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Alkinylation reactions of benzaldehyde by ethynylbenzene in the presence of some catalysts

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ALKINYLATION REACTIONS OF BENZALDEHYDE BY ETHYNYLBENZENE
IN THE PRESENCE OF SOME CATALYSTS

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The synthesis of acetylene alcohol 1,3-diphenyl propin-2-ol-1, which has several reaction centers in the molecule, is studied. This product was obtained for the first time from a representative of aromatic hydrocarbons of benzaldehyde with phenylacetylene based on an alkynylation reaction in the presence of stereoselective catalysts - $ZnEt_2/Ti(OiPr)_4/PhMe$ and $Sn(OTf)_2/NEt_3/MeCN$. The influence of the activity, stability, and selectivity of the selected catalysts on the yield of products, as well as, the rate of the main reactions, along with side reactions was analyzed. The optimal conditions for the alkynylation reaction and the selectivity of the process are determined. The main and by-products formed in this process are identified. Suggestions are made for the formation of unstable intermediate compounds - carbocations, carbanions, radicals, as well as, active complexes of reactions and catalytic modifications formed in the transition state. A number of efficiencies have been developed for catalysts for the enantioselective alkynylation reaction.

Keywords: phenylacetylene, benzaldehyde, alkynylation reaction, acetylene alcohols, catalysts, selectivity, reaction mechanism, yield products

РЕАКЦИИ АЛКИНИЛИРОВАНИЯ БЕНЗАЛЬДЕГИДА ЭТИНИЛБЕНЗОЛОМ
В ПРИСУТСТВИИ НЕКОТОРЫХ КАТАЛИЗАТОРОВ

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Исследован синтез ацетиленового спирта 1,3-дифенил пропина-2-ола-1, имеющего в молекуле несколько реакционных центров. Данный продукт был получен впервые из представителя ароматических углеводородов бензальдегида с фенилацетиленом на основе реакции алкинирования с присутствием стереоселективных катализаторов - $ZnEt_2/Ti(OiPr)_4/PhMe$ и $Sn(OTf)_2/NEt_3/MeCN$. Проанализировано влияние активности, стабильности и селективности выбранных катализаторов на выход продуктов, а также скорость основных реакций, наряду с побочными реакциями. Определены оптимальные условия реакции алкинирования и селективность процесса. Идентифицированы основные и побочные продукты образующиеся в данном процессе. Приведены предложения об образовании в качестве неустойчивых промежуточных соединений - карбокатионов, карбанионов, радикалов, а также активных комплексов образующихся в переходном состоянии реакций и каталитических модификаций. Разработан ряд эффективностей для катализаторов реакции энантиоселективного алкинирования.

Ключевые слова: фенилацетилен, бензальдегид, реакции алкинирования, ацетиленовые спирты, катализаторы, селективность, механизм реакции, выход продукты

TURLI KATALIZATORLAR ISHTIROKIDA BENZALDEGIDNI ETINILBENZOL
BILAN ALKINILLASH REAKSIYALARI

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Ilk bor benzaldegidni fenilasetilen bilan turli stereoselektiv katalizatorlar - $ZnEt_2/Ti(OiPr)_4/PhMe$ va $Sn(OTf)_2/NEt_3/MeCN$ ishtirokida alkinillash reaksiyasi asosida molekulasida bir neshita faol markaz saqlagan aromatik atsetilen spirti 1,3-difenilpropin-2-ol-1 sintez qilingan. Tanlangan katalizatorlarning faolligi, stabillic va selektivligining asosiy reaksiyalar bilan bir qatorda qo'shimcha reaksiyalar tezligiga hamda mahsulot unumiga ta'siri tahlil qilingan. Alkinillash reaksiyasi muqobil sharoiti va samaradorligi aniqlangan. Jarayonda hosil bo'ladigan asosiy va qo'shimcha mahsulotlar identifikatsiya qilingan. Beqaror oraliq birikmalar sifatida karbanoion, karbkation va radikal hamda reaksiyaning o'tish holatida hosil bo'lgan faollangan komplekslar va katalitik modifikatsiyalar to'g'risida takliflar keltirilgan. Enantioselektiv alkinillash reaksiyasi uchun katalizatorlarning samaradorlik qatori ishlab chiqilgan.

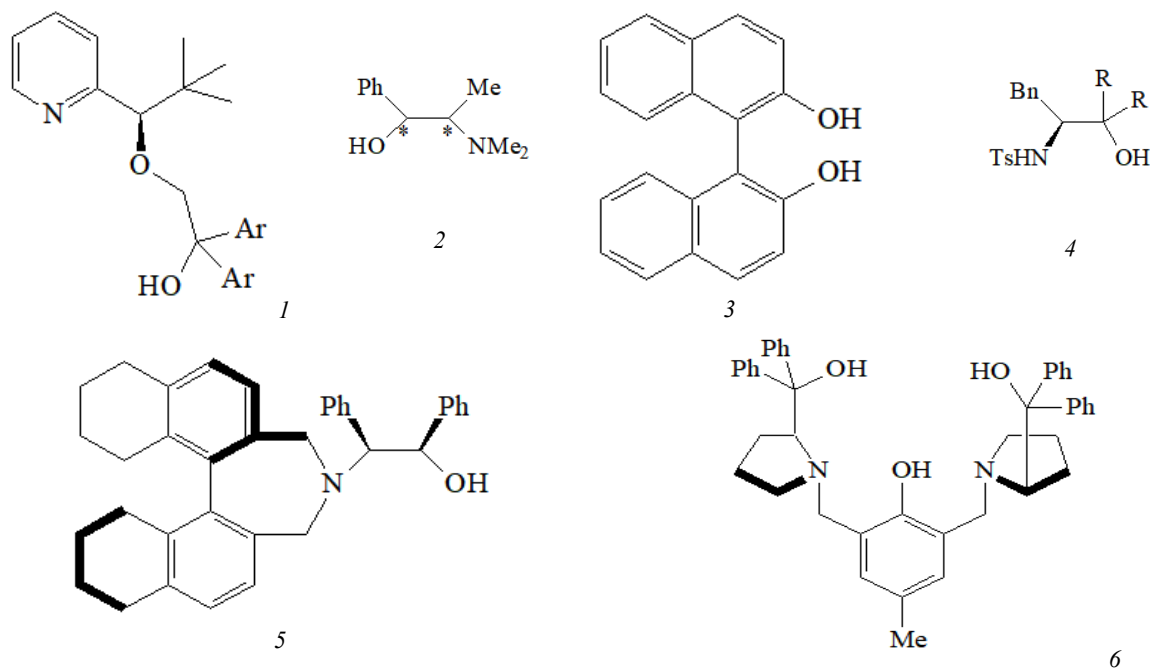
Kalit so'zlar: fenilasetilen, benzaldegid, alkinillash reaksiyasi, atsetilen spirti, katalizatorlar, selektivlik, reaksiya mexanizmi, mahsulot unumi

Kirish

Katalizator sifatida molekulasida bir nechta reaksiya markaz saqlagan tabiiy aminokislotalar va aminospirtlar asosida tayyorlangan, tanlab ta'sir etuvchi xiral oksazolin hosilalari [1] va rux dialkillar asosida tayyorlangan katalitik komponentlar yordamida aromatik aldegidlarning terminal alkinlar bilan assimetrik alkinillash, yoki dixlormetan eritmasida trimetilgalliy ishtirokida etinillash reaksiyasi bo'yicha ko'p qirrali amaliy ahamiyatga ega, biologik faol bo'lgan yangi xiral propargil spirtlari sintez (85-99%) qilingan [2, 3]. Xiral siklopropan asosidagi

aminospirtlar va bisoksozolidin ishtirokida rux atsetilenidlarning aldegidlar bilan toluol eritmasida xona haroratida enantioselektiv birikish reaksiyasi asosida yangi atsetilen spirtlari 79-94% unum bilan sintez qilingan. Bunda siklopropilaminospirti (prolinol) foydalanilganda mahsulot unumi past (22%), ammo prolinol molekulasidagi gidroksil guruhi vodorodni uchlamchi butildimetilsilil xlorid, uchlamchi butildifenilsilil xlorid ligandlariga almashtirilsa mahsulot unumi 90% atrofida hosil bo'lishi kuzatilgan [4]. Ilk bor Osamu Hoshino tomonidan siklogeksankarbaldegid yoki

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ТЕХНОЛОГИЯ КАТАЛИЗА И РЕАКЦИЙ
TEKNOLOGIK KATALIZ VA REAKTSIYALAR

benzaldegidni rux alkinillar va katalizator sifatida xiral ligand 2-[2,2-dimetil-1-(2-pyridyl)propoksi]-1,1-diaryletanol (1) yordamida enantiosektiv alkinillash orqali atsetilen spirtlari sintez qilingan [5]. Bir qator katalitik komponentlar yordamida terminal alkinlarning aldegid va ketonlar bilan nukleofil birikish reaksiyasi asosida biologik faol atsetilen spirtlarini sintez qilish jarayonlari tadqiq qilingan, jumladan quyida keltirilgan (+)- yoki (-)-*N*-metilefedrin (2), (*R*)- yoki (*S*)-BINOL (3), β -sulfonamid spirtlari (4), molekulasida bir nechta reaksiyon markaz yaqinida katta o'rinbosarlar tutgan aminospirtlar hosilalari (5), bifunksional katalitik kompozitsiya ProPhenol (6) kabi nanosektiv katalizatorlarning koordinatsion gomogen katalitik reaksiyalari bo'yicha yuqori unum bilan ikkilamchi va uchlamchi atsetilen spirtlari hamda diollari sintez qilingan [6-10].

Gomogen-katalitik oksidlanish-qaytarilish reaksiyalari bo'yicha terminal aromatik alkinlarlarning aromatik aldegid va ketonlar bilan yuqori enantiosektiv reaksiyalari asosida diaromatik atsetilen spirtlari sintez qilingan. Jarayonda katalizator sifatida reaksiyon sistemaga tuz holda kiritilgan metallarning oddiy va murakkab ionlarini hosil qiladigan turli kombinatsiyalar hosil qiluvchi N -MeEph-Zn (ODf)₂-Et₃N [11], BINOL-ZnEt₂-Ti(OiPr)₄ [12], 4-phenylquinazolin- ZnEt₂-Ti(OiPr)₄-THF [13], Oxazaborolidin Ligand-SnBu₄-Me₂BBr-PhMe [14] kabi katalitik kompozitsiyalar qo'llanilgan [15-16]. Oxirgi vaqtlarda atsetilen spirtlaridan meditsinada, qishloq xo'jaligida, neft-gaz va farmatsevtika sanoatida turli maqsadlarda foydalanilayotganligi ushbu turkum birikmalarning amaliy ahamiyati yuqoriligidan dalolat beradi [15-18].

Olingan natijalar tahlili

Ushbu ishda ilk bor benzaldegid va fenilatsetilen asosida atsetilen spirti-1,3-difenilpropin-2-ol-1 ni ZnEt₂/Ti(OiPr)₄/PhMe va Sn(OTf)₂/NEt₃/MeCN katalizatorlari yordamida sintez qilish reaksiyasi ximizmi o'rganilgan. Tanlangan aldegidni alkinillash jarayonida qo'llanilgan katalizatorlarning selektivligi, stabilligi va faolliklari olingan natijalar asosida tahlil qilingan.

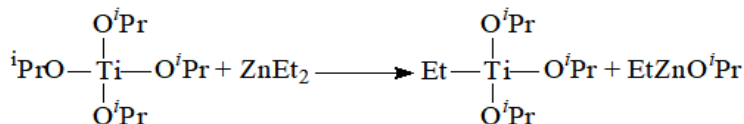
Atsetilen spirtini sintez qilishda boradigan qo'shimcha reaksiyalar, jarayonda hosil bo'ladigan oraliq va qo'shimcha mahsulotlar to'g'risida takliflar kiritilgan, tanlangan katalitik kompozitsiyalarning samaradorligi aniqlangan, yuqori unum bilan mahsulot olish uchun reaksiyalar turli haroratda, bosimda va reaksiya davomiylıklarida olib borildi.

Olingan natijalar asosida atsetilen spirtini sintez qilish reaksiyalari uchun eng muqobil sharoitlar topilgan.

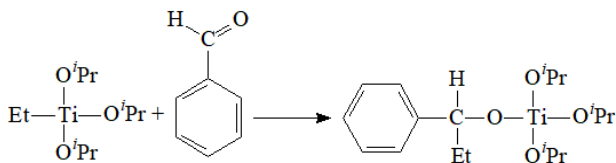
Ilmiy adabiyotlar tahlili va olib borilgan tajribalar natijalari asosida 1,3-difenilpropin-2-ol-1 ni sintez qilish reaksiyalarini olib borish usullari, ularni nazorat qilish va boshqarish yo'llari hamda ximizm (reaksiya mexanizm) lari to'g'risida takliflar berildi.

Jumladan benzaldegidni ZnEt₂/Ti(OiPr)₄/PhMe katalitik sistemasi orqali fenilatsetilen bilan etinillash orqali 1,3-difenilpropin-2-ol-1 sintez qilish reaksiyasi tahlil qilingan. Reaksiya sxemasi quyidagicha taklif etildi.

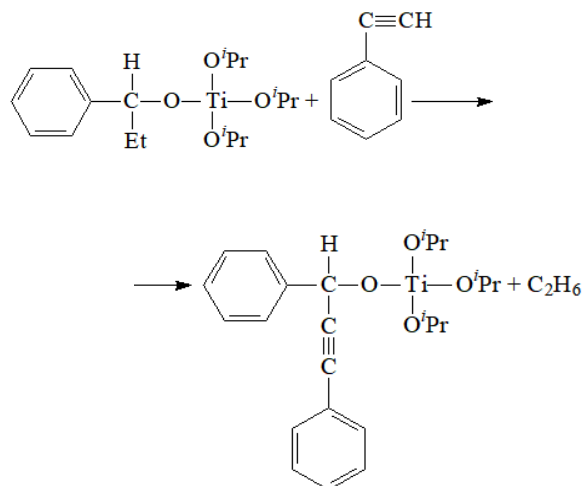
Jarayon ximizmi: Jarayonda dastlab katalizator sifatida tanlangan Ti(OiPr)₄ toluol eritmasida ZnEt₂ bilan ta'sirlashib uzoq vaqt faolligini saqlab turuvchi, selektivligi stabil bo'lgan katalitik komponent EtTi(OiPr)₃ ni hosil qiladi.



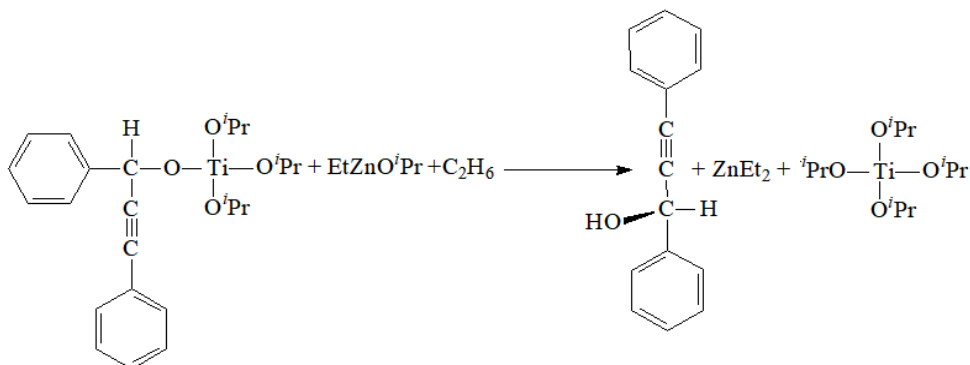
EtTi(O^{*i*}Pr)₃ o'z navbatida benzaldegid bilan birikish reaksiyasiga kirishib oraliq birikmaga aylanadi, bunda EtTi(O^{*i*}Pr)₃ tarkibidagi etil radikali karbonil guruhining uglerod atomiga, titan trioksiizopropil ioni esa kislorod atomiga bog'lanib katalitik faol murakkab modifikatsiyasini hosil qiladi.



Fenilatsetilenning harakatchan vodorodi katalitik komponent molekulasidagi etil radikali bilan feniletinil radikali esa elektron zichligi tanqis bo'lgan uglerodga borib birikishi natijasida dastlab atsetilen spirtining trioksiizopropiltitan hosilasi, so'ngra EtZnO^{*i*}Pr ta'sirida atsetilen spirti 1,3-difenilpropin-2-ol-1 hosil bo'ladi.

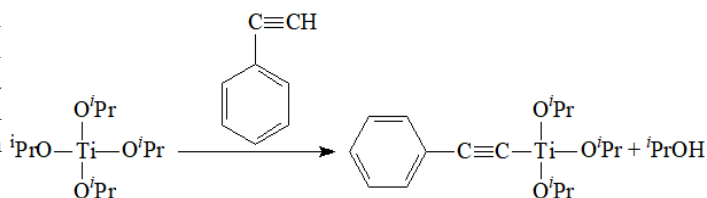


Jarayonni olib borishda sistemadagi ZnEt₂ fenilatsetilen bilan ta'sirlashib atsetilenid, 1,3-difenilpropin-2-ol-1 bilan alkogolyat hosil bo'

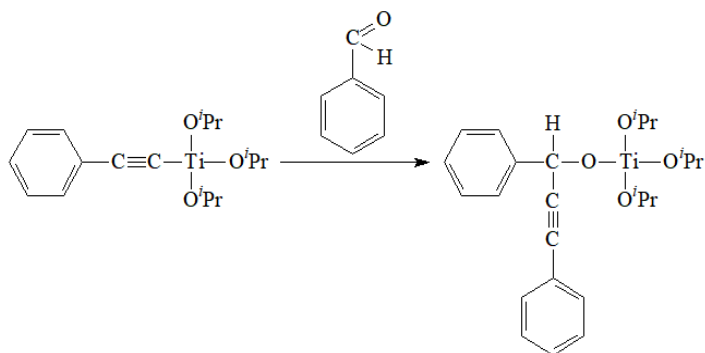


lishi natijasida katalizatorning faol markazlarining bir qismini berkitib katalitik zaharlanish kuzatilishi kerak edi, ammo rux alkogolyat o'z navbatida juda tez gidrolizlanishi yoki sistemadagi erkin vodorod bilan almashinib yuqori unum bilan atsetilen spirtlari hosil bo'lishiga xizmat qilishi kuzatildi.

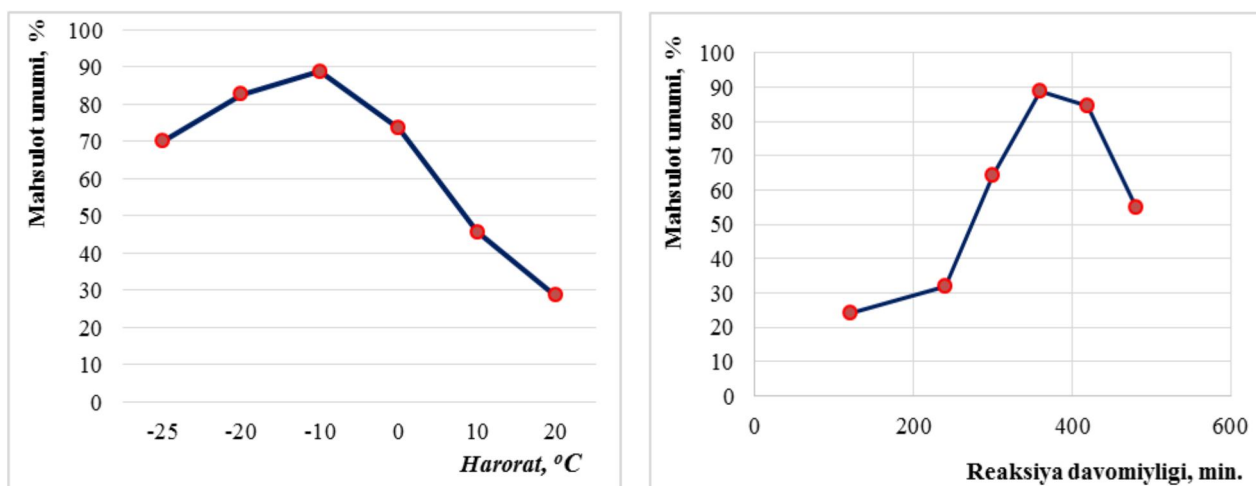
Olingan natijalarni fizik-kimyoviy tadqiq qilish asosida aldegilarni alkinillash jarayonining keyingi bosqichida (parallel ravishda) dastlab toluol eritmasida guruh selektivlik namoyon qiluvchi Ti(O^{*i*}Pr)₄ katalizator fenilatsetilen bilan reaksiyaga kirishib selektivligi va faolligi juda yuqori bo'lgan PhCCTi(O^{*i*}Pr)₃ katalitik kompozitsiyani hosil qiladi [19].



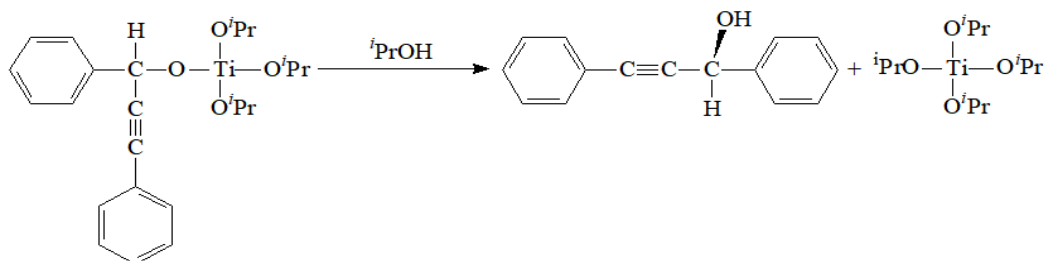
Sistemadagi barqaror PhCCTi(O^{*i*}Pr)₃ katalitik kompozitsiyaga benzaldegidning kuchli qutblangan C=O guruhining hujumi ya'ni o'zida ortiqcha elektron zichlik saqlagan kislorod atomi PhCCTi(O^{*i*}Pr)₃ molekulasidagi uchbog' saqlagan feniletinil radikaliga tanlab ta'sir qilishi natijasida dastlab oraliq birikmaga, so'ngra atsetilen spirtiga aylanadi [20].



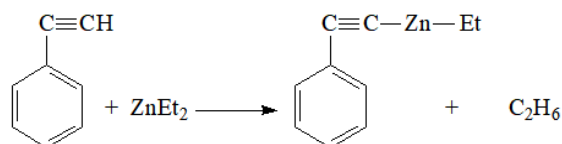
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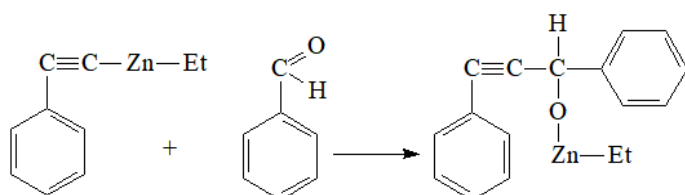
1-Rasm. 1,3-difenilpropin-2-ol-1 unumiga harorat va reaksiya davomiyligi ta'siri (erituvchi PhMe, boshlang'ich moddalar (PhCCH:RCHO) mol miqdori 3:1 nisbatda).



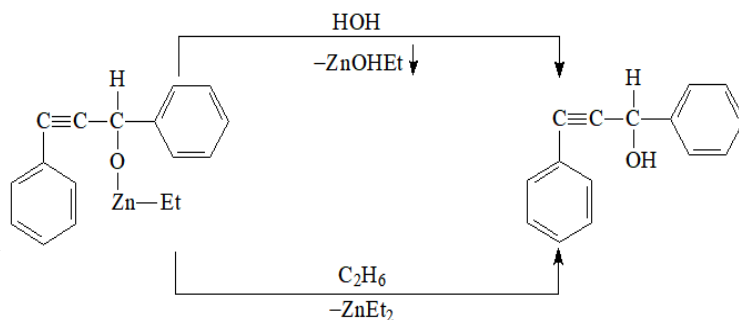
ZnEt₂/Ti(OiPr)₄ universal selektiv namoyon qiluvchi katalizator bo'lganligi uchun unda faol markazlar soni ham bir nechta bo'lib, jumladan alkinlash jarayonida ZnEt₂ terminal alkin molekulasida harakatchan vodorod bilan ta'sirlashib PhCCZnEt hosil qiladi.



Sistemada hosil bo'lgan ruh etilfenilatsetilenid benzaldegid bilan reaksiyaga kirishib oraliq birikmaga aylanadi [21]. Aldegidning kislorod atomiga ZnEt⁺ ning kelib birikishi natijasida katalitik faol komponent (oraliq birikma) hosil bo'ladi. Bunda oraliq komponent miqdori qanchalik ko'p hosil bo'lishi, mahsulot hosil bo'lish samaradorligining ortishiga xizmat qilishi kuzatildi.

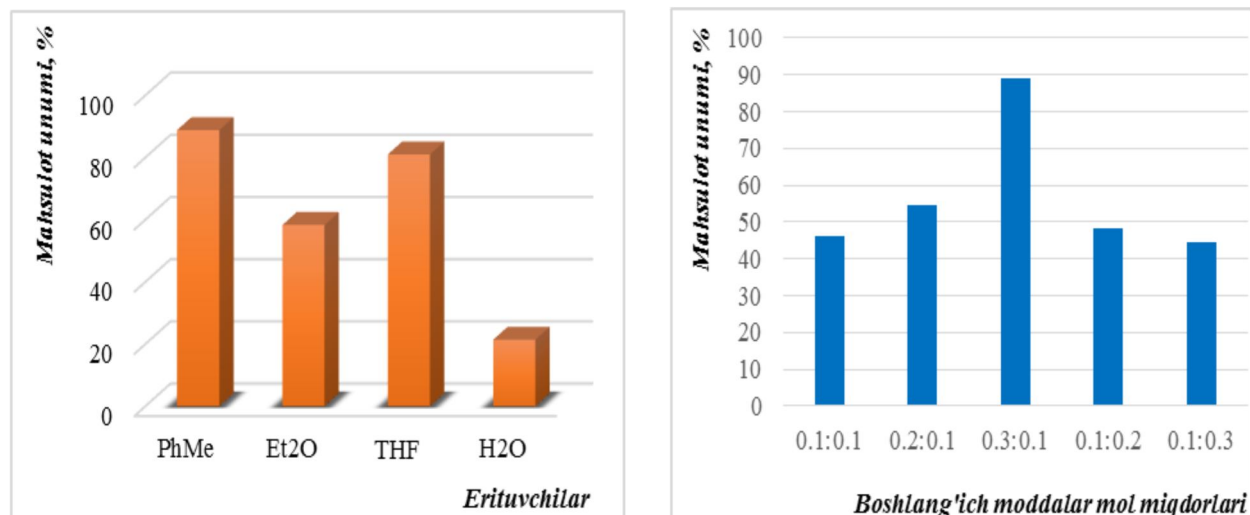


Katalizat tarkibidagi oraliq faol birikma bir vaqtning o'zida ham gidrolizga uchraydi, ham sistemadagi etan bilan ta'sirlashadi, reaksiya natijasida ZnOHEt va 1,3-difenilpropin-2-ol-1 ni hosil qiladi [22].

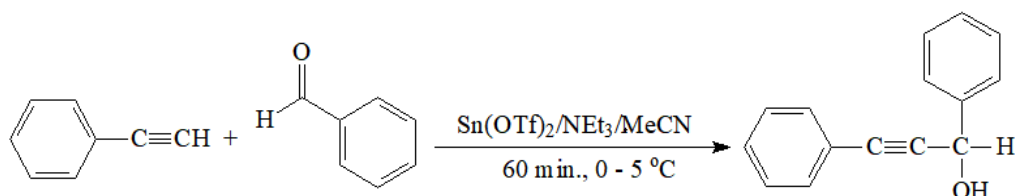


Mahsulot unumiga tanlangan aldegidning tabiati, uning molekulasini fazaviy tuzilishi va optik faolligi ta'siri o'rganilgan. 1,3-difenilpropin-2-ol-1 hosil bo'lish samaradorligi va kimyoviy reaksiyalarning borishiga harorat, reaksiya davomiyligi, erituvchilar va katalizatorlar tabiati, boshlang'ich moddalar konsentratsiyasi hamda mol miqdorlari ta'siri tizimli tahlil qilindi.

Tanlangan intervallarda haroratning -25 °C dan -10 °C gacha oshib borishi bilan mahsulot unumining samaradorligi ham ortishi (70,1 dan 88,8% ga) kuzatildi. Ammo harorat -10 dan 20 °C gacha oshirilishi bilan Ti(OiPr)₄ dimer



2-Rasm. 1,3-difenilpropin-2-ol-1 unumiga erituvchilar tabiati va boshlang'ich moddalar mol miqdorlari ta'siri (reaksiya davomiyligi 360 minut, harorat -10°C).



kompleksga aylanib katalitik faolligini yo'qotishi, katalizator etishmovchiligi natijasida ko'p miqdorda oraliq va sistemadagi atsetilen spirti kompleks tuzlari hosil bo'lishi natijasida mahsulot unumining keskin ravishda kamayishi (88,8 dan 28,7% ga) kuzatildi. Reaksiya davomiyligi 360 minut davomida olib borilganda 1,3-difenilpropin-2-ol-1 eng maksimum unum bilan sintez qilindi. Reaksiya uzoq vaqt (400-480 minut) davomida olib borilgan qo'shimcha reaksiyalar (kondensatsiya, polimerlanish, oligomerlanish, gidroliz) ketishi, oraliq mahsulotlarning boshqa birikmalarga aylanishi natijasida atsetilen spirti unumida kamayish kuzatildi.

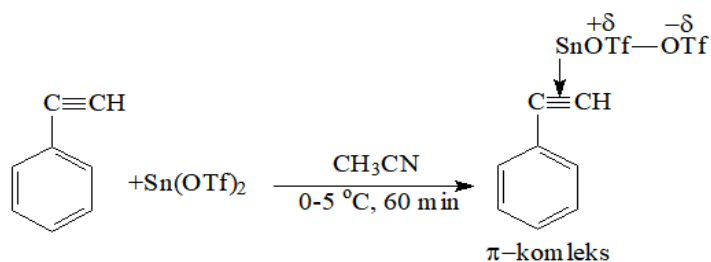
2-Rasmda 1,3-difenilpropin-2-ol-1 unumiga erituvchilar tabiati va boshlang'ich moddalar mol miqdorlari ta'siri o'rganilgan bo'lib, reaksiya aproton erituvchilar hisoblangan dietilefir (Et_2O) va tetragidrofuran (THF) da olib borilganda, dielektrik doimiyligi va dipol momenti yuqori bo'lgan THF mahsulot unumi yuqori chiqishi aniqlandi. Buning sababi Et_2O eritmasidagi Ti(OiPr)_4 ga ZnEt_2 ta'sir ettirilganda reaksiya juda sekin borishi, THF eritmasida jarayon juda tez borishi, katalitik faol va selektivligi yuqori bo'lgan TiEt(OiPr)_3 ning hosil bo'lishi benzaldegidning faollashiga olib keladi. Jarayon PhMe eritmasida olib borilganda fenilatsetilenning benzaldegid bilan optik faol to'qnashuvdan jarayonda oraliq va qo'shimcha mahsulotlarning hosil bo'lishi va ular faollik bilan atsetilen spirtlariga aylanishi uchun sistemada qulay kompleks gomogen-koordinatsion katalitik muhitni

yaratib berganligi sababli atsetilen spirti yuqori unum bilan hosil bo'lishi kuzatildi.

Olingan natijalar asosida jarayon toluol eritmasida, 360 minut davomida, -10°C haroratda, boshlang'ich moddalar va katalizatorlar ($\text{PhCCH}:\text{RCHO}:\text{ZnEt}_2:\text{Ti(OiPr)}_4$) mol miqdori 3:1:3:0,25 nisbatda olib borilganda eng yuqori (88,8%) unum bilan 1,3-difenilpropin-2-ol-1 sintez qilindi va ushbu holat reaksiyaning eng muqobil sharoiti sifatida taklif qilindi.

Tadqiqot maqsadidan kelib chiqib mahsulot unumiga katalizatorlar tabiatining ta'sirini va eng selektiv katalizatorni aniqlashdan iboratligini e'tiborga olib 1,3-difenilpropin-2-ol-1 ni triflormetilsulfonat kislotasi asosida tayyorlangan $\text{Sn(OTf)}_2/\text{NEt}_3/\text{MeCN}$ katalitik muhitida sintez qilish jarayoni o'rganildi. Reaksiya sxemasi va mexanizmi quyidagicha taklif qilindi.

Jarayon ximizmi: Aromatik atsetilen spirti sintez qilishda dastlab qalay triflormetilsulfonat fenilatsetilen molekulasidagi uchbog'ga orientatsion ta'sir etadi va natijada vodorod atomining harakatchanligini yanada oshirib, π -kompleks hosil qiladi.

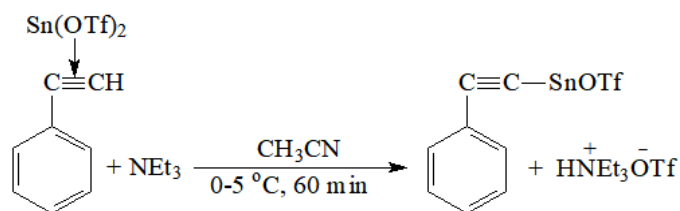


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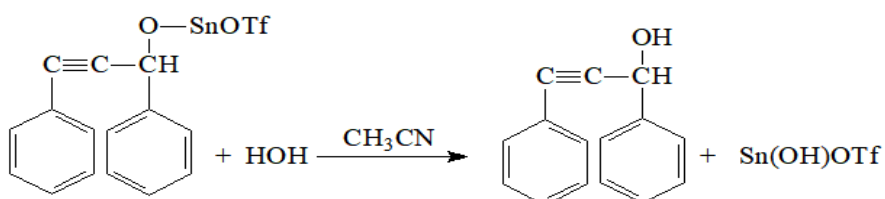
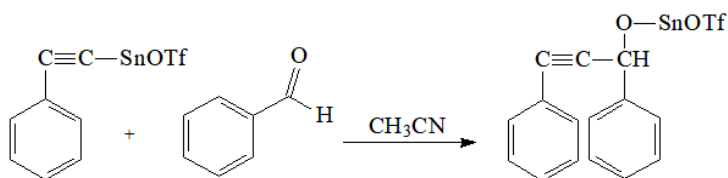
ТЕХНОЛОГИЯ КАТАЛИЗА И РЕАКЦИЙ
TEKNOLOGIK KATALIZ VA REAKTSIYALAR1,3-Difenilpropin-2-ol-1 unumiga reaksiya
davomiyligi ta'siri
(erituvchi atsetonitril, harorat -10 °C)

Reaksiya davomiyligi, minut	PhCCH:Sn(OTf) ₂ mol miqdori	Mahsulot unumi, %
40	1:1	46,3
60		57,1
80		55,5
40	2:1	80,3
60		92,0
80		86,0
40	1:2	73,0
60		78,2

Hosil bo'lgan oraliq mahsulot (π -kompleks) atsetonitril eritmasida trietilamin bilan reaksiyaga kirishadi va sistemada oraliq mahsulot fenilatsetilenning qalay triftoformetil-sulfonatli tuzi va HNEt₃OTf hosil bo'ladi.



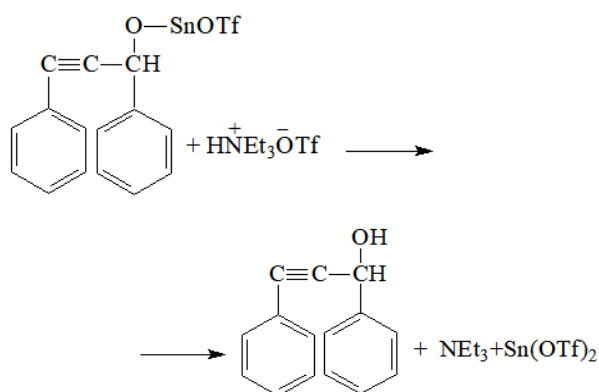
Oraliq mahsulot sifatida hosil bo'lgan fenilatsetilenning qalay triftoformetil-sulfonatli tuzi molekulasidagi SnOTf⁺ kationning harakatchanligi faol bo'lganligi uchun benzaldegid molekulasidagi kislorod atomiga kuchli hujum qilishi natijasida atsetilen spirtining qalay triftoformetil-sulfonatli tuzini hosil qiladi.



Hosil bo'lgan tuz suv ta'sirida gidrolizga uchrashi natijasida 1-(2-feniletinil)siklogeksanolga aylanadi.

Jarayonda fenilatsetilenning qalay triftoformetil-sulfonatli tuzi va 1-(2-feniletinil)-siklogeksanolning qalay triftoformetil-sulfonatli tuzi hosil bo'lishi qanchalik tez va ko'p miqdorda hosil bo'lsa, mahsulot unumining ham yuqori chiqishi kuzatiladi.

Reaksiyada hosil bo'lgan oraliq mahsulot-fenilatsetilenning qalay triftoformetil-sulfonatli tuzi bir vaqtning o'zida sistemadagi oraliq mahsulot HNEt₃OTf bilan ta'sirlashuvidan atsetilen spirtiga aylanadi [23, 24].

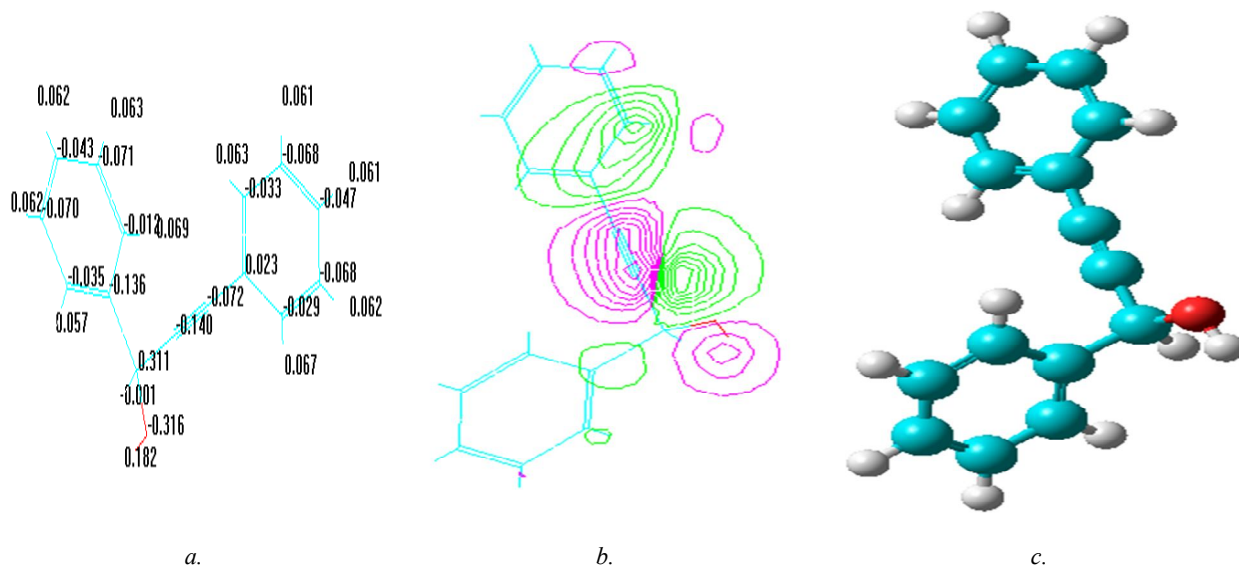


Olib borilgan tajriba natijalarini tahlil qilish asosida jarayonda reaksiyaga kirishmagan fenilatsetilen, benzaldegid borligi kuzatildi, bundan tashqari sistemada stannum fenilatsetilenid, 1,3-difenilpropin-2-ol-1 fenilviniloksi efiri, alkogolyati va kompleks tuzlari hamda smola mahsulotlar borligi fizik-kimyoviy usullarda aniqlandi.

Jadvaldan ko'rinib turibdiki reaksiya 60 minut davomida, PhCCH:Sn(OTf)₂ mol miqdori 2:1 nisbatda olinganda mahsulot unumi eng yuqori unum bilan chiqishi kuzatildi.

Reaksiya davomiyligining ortishi bilan sistemada alkogolyatlar, atsetilenidlar va polimer smola mahsulotlarining hosil bo'lishi natijasida mahsulot unumining minimallasuvi aniqlandi.

Jarayonda katalizator miqdorini oshirish natijasida aldegidning kondensatsiyalanishi, qalay atsetilenid, triftoformetil-sulfon kislota va qalay gidroksidi miqdorining ortishi kuzatildi, natijada sistemadagi atsetilen spirtining turli



3-Rasm. 1,3-difenilpropin-2-ol-1 ning ayrim fazoviy tuzilishlari.

hosilalarga (efir, alkogolyat, atsetal, qisman oksinitril) aylanishi hisobiga mahsulot unumining pasayishiga olib kelishi aniqlandi.

Sintez qilingan 1,3-difenilpropin-2-ol-1 ning tuzilishi spektroskopik usullarda tahlil qilindi: $^1\text{H-NMR}$ (CDCl_3): δ 7.82-7.74 (m, 2H), 7.55-7.42 (m, 6H), 5.88 (d, $J=5.8$ Hz, 1H), 2.42(d, $J=5.9$ Hz, 1H). $^{13}\text{C-NMR}$: δ 140.4, 131.2, 128.3, 128.7, 128.3, 128.2, 126.6, 122.5, 88.5, 86.8, 65.2.

Xulosa

Ilk bor kompleks gomogen-koordinatsion katalitik sistemalar ishtirokida fenilatsetilen va benzaldegid asosida aromatik atsetilen spirti 1,3-difenilpropin-2-ol-1 sintez qilish usuli ishlab

chiqildi.

Olib borilgan tajribalar asosida tanlangan kompleks gomogen-koordinatsion katalitik sistemalar $\text{ZnEt}_2/\text{Ti}(\text{OiPr})_4/\text{PhMe}$ va $\text{Sn}(\text{OTf})_2/\text{NEt}_3/\text{MeCN}$ orqali aldegidlarni terminal atsetilen uglevodorodlari bilan enantiosektiv alkinillash reaksiyalari mexanizmlari taklif etildi.

Alkinillash reaksiyalarning borishida harorat, reaksiya davomiyligi, erituvchi va katalizatorlar tabiati, boshlang'ich moddalar mol nisbatlari ta'sirini tizimli tahlil qilindi.

Tanlangan katalizatorlar orasida $\text{Sn}(\text{OTf})_2/\text{NEt}_3/\text{MeCN}$ ni kislotalilik xossasi yuqoriligi, ya'ni xohlagan asosni protonlash xossasiga ega bo'lganligi sababli $\text{ZnEt}_2/\text{Ti}(\text{OiPr})_4/\text{PhMe}$ ga nisbatan katalitik faolligi aniqlandi.

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