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REGIOSELECTIVE HYDROALKOXYCARBONYLATION OF 1.3-BUTADIENE, 1.5-HEXADIENE, AND 1.7-OCTADIENE USING PALLADIUM-PHOSPHINE CATALYTIC SYSTEMS

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Abstract: Hydroalkoxycarbonylation of dienes offers a straightforward and atom-economic route to valuable esters derived from simple unsaturated feedstocks and carbon monoxide. In this work, we investigated the regioselective hydroalkoxycarbonylation of three representative substrates: 1.3-butadiene, 1.5-hexadiene, and 1.7-octadiene, using palladium-phosphine catalysts in ethanol at 120°C under 2.5 MPa CO. Two catalysts, [$PdCl_2(PPh_3)_2$] and [$Pd(PPh_3)_4$], were tested in combination with additional PPh_3 and p-toluenesulfonic acid. Across all three dienes, the reactions consistently favored formation of the linear ester, with yields increasing as the diene chain length grew and conjugation decreased: from 2.31% for ethyl 4-pentenoate (from 1.3-butadiene) up to 32.08% for ethyl 8-nonenoate (from 1.7-octadiene). The superior performance of $Pd(PPh_3)_4$ compared with $PdCl_2(PPh_3)_2$ highlights the importance of electron-rich Pd(0) species in stabilizing acyl intermediates and sustaining catalytic turnover. These findings not only clarify how catalyst structure and substrate features influence reactivity in diene hydroalkoxycarbonylation but also provide practical guidance for tailoring conditions to enhance linear selectivity. Such insights expand the synthetic potential of this methodology for producing C_5-C_{10} esters relevant to polymer, plasticizer, fragrance, and fine-chemical applications.

Keywords: alkadienes, hydroalkoxycarbonylation, palladium catalysts, ethyl esters, regioselectivity

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1. Introduction

Carbonylation reactions are widely applied for the direct synthesis of carboxylic acid derivatives from unsaturated compounds in the presence of carbon monoxide. Among them, hydroalkoxycarbonylation involves the addition of an alcohol and CO across a C=C bond under palladium catalysis. This transformation provides an efficient route to unsaturated esters and diesters and is valued for its high atom economy, broad substrate scope, and simple reaction setup. The resulting products are used as solvents and as intermediates for polymers, plasticizers, and fine chemicals. Recent work has also focused on improving the environmental profile of hydroalkoxycarbonylation, for example by employing formic acid as an in-situ source of CO [1].

1,3-Dienes and non-conjugated dienes are challenging substrates for hydroalkoxycarbonylation. The presence of two C=C bonds allows several competing pathways, including mono- and bis-carbonylation, 1,2- or 1,4-addition, formation of linear or branched esters, and intramolecular cyclo(oxy)carbonylation. At the same time, these systems are prone to double-bond migration and to alternative insertion sequences. High selectivity therefore requires careful choice of catalyst and reaction medium to control oxidative addition, migratory insertion, and nucleophile attack [2,3].

For 1.3-butadiene, both early and recent studies have shown that Pd-phosphine catalysts promote regioselective mono-hydroalkoxycarbonylation to give 3-alkenoate esters such as methyl 3-pentenoate via η^3-allyl-palladium intermediates. Mechanistic investigations identified crotylpalladium complexes and clarified the sequence of oxidative addition, CO insertion, and nucleophilic attack, demonstrating that ligand steric and electronic properties and the reaction medium determine which allyl fragment undergoes carbonylation. Later work revealed that solvent and ligand effects, including the use of bulky bisphosphines like dtbpx, can strongly influence selectivity in diene carbonylations. In parallel, dicarbonylation of butadiene has been explored as a direct approach to adipate diesters, compounds relevant to adipic-acid production. Recent mechanistic analyses have even suggested refinements to the classic mono-hydroalkoxycarbonylation pathway, emphasizing the role of basic additives and off-cycle equilibria. These findings highlight both the synthetic utility and the unresolved challenges of achieving full regio- and chemoselective control in the carbonylation of conjugated dienes [4–6].

In contrast, non-conjugated dienes such as 1.5-hexadiene and 1.7-octadiene present distinct patterns of reactivity and selectivity. Early investigations showed that 1.5-hexadiene can undergo regioselective cyclocarboxylation under Pd/PPh_3 catalysis in alcoholic media to give oxa- and carbocyclic products bearing ester groups. Subsequent studies revealed that variations in CO pressure and the nature of the nucleophile can shift the outcome between acyclic mono- or diesters and cyclized products, reflecting competition between intramolecular trapping of allyl-palladium intermediates and linear chain growth. Although these C_6 and C_8 dienes are valuable industrial feedstocks, systematic data on the hydroalkoxycarbonylation regioselectivity of 1.5-hexadiene and 1.7-octadiene with phosphine-ligated palladium catalysts remain limited, indicating the need for further detailed investigation [7,8].

Across both conjugated and non-conjugated dienes, the nature of the phosphine ligand and the reaction medium are key factors governing reactivity and selectivity. Bulky, strongly donating bisphosphines such as dtbpx can promote hydroalkoxycarbonylation under acid-free conditions for conjugated substrates, whereas monodentate systems based on PPh_3 typically require Brønsted or Lewis acids (for example, p-toluenesulfonic acid or $AlCl_3$) to enhance catalyst turnover and influence the site of insertion. More recent work has optimized Hemaraphos-type ligands for the dicarbonylation of butadiene, with kinetic studies correlating ligand robustness to both activity and selectivity. The choice of solvent also plays a decisive role by affecting ion pairing, nucleophile reactivity, and the solubility of carbon monoxide, and can therefore shift the chemoselectivity observed in diene carbonylations [2,9,10].

Despite recent advances, achieving reliable control over regioselectivity in diene hydroalkoxycarbonylation remains difficult. Competing allyl- and alkyl-palladium pathways, reversibility of key elementary steps, and subtle interactions among solvent, acid, and ligand can direct the reaction toward linear or branched esters, mono- and dicarbonylation, or cyclized products. Computational and experimental studies indicate that several catalytic cycles may operate simultaneously even with simple alkenes, and that mechanistic insights from mono-olefin carbonylation cannot be directly extrapolated to 1.3-butadiene. These factors underscore the value of a systematic comparison of conjugated and non-conjugated dienes, ligand frameworks, acid co-catalysts, and solvents under unified reaction conditions [6,11].

In this work we present a comparative study of the regioselective hydroalkoxycarbonylation of 1.3-butadiene, 1.5-hexadiene, and 1.7-octadiene catalyzed by well-defined palladium-phosphine complexes. By varying the ligand environment (bidentate vs monodentate), the type of Brønsted or Lewis acid additive, and the alcohol combination, we examine how these factors influence product distribution and regioselectivity. The study identifies conditions that favor linear mono-hydroalkoxycarbonylation, such as 3-alkenoate formation from 1.3-butadiene, as well as conditions that lead to dicarbonylation or intramolecular cyclocarboxylation with non-conjugated dienes. These findings provide practical guidance for controlling selectivity in diene carbonylations and demonstrate efficient access to C_5-C_{10} ester intermediates under straightforward, scalable conditions.

2. Experimental part

1.3-butadiene, 1.5-hexadiene, 1.7-octadiene, triphenylphosphine (PPh_3), p-toluenesulfonic acid (p-TsOH), $PdCl_2(PPh_3)_2$, and $Pd(PPh_3)_4$ were purchased from MERYER Chemical Technology Co. and used without further purification.

Carbon monoxide (supplied in cylinders) was employed without additional purification.

Hydroalkoxycarbonylation reactions were performed in a 100 mL stainless-steel autoclave equipped with a magnetic stirrer, CO inlet and outlet valves, pressure gauges, an electric heater, and a thermoregulator. The setup allowed for repeated purging of the reaction volume with CO and precise control of temperature and pressure. After charging the autoclave with the corresponding alkadiene, ethanol, palladium catalyst ($PdCl_2(PPh_3)_2$ or $Pd(PPh_3)_4$), additional PPh_3, and p-TsOH, the reactor was sealed and purged three times with carbon monoxide. The system was then pressurized with CO to 2.5 MPa and heated with stirring to 120°C. The reactions were maintained at this temperature and pressure for 5 h. After completion, the autoclave was cooled to room temperature and depressurized.

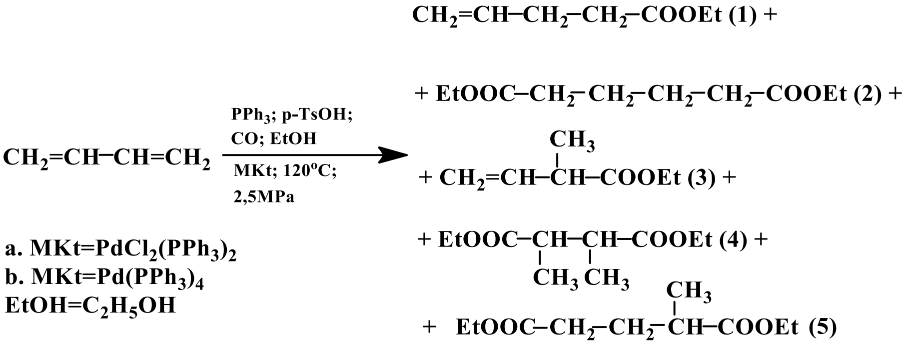
In each case of hydroalkoxycarbonylation of 1.3-butadiene, 1.5-hexadiene, and 1.7-octadiene, the autoclave was charged at room temperature with $3.31*10^{-2}$ mol of alkadiene (1.79 g of 1.3-butadiene, 2.71 g of 1.5-hexadiene and 3.64 g of 1.7-octadiene), 0.761 g ($1.65*10^{-2}$ mol) of ethanol, 0.026 g ($3.8*10^{-5}$ mol) of $PdCl_2(PPh_3)_2$ (or an equimolar amount of $Pd(PPh_3)_4$), 0.060 g ($2.28*10^{-4}$ mol) of PPh_3, and 0.058 g ($7.06*10^{-4}$ mol) of p-TsOH, corresponding to a molar ratio of [alkadiene]:[C_2H_5OH]:[Pd]:[PPh_3]:[p-TsOH] = 870:435:1:6:9.

Product compositions were analyzed on an Agilent 7890A gas chromatograph equipped with an Agilent 5975C mass-selective detector (Santa Clara, CA, USA). Helium served as the carrier gas. Injection was performed at 300°C with a split ratio of 1000:1. The oven program started at 40 °C (hold 1 min), then increased at 5 °C min^{-1} to 250°C and held for 1 min, giving a total run time of 44 min. Detection was carried out in electron-impact mode. Separation employed an HP-FFAP capillary column with a nitroterephthalic acid-polyethylene glycol stationary phase.

3. Results and discussion

The hydroalkoxycarbonylation of 1.3-butadiene, 1.5-hexadiene, and 1.7-octadiene with ethanol and CO was investigated using two palladium-based catalytic systems: [$PdCl_2(PPh_3)_2$]: PPh_3:p-TsOH and [$Pd(PPh_3)_4$]:PPh_3:p-TsOH. Across all substrates, we observed a consistent preference for linear over branched esters, with activity increasing from the conjugated diene (1.3-butadiene) to the non-conjugated dienes (1.5-hexadiene and 1.7-octadiene).

Hydroalkoxycarbonylation of 1.3-butadiene. 1.3-butadiene afforded a mixture of five possible products: two linear esters (ethyl 4-pentenoate (1) and ethyl 2-methyl-3-butenoate (2)) and three branched products (diethyl 2-methyl-pentanedioate (3), diethyl 2,3-dimethylbutanedioate (4), diethyl hexanoate (5)):



From the chromatograms obtained, it was found that the hydroalkoxycarbonylation of 1.3-butadiene in the presence of $PdCl_2(PPh_3)_2$ and $Pd(PPh_3)_4$ catalysts yielded predominantly ethyl 4-pentenoate with 1.69% and 2.31% yields, respectively. Minor amounts of ethyl 2-methyl-3-butenoate (0.03% and 0.02%), diethyl 2-methyl-pentanedioate (0.01% and 0.03%), and diethyl hexanoate (0.02% and 0.023%) were also detected, while diethyl 2.3-dimethylbutanedioate was not observed under the applied reaction conditions. (Table 1). The low absolute yields are consistent with the known lower reactivity of conjugated dienes in PPh_3/acid media and with the susceptibility of such systems to off-cycle palladium deactivation (e.g., Pd black formation) under strongly protic/acidic conditions. In contrast, tailored bisphosphine ligands and appropriate solvent choice can dramatically elevate both conversion and selectivity. For example, Yang and co-workers demonstrated that with dtbpx ligation the dicarbonylation of 1.3-butadiene to adipate diesters proceeds with up to 97% selectivity and high yield in toluene, whereas the same catalyst in methanol strongly suppresses the first carbonylation cycle, an illustrative solvent switch between mono- and bis-carbonylation regimes. Their data also show that in toluene the monocarbonylation intermediate is only detectable in trace amounts, indicating fast turnover to the diester under these conditions [5].

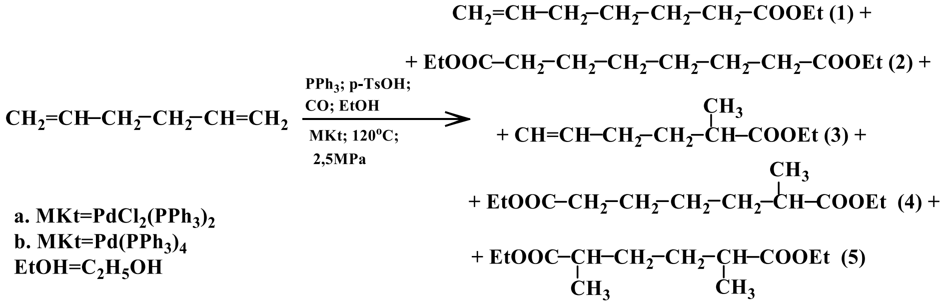
Table 1 – Product yield of the reaction of hydroalkoxycarbonylation of butadiene-1.3

Product	with $PdCl_2(PPh_3)_2$ cat. product yield, %	with $Pd(PPh_3)_4$ cat. product yield, %
ethyl 4-pentenoate	1.69	2.31
ethyl 2-methyl-3-butenoate	0.03	0.02
diethyl 2-methyl-pentanedioate	0.01	0.03
diethyl 2.3-dimethylbutanedioate	0	0
diethyl hexanoate	0.02	0.023

Beyond dtbpx, Xantphos-type ligation under base-assisted conditions has been shown to enable selective methoxycarbonylation of 1.3-butadiene to methyl 3-pentenoate, with mechanistic experiments isolating or inferring η^3-allyl and acyl-Pd intermediates and highlighting the role of external base in accelerating alcoholysis of the acyl complex. These observations align with our linear preference and suggest that in our PPh_3/p-TsOH system, slow alcoholysis and acid-promoted off-cycle pathways likely limit overall yield [12].

This interpretation fits within the broader mechanistic framework recently described for Pd-catalyzed alkoxycarbonylations. Two parallel catalytic cycles are generally proposed: a Pd-OR ("alkoxy") pathway, which favors unsaturated linear esters, and a Pd-H ("hydride") pathway, which can lead to saturated or branched products. When the reaction medium and ligand environment promote rapid CO insertion and alcoholysis from a less hindered acyl intermediate, the Pd-OR cycle predominates, accounting for the preference for linear products observed for conjugated dienes [11]. Our own combination of PPh_3, p-TsOH, and ethanol therefore represents a practical baseline that reveals the intrinsic linear bias of 1.3-butadiene hydroalkoxycarbonylation, even though it underperforms compared with state-of-the-art bisphosphine/toluene protocols. Literature precedents indicate that improvements are achievable by switching to bulkier bidentate ligands such as dtbpx or Xantphos, reducing medium acidity or adding a non-nucleophilic base, and employing less coordinating, apolar solvents each of which has been shown to enhance both catalytic activity and linear selectivity [5].

Hydroalkoxycarbonylation of 1.5-hexadiene. Under identical reaction conditions, hydroethoxycarbonylation of 1.5-hexadiene gave a distribution of five detectable products. The major species were the linear esters, with ethyl 6-heptenoate (1) dominating the mixture, accompanied by a minor amount of ethyl 2-methyl-5-hexenoate (2), in addition, three branched diesters: diethyl 2-methyl-heptanedioate (3), diethyl 2.5-dimethyl-hexaneoate (4), and a trace of diethyl octanedioate (5) were observed:



$$CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2 \xrightarrow[\text{MKt; 120°C; 2,5MPa}]{PPh_3\text{; p-TsOH; CO; EtOH}} CH_2{=}CH{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}COOEt\ (1) +$$

$$+\ EtOOC{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}COOEt\ (2) +$$

$$+\ CH{=}CH{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle CH_3}{|}}{C}H{-}COOEt\ (3) +$$

$$+\ EtOOC{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle CH_3}{|}}{C}H{-}COOEt\ (4) +$$

$$+\ EtOOC{-}\underset{\underset{\displaystyle CH_3}{|}}{C}H{-}CH_2{-}CH_2{-}\underset{\underset{\displaystyle CH_3}{|}}{C}H{-}COOEt\ (5)$$

a. MKt=$PdCl_2(PPh_3)_2$
b. MKt=$Pd(PPh_3)_4$
EtOH=C_2H_5OH

Chromatographic analysis of the hydroalkoxycarbonylation of 1.5-hexadiene in the presence of $PdCl_2(PPh_3)_2$ and $Pd(PPh_3)_4$ catalysts showed that ethyl 6-heptenoate was the major product, obtained in 8.59% and 11.06% yields, respectively. Minor products included ethyl 2-methyl-5-hexenoate (0.06% and

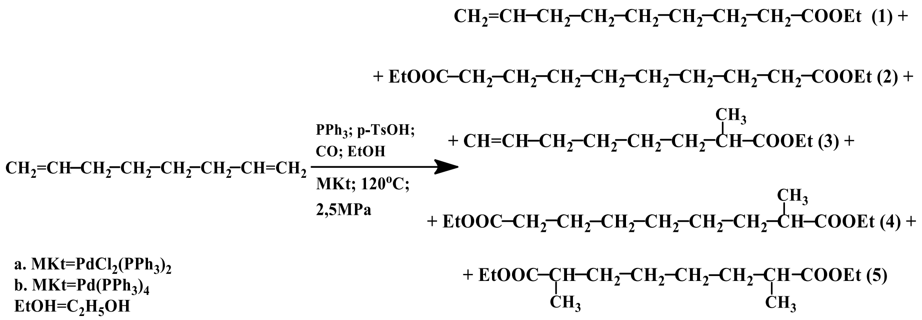
0.05%), diethyl 2-methyl-heptanedioate (0.56% and 0.84%), diethyl 2,5-dimethyl-hexanoate (0.07% and 0.09%), and diethyl octanedioate (5.9% and 5.65%). (Table 2). The superiority of the non-conjugated diene is consistent with the reduced electronic stabilization of η^3-allyl off-cycle species and more accessible terminal hydropalladation relative to 1.3-butadiene.

Earlier studies on 1.5-dienes show another layer of selectivity: under Pd catalysis these substrates can isomerize and then undergo hydrocarbonylative cyclization, giving five-membered ring products instead of simple linear esters. Whether this pathway dominates depends strongly on the ligand, the amount of acid, and the CO pressure. Milder acidity and ligands that make intramolecular trapping less favorable help keep the reaction on the acyclic, linear path, while stronger acids or conditions that favor a more cationic Pd species tend to promote cyclocarbonylation. In our experiments we mainly observed linear esters with only a small amount of diester, which is consistent with conditions that do not strongly promote the ring-forming route. Reviews of non-conjugated alkene and diene carbonylations report similar trends, noting that a higher linear-to-branched ratio is usually achieved when the phosphine ligands are bulkier and when the system contains chloride or has a lower acid load, factors that steer the key hydropalladation step toward terminal insertion and match well with the selectivity we observed [13,14].

Table 2 – Product yield of the reaction of hydroalkoxycarbonylation of hexadiene-1.5

Product	with $PdCl_2(PPh_3)_2$ cat. product yield, %	with $Pd(PPh_3)_4$ cat. product yield, %
ethyl 6-heptenoate	8.59	11.06
ethyl 2-methyl-5-hexenoate	0.06	0.05
diethyl 2-methyl-heptanedioate	0.56	0.84
diethyl 2.5-dimethyl-hexanoate	0.07	0.09
diethyl octandioate	5.9	5.65

Hydroalkoxycarbonylation of octadiene-1.7. The longest-chain substrate, 1.7-octadiene, underwent hydroethoxycarbonylation to yield a broader but still regioselective product spectrum. The reaction primarily furnished ethyl 8-nonenoate (1), with smaller amounts of ethyl 2-methyl-7-octenoate (2). Three branched dicarboxylates: diethyl 2-methyl-nonanedioate (3), diethyl 2,7-dimethyl-octanedioate (4), and a fraction of diethyl decanedioate (5) were also detected:



From the chromatograms obtained, it was observed that the hydroalkoxycarbonylation of 1.7-octadiene manifested even higher regioselectivity and yield for the linear ester, ethyl 8-nonenoate: 22.5% with $PdCl_2$ and an outstanding 32.08% with $Pd(PPh_3)_4$. Minor peaks in the chromatograms corresponded to ethyl 2-methyl-7-octenoate (7.47% and 10.07%), diethyl 2-methyl-nonanedioate (0.88% and 1.97%), diethyl 2,7-dimethyl-octanedioate (0.5% and 0.71%), and diethyl decanoate (9.48% and 8.79%) (Table 3). The larger C8 backbone minimizes internal steric congestion during linear acyl formation and facilitates alcoholysis, rationalizing the observed boost in both conversion and linear selectivity. The superior performance of $Pd(0)/PPh_3$ relative to $Pd(II)/PPh_3$ is in line with multiple studies where electron-rich, robust Pd(0) sources stabilize the acyl-Pd resting state and resist aggregation/deactivation, thereby enhancing turnover frequency. Complementary literature on diene di-methoxycarbonylation and on the assisting role of anions further supports that subtle medium and counter-ion effects modulate acyl stability and product distribution - factors that could be leveraged to further increase the mono-hydroalkoxycarbonylation channel toward linear esters [15].

Table 3 – Product yield of the reaction of hydroalkoxycarbonylation of octadiene-1,7

Product	with $PdCl_2(PPh_3)_2$ cat. product yield, %	with $Pd(PPh_3)_4$ cat. product yield, %
ethyl 8-nonenoate	22.5	32.08
ethyl 2-methyl-7-octenoate	7.47	10.07
diethyl 2-methyl nonanedioate	0.88	1.97
diethyl 2,7-dimethyl octanedioate	0.5	0.71
diethyl decanoate	9.48	8.79

4. Conclusion

This study shows that palladium-phosphine catalysts promote the hydroalkoxycarbonylation of both conjugated and non-conjugated dienes with ethanol and CO, giving a clear preference for linear esters over branched products. Among the substrates, 1.3-butadiene was the least reactive, whereas 1.5-

hexadiene and especially 1.7-octadiene underwent conversion more readily and with stronger selectivity for the linear isomer. The $Pd(PPh_3)_4$ catalyst consistently outperformed $PdCl_2(PPh_3)_2$, underscoring the value of an electron-rich Pd(0) center for stabilizing acyl intermediates and sustaining turnover. Taken together with prior reports, the data highlight three main elements that govern selectivity in these reactions: the nature of the diene (conjugated and non-conjugated), the steric and electronic properties of the ligand, and medium effects such as acidity and solvent polarity. Adjusting these factors allows higher yields and tighter control of product distribution, offering a practical route to C_5-C_{10} esters useful in materials, fragrance, and fine-chemical applications.

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Conflict of Interest: All authors declare that they have no conflict of interest.

РЕГИОСЕЛЕКТИВНОЕ ГИДРОАЛКОКСИКАРБОНИЛИРОВАНИЕ 1.3-БУТАДИЕНА, 1.5-ГЕКСАДИЕНА И 1.7-ОКТАДИЕНА С ИСПОЛЬЗОВАНИЕМ КАТАЛИТИЧЕСКИХ СИСТЕМ ПАЛЛАДИЯ-ФОСФИНА

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Резюме: Гидроалкоксикарбонилирование диенов представляет собой простой и атомарно-экономичный способ получения ценных сложных эфиров, полученных из простого ненасыщенного сырья и монооксида углерода. В этой работе мы исследовали региоселективное гидроалкоксикарбонилирование трех типичных субстратов: 1.3-бутадиена, 1.5-гексадиена и 1.7-октадиена с использованием палладий-фосфиновых катализаторов в этаноле при 120°C и давлении 2.5 МПа. Два катализатора, $[PdCl_2(PPh_3)_2]$ и $[Pd(PPh_3)_4]$, были протестированы в комбинации с дополнительным PPh_3 и п-толуолсульфоновой кислотой. Для всех трех диеновых соединений реакции неизменно благоприятствовали образованию линейного сложного эфира, причем выходы увеличивались по мере увеличения длины диеновой цепи и уменьшения конъюгации: с 2.31% для этил-4-пентеноата (из 1.3-бутадиена) до 32.08% для этил-8-ноненоата (из 1.7-октадиена). Превосходные характеристики $Pd(PPh_3)_4$ по сравнению с $PdCl_2(PPh_3)_2$ подчеркивают важность обогащенных электронами соединений Pd(0) для стабилизации ацильных промежуточных продуктов и поддержания каталитического цикла. Эти результаты не только проясняют, как структура катализатора и особенности субстрата влияют на реакционную способность при гидроалкоксикарбонилировании диена, но и дают практическое руководство по подбору условий для повышения линейной селективности. Такие выводы расширяют синтетический потенциал этой методики для получения сложных эфиров C_5-C_{10}, востребованных при производстве полимеров, пластификаторов, ароматических веществ и тонкой органической химии.

Ключевые слова: алкадиены, гидроалкоксикарбонилирование, палладиевые катализаторы, этиловые эфиры, региоселективность

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ПАЛЛАДИЙ-ФОСФИННІҢ КАТАЛИТИКАЛЫҚ ЖҮЙЕЛЕРІН ПАЙДАЛАНА ОТЫРЫП, 1.3-БУТАДИЕНДІ, 1.5-ГЕКСАДИЕНДІ ЖӘНЕ 1.7-ОКТАДИЕНДІ РЕГИОСЕЛЕКТИВТІ ГИДРОАЛКОКСИКАРБОНИЛДЕУ

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Түйіндеме: Диендердің гидроалкоксикарбонилденуі қарапайым қанықпаған шикізаттар мен көміртек оксидінен бағалы эфирлерді алудың тікелей және атом-экономикалық тәсілін ұсынады. Бұл жұмыста 1.3-бутадиен, 1.5-гексадиен және 1.7-октадиен сияқты үш үлгілік қосылыстың этанолда 120°C температурада және 2.5 МПа CO қысымында палладий-фосфинді катализаторлар қатысында региоселективті гидроалкоксикарбонилденуі зерттелді. Катализаторлар ретінде $[PdCl_2(PPh_3)_2]$ және $[Pd(PPh_3)_4]$ қосымша PPh_3 және п-толуолсульфон қышқылымен бірге қолданылды. Барлық диендер үшін реакциялар негізінен сызықты эфирлердің түзілуімен жүрді, ал шығымдар тізбектің ұзындығына қарай артып, қос байланыстың конъюгациясы азайған сайын жоғарылады: 1.3-бутадиеннен алынған этил-4-пентеноат үшін 2.31%-дан бастап, 1.7-октадиеннен алынған этил-8-ноненат үшін 32.08%-ға дейін жетті. $PdCl_2(PPh_3)_2$ -мен салыстырғанда $Pd(PPh_3)_4$ жүйесінің жоғары белсенділігі Pd(0)-дің электронға бай түрлерінің ацил аралық қосылыстарды тұрақтандырудағы және каталитикалық циклді қолдаудағы маңызын көрсетті. Бұл нәтижелер катализатор құрылымының және субстрат ерекшеліктерінің диендердің гидроалкоксикарбонилдену реакциясына әсерін түсіндіреді және жоғары селективтілікке қол жеткізуге мүмкіндік беретін практикалық жағдайларды анықтайды. Мұндай қорытындылар C_5-C_{10} эфирлерін синтездеудің тиімді жолдарын ашып, оларды полимерлер, пластификаторлар, хош иісті заттар және жұқа органикалық синтезде қолдануға жол ашады.

Түйінді сөздер: алкадиендер, гидрококсикарбонилдеу, палладий катализаторлары, этил эфирлері, региоселективтілік

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