortified with

N-heterocyclic carbene has shown effective catalytic activity in an aqueous medium [9]. The Pd catalyst, stabilized by N-heterocyclic carbene in magnetic nanoparticles, demonstrated high activity and the possibility of reuse [10]. Fenanthrolin fragments were placed in porous polymer nanotubes and demonstrated high catalytic efficiency [11]. It has been established that carrier functionalization in graphene oxide-based Pd nanocomposites significantly alters catalytic activity [12]. It was also found that single Pd centers stabilized by phospholimobdate are active on the surface of ZrO_2 [13], and the catalytic activity in the $PdCu/Ti_3C_2$ system can also be controlled in the presence of a carrier and a second metal [14]. Pd reinforcement in the functional hypercross-linked polymer allowed for the effective conduct of the Suzuki-Miyaura reaction while reducing metal release [15].

Thus, modern research shows that the composition of the catalyst, solvent, base, temperature, and reaction time are of decisive importance in the processes of Pd-catalytic C-C bond formation. However, the analysis of various metal-oxide catalytic systems in the process of producing valuable vinyl compounds of tetracen isolated from pyrolysis resin has not been studied. Therefore, the main attention was paid to obtaining mono- and divinyl compounds by bromination of tetracen and subsequent catalytic vinylation, as well as to determining the optimal catalytic system and reaction conditions for the process.

MATERIALS AND METHODS

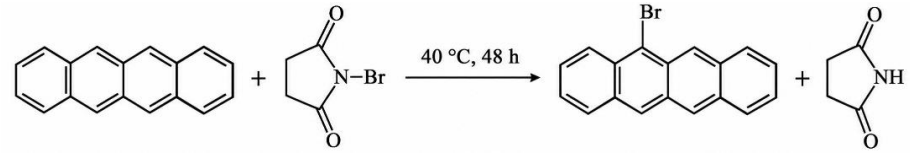
Tetracen, separated from pyrolysis resin, was initially brominated, and vinyl derivatives of tetracen were obtained from the resulting bromine compounds. For bromination, 228.3 g of tetracene and 195.8 g of N-bromsuccinimide were obtained. The amount of NBS was determined to be 10 % higher than that of tetracen. The reaction was continued at 40 °C for 48 hours. Upon completion of the process, the mixture was cooled, the organic part was separated, washed, and dried. The solvent was evaporated at low pressure, and the resulting bromine tetracene was transferred to the next vinylation stage. Vinilboric acid CH_2=CH-B $(OH)_2$ was used to introduce the vinyl group during the vinylation of bromine tetracen. The reaction was carried out in the presence of a palladium catalyst and a carbonate base. To determine the effect of temperature in the Pd-Co_3O_4/K_2CO_3 system, experiments were conducted at 40, 50, 60, and 70 °C, with reaction times of 2, 4, 6, and 8 hours. When evaluating the effect of the solvent, toluene, THF, and 2-MeTHF were compared separately. The influence of the reaction time and the amount of Cs_2CO_3 in a 2-MeTHF medium was also studied. To determine the effect of the catalyst composition, systems of palladium with various metal oxides were studied. The experiments were conducted for 6 hours. Once the reaction was complete, the mixture was cooled to room temperature. The solid catalyst was separated by filtration. The resulting product was separated using an organic solvent, washed, and dried. The solvent was then evaporated at low pressure. The reaction results were evaluated based on the amount of tetrasene reacted, the degree of formation of the desired product, and the product yield.

RESULTS AND DISCUSSION

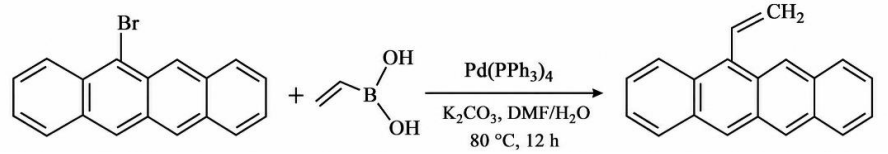
The process of obtaining vinyl compounds of tetracen was carried out in two stages. Initially, monovinyltetracen was synthesized by monobroming tetracen followed by

vinylation, and divinyltetracen was synthesized from the dibromo derivative of tetracen. Thus, the possibility of obtaining targeted mono- and divinyl compounds of tetracen by controlling the degree of bromination and subsequent vinylation stages was investigated.

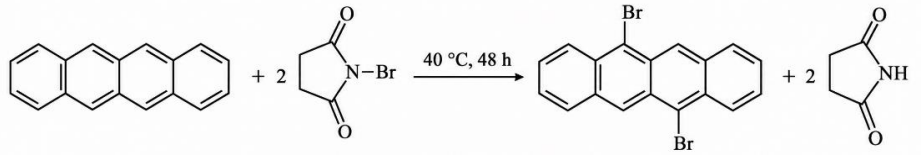
Initially, a monobromated intermediate compound was obtained to prepare tetracen for the next stage of functioning. For this purpose, tetracen was brominated with N-bromsuccinimide (NBS) to obtain monobrometetracen.



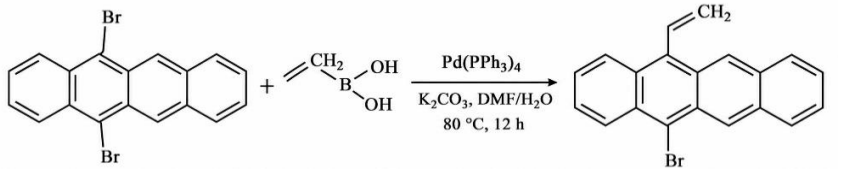
At the next stage, the resulting monobrometetracen was introduced into the vinylation reaction. Under the influence of a palladium catalyst in the presence of vinylboric acid, a C-C bond was formed in place of the C-Br bond, a vinyl group was introduced into the tetracenic ring, and monovinyltetracen was obtained.



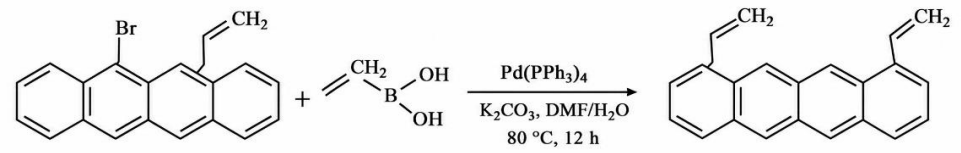
In the second direction of the synthesis, the dibromation of tetracen was carried out to obtain the divinyl derivative. At the same time, the amount of NBS was increased, and the intermediate product dibromotetracen, necessary for the subsequent two-stage vinylation, was formed.



The resulting dibromohydrate was first introduced into the vinylation reaction at the next stage. At this stage, one of the bromine atoms is replaced by a vinyl group, forming a bromine-vinyl tetrasene intermediate product that simultaneously contains bromine and vinyl groups in the molecule.



At the final stage of the synthesis, bromine-vinyl tetrachene was introduced into the vinylation reaction for the second time. Divinyltetracen was formed as a result of the replacement of the remaining bromine atom with a vinyl group. Thus, a scheme for the targeted production of monovinyl- and divinyltetracen compounds was formulated by controlling the degree of bromination of tetracen and sequential vinylation of the brominated intermediate products.



Tetracene isolated from pyrolysis resin was used as the initial polycyclic aromatic substrate, NBS as the brominating reagent, and CH_2=CH-B $(OH)_2$ as the source of the vinyl fragment. The main substrate of the Pd-catalytic vinylation step was 5-bromotetracen, which was formed as a result of monobroming. Carbonate bases K_2CO_3 and Cs_2CO_3 were used to form the reaction medium, and toluene, THF, and 2-MeTHF were used as solvents. Particular attention was paid to heterogeneous metal-oxide systems based on the Pd active center during the vinylation of tetracenes. The influence of temperature and reaction duration was studied in the Pd-Co_3O_4/K_2CO_3 system, followed by the change of the metal-oxide component at the same 80 °C and 6 hours, and the influence of the Pd-Co_3O_4, Pd-Mn_2O_4, Pd-NiO_2, Pd-CeO_2, and Pd-TiO_2 systems on the product yield was studied. ° The influence of temperature and reaction duration on the vinylation of tetracene in the Pd-Co_3O_4/K_2CO_3 system was studied at 40-70 °C and within 2-8 hours (Table 1).

Table 1

Influence of temperature and reaction duration on the vinylation of tetracene in the Pd-Co_3O_4/K_2CO_3 system

T, °C	t, h	Conversion, %	Selectivity, %	Yield, %
40	2	41.8	99.0	37.7
40	4	53.6	99.0	48.3
40	6	65.4	99.0	58.9
40	8	77.2	98.3	69.1
50	2	50.0	98.2	44.7
50	4	61.8	98.2	55.2
50	6	73.6	98.2	65.8
50	8	85.4	97.5	75.8
60	2	58.2	97.4	51.6
60	4	70.0	97.4	62.0
60	6	81.8	97.4	72.5
60	8	93.6	96.7	82.4
70	2	66.4	96.6	58.4
70	4	78.2	96.6	68.7
70	6	90.0	96.6	79.1
70	8	96.0	95.9	83.8

The table results showed that in the Pd-Co_3O_4/K_2CO_3 system, the conversion rate and product yield increase steadily as temperature and reaction duration increase. At 40 °C and 2 hours, conversion was 41.8 %, and yield was 37.7 %, while at 70 °C and 8 hours, these indicators reached 96.0 % and 83.8 %, respectively. At the same time, selectivity remained high across the entire studied range at 95.9-99.0 %. The study also analyzes the influence of solvent, reaction duration, and base amount on product yield. To select the most suitable solvent for the reaction, experiments were conducted in various solvents at 25-30 °C for 48 hours. After obtaining the best results in the 2-MeTHF medium, further experiments were continued in the same solvent, and the influence of reaction time and Cs_2CO_3 content on product yield was studied (Table 2).

Table 2.

Influence of solvent, reaction duration, and base amount on product yield

Solvent and mode	T, °C	t, h	Yield, %
Toluene	25-30	48	0
THF	25-30	48	94
2-MeTHF	25-30	48	98
2-MeTHF	25-30	36	69
2-MeTHF, Cs2CO3	25-30	48	6

At the same temperature and 48-hour duration, the target product was not detected in the toluene medium; the yield in THF was 94 %, and in 2-MeTHF, it was 98 %. Consequently, 2-MeTHF provided the highest result among the tested solvents. Reducing the time from 48 to 36 hours in 2-MeTHF reduced the yield from 98 % to 69 %. When Cs_2CO_3 was applied in an amount of 0.5 eq., the yield after 48 hours was 6 %, which reflects the inefficiency of the tested low-quantity regimen rather than the general inefficiency of Cs_2CO_3. To evaluate the effect of the metal-oxide component on catalytic activity, five Pd-based systems were compared under identical conditions at 80 °C and 6 hours. In this case, conversion, selectivity, and GC yield were evaluated as the main criteria.

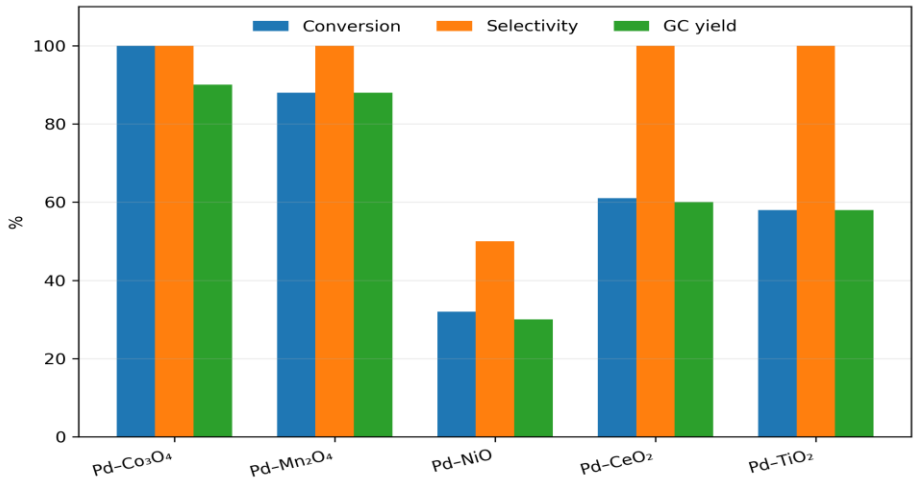


Figure 1. Efficiency of metal oxide catalysts.

The results showed that the catalyst composition significantly affects the efficiency of the reaction. Pd-Co_3O_4 exhibited the highest activity, yielding 100% conversion, 100% selectivity, and 90% GC yield. High results were also observed in the Pd-Mn_2O_4 system, where conversion and yield were 88 % and 88 %, respectively. Although selectivity was maintained at 100 % for Pd-CeO_2 and Pd-TiO_2, the yield was limited to 60 and 58 %, respectively. The lowest result was observed in the Pd-NiO system, with conversion at 32 %, selectivity at 50 %, and yield at 30 %. On this basis, Pd-Co_3O_4 was selected as the most effective system among the studied metal-oxide systems.

Conclusion

A pathway for obtaining a target vinyl derivative was formulated by brominating the tetracen isolated from the pyrolysis resin with NBS and introducing the resulting 5-bromotetracen into Pd-catalytic cross-linking in the presence of vinyl boric acid. In the Pd-Co_3O_4/K_2CO_3 system, increasing the temperature and reaction duration in the range of 40-70

°C and 2-8 hours increased conversion and product yield; in the studied range of 70 °C and 8 hours, an 83.8 % yield was recorded. Screening of the reaction medium showed the highest yield of 2-MeTHF at 48 hours with a yield of 98 %. In the independent comparison of metal-oxide systems at 80°C and 6 hours, Pd-Co_3O_4 was the most effective system with 100 % conversion, 100 % selectivity, and a 90 % GC yield. The results obtained indicate the need for a comprehensive selection of the composition of the reaction medium and catalytic system during the vinylation of tetracen.

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