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SYNTHESIS OF INTERNAL ACETYLENE ALCOHOLS BASED ON THE SONOGASHIRA REACTION OF TERMINAL ACETYLENE ALCOHOLS AND BENZOLCHLORIDE

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The purpose of the study is to develop a new catalytic system for the synthesis of internal acetylene alcohols from the Sonogastric coupling reaction of terminal acetylene alcohols and benzolchloride. For the first time in this work, internal acetylene alcohols have been synthesized based on reactions of some terminal acetylene alcohols – 3,4-dimethylpentin-1-ol-3, 3,4,4-trimethylpentin-1-ol-3, 1-ethynylcyclohexanol-1, 2-ethynyladamantanol-2, 2-phenylbutin-3-ol-2, 2-(naphthyl-2)butyn-3-ol-2, 2-(furanyl-2)butyn-3-ol-2 and 2-(pyridinyl-4)butyn-3-ol-2 with chloridebenzene. In order to achieve high product productivity in the Sonogashira reaction, alternative conditions have been identified by studying the molar ratios, spatial structure, induction effects of substituents, solvent and catalyst nature, as well as temperature, reaction duration effects, and the reaction mechanism has been proposed on the basis of literature sources.

Keywords: catalytic system, chloridebenzene, copper(I)-salt, Pd(II)-salt, triethylamine, product yield, solvents

СИНТЕЗ ИНТЕРНАЛЬНЫХ АЦЕТИЛЕНОВЫХ СПИРТОВ НА ОСНОВЕ РЕАКЦИИ СОНОГАШИРЫ ТЕРМИНАЛЬНЫХ АЦЕТИЛЕНОВЫХ СПИРТОВ И БЕНЗОЛХЛОРИДА

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Целью исследования является разработка новой каталитической системы для синтеза концевых ацетиленовых спиртов и внутренних ацетиленовых спиртов из реакции присоединения хлоридабензол реакции Соногашира. В этой работе впервые были использованы некоторые концевые ацетиленовые спирты с использованием каталитической системы $Pd(OAc)_2/CuCl/Et_3N/MeCN/H_2O$ – 3,4-диметилпентин-1-ол-3, 3,4,4-триметилпентин-1-ол-3, 1-этинилциклогексанол-1, 2-этиниладамантанол-2, 2-фенилбутин-3-ол-2, 2-(нафтил-2)бутин-3-ол-2, 2-(фуранил-2)бутин-3-ол-2 и 2-(пиридинил-4)бутин-3-ол-2 на основе реакций с бензолхлоридом синтезированы внутренние ацетиленовые спирты. Альтернативные условия были определены путем изучения мольных соотношений исходных веществ, пространственной структуры, индукционных эффектов заместителей, природы растворителя и катализатора, а также влияния температуры, продолжительности реакции для достижения более высокого выходного эффекта в реакции Соногашира, а механизм реакции был предложен на основе литературных источников.

Ключевые слова: каталитическая система, хлоридбензол, медь(I)-соль, Pd(II)-соль, триэтиламин, выход продукта, растворители

TERMINAL ATSETILEN SPIRTLARI VA BENZOLXLORIDNING SONOGASHIRA REAKSIYASI ASOSIDA INTERNAL ATSETILEN SPIRTLARI SINTEZI

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Tadqiqotning maqsadi terminal atsetilen spirtlari va benzolxloridning Sonogashira birikish reaksiyasidan internal atsetilen spirtlari sintez qilish uchun yangi katalitik sistemasi ishlab chiqishdan iborat. Ushbu ishda ilk bor $Pd(OAc)_2/CuCl/Et_3N/MeCN/H_2O$ katalitik sistemasi yordamida ayrim terminal atsetilen spirtlari – 3,4-dimetilpentin-1-ol-3, 3,4,4-trimetilpentin-1-ol-3, 1-etinilsiklogeksanol-1, 2-etiniladamantanol-2, 2-fenilbutin-3-ol-2, 2-(naftil-2)butin-3-ol-2, 2-(furanil-2)butin-3-ol-2 va 2-(piridinil-4)butin-3-ol-2ning xlorbenzol bilan reaksiyalari asosida internal atsetilen spirtlari sintez qilingan. Sonogashira reaksiyasida yuqori mahsulot unumiga erishish uchun boshlang‘ich moddalar mol nisbatlari, fazoviy tuzilishi, o‘rinbosarlarning induksion ta’siri, erituvchi va katalizator tabiati, shuningdek, harorat, reaksiya davomiyligi ta’sirini o‘rganish orqali muqobil sharoit aniqlangan va reaksiya mexanizmi adabiyot manbaalari asosida taklif etilgan.

Kalit so'zlar: katalitik sistema, xlorbenzol, mis(I)-tuzi, Pd(II)-tuzi, trietilamin, mahsulot unumi, erituvchilar

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Kirish

Yangi C–C bog‘ hosil qilishning universal, regioselektiv va sterioselektiv usulining asosida metalorganik birikmalarning galogen-alkanlar, gagalogenalkenlar, galogenarillar va boshqalar bilan oraliq metallarning kompleks katalizatorlari ishtirokida boradigan kors-birikish reaksiyalari yotadi [1-6].

Ilk bor Chow va uning ilmiy jamoasi tomonidan 2001-yil $PdCl_2(PPh_3)_2/CuJ$ katalitik sistema yordamida aromatik atsetilen spirtlarini brombenzol bilan Sonogashira reaksiyasi asosida diaril atsetilenlar sintezi amalga oshirilgan [7]. Keyinchalik ushbu reaksiyani Hua va uning hamkasblari xlorbenzol bilan $PdCl_2(PCy_3)_2$ katalitik sistemada [8], Tsai esa yodbenzol bilan $FeCl_3$ katalizatori yordamida amalga oshirgan [9]. Sonogashira reaksiyasi asosida internal aromatik atsetilen spirtlarining xlorbenzol bilan birikish reaksiyasi $Palladacycle/Xphos/K_2CO_3$ katalitik sistema yordamida azot atmosferasida, atsetonitril eritmasida 110 ^oC haroratda olib borilgan va 99% unumgacha 31 xil turdagi diarillar sintez qilingan [10]. Mis (I) kompleks tuzlari ishtirokida o-yodanilin bilan terminal alkinlarning Sonogashira kross-birikish reaksiyalari havo atmosferasida amalga oshirilgan 56-99% unum bilan biologik, farmakologik faol etinilanilin hosilalari olingan [11]. Terminal alkinlar asosida kross-birikish reaksiyasidan silikonorganik birikmalarning muhim sinfi, allenil birikmalarning boshlang‘ich reagenti hisoblangan aromatik propargilsilanlar sintezi toluol eritmasida 80 ^oC haroratda 4 soat davomida $Pd_2dba_3{\cdot}CHCl_3$ katalitik sistemada amalga oshirilgan. [12]. Rossiya olimlari Y.Kotovshchikov uchlamchi propargil spirtlari va aril(getaril)galogenidlardan mis tuzlari ishtirokida 34 turdagi internal diarillar maksimum 94% unumgacha sintez qilingan [13]. $PdCl_2(PPh_3)_2Cl_2/CuJ$ katalitik sistema yordamida terminal atsetilen spirlari va 3-yodalken-2-ol-1 ning Sornogashira birikish reaksiyasi asosida yenindiollar sintez qilingan va olingan birikmalarning sikloizomerizatsiya, degidrotsiklizatsiya reaksiyalari natijasida 2-(1-alkenil)furanlar sintezi tadqiq qilingan [14]. $Pd(OAc)_2/MeCN$ katalitik sistemada 24 ^oC haroratda 17 soat davomida fenilatsetilenning birlamchi atsetilen spirtlariga birikish reaksiyalari olib borilgan, alkinning selektiv dimerlanishi natijasida turli yeninol, yenindiol, yenindiaril birikmalar olingan [15]. 3-bromanilin va 2-metil-3-butin-2-oldan Sonogashira reaksiyasi asosida o‘pka, oshqozon, buyrak, jigar va ko‘krak saratonida o‘simtani epidemial o‘sish omili retseptorlariga qarshi ingibitor xisoblangan farmokologik faol birikma Erlotinib sintezi amalga oshirilgan [16].

Tadqiqot usuli

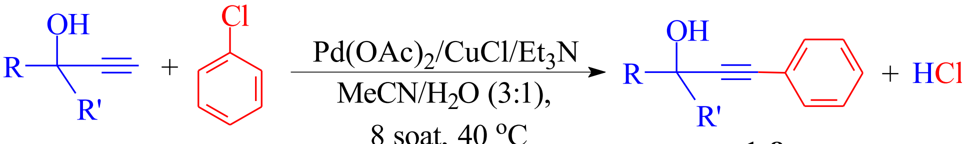
$CuCl/Pd(OAc)_2/Et_3N/MeCN/H_2O$ katalitik sistemasida 1-(feniletinil) siklogeksanol-1 sintezi. Terminal atsetilen spirtlaridan internal aromatik atsetilen spirtlari sintez qilish jarayoni hajmi 500 ml bo‘lgan besh og‘izli kolbada amalga oshirildi. Ushbu kolbaga tomizgich voronka, mexanik aralashtirgich, termometr va qaytarma sovutgich o‘rnatildi. Dastlab kolbaga 18,6 g (0,15 mol) 1-etinilsiklogeksanol-1 va 0,10 g (0,01 mol) CuCl solindi. Keyin 2,24 g (0,01 mol) palladiy(II)-atsetat ($Pd(OAc)_2$)ning 15 ml MeCN va 5 ml H_2O (3:1 nisbatda) erituvchilar yordamida tayyorlangan suspensiyasi aralashtirilgan holatda qo‘shildi. Bunda kolbadagi harorat 30-40 ^oC da bo‘lishi kerak. Hosil bo‘lgan aralashmaga 11,25 g (0,10 mol) xlorbenzol (C_6H_5Cl) va 20 g (0,2 mol, 15 ml) trietilamin bilan tayyorlangan suspensiyasi 30 minut davomida tomchilatib qo‘shildi. So‘ngra aralashma 40 ^oC haroratda 7,5 soat davomida bir meyorda aralashtirildi. Hosil bo‘lgan reaksiya mahsuloti 30 minutga tindirishga qo‘yildi. So‘ngra 75 ml (3×25) sovuq suv yordamida gidroliz qilinib, katalitik qism ajratib olinadi va qolgan organik qismi esa dixlorometan 60 ml (3×20) yordamida qayta-qayta ekstraksiya qilindi. Organik qismi $CaCl_2$ yordamida bir sutka davomida quritilib, filtrlab olindi va erituvchi oddiy haydab olindi va qolgan qism vakuumda haydaldi. Reaksiya mahsulotlari Silikagel 60 kolonkali xromatografiya yordamida AcOEt/geksan (1:4) eluentlar o‘tkazilib, R_f qiymati aniqlandi va mahsulot toza holatda ajratib olindi. Natijada 26,1 g rangsiz suyuq modda 1-(feniletinil)siklogeksanol-1 (87%) unum bilan sintez qilindi.

Ushbu usul bo‘yicha 3,4-dimetilpentin-1-ol-3, 3,4,4-trimetilpentin-1-ol-3; 2-etiniladamantanol-2, 2-fenilbutin-3-ol-2, 2-(naftil-2)butin-3-ol-2, 2-(furanil-2)butin-3-ol-2 va 2-(piridinil-4)butin-3-ol-2 kabi terminal atsetilen spirtlarining Sonogashira birikish reaksiyasi asosida mos ravishdagi internal aromatik atsetilen spirtlari, jumladan 84% unum bilan 3,4-dimetil-1-fenilpentin-1-ol-3, 82% unum bilan 3,4,4-trimetil-1-fenilpentin-1-ol-3, 79% unum bilan 2-(1-feniletinil)adamantanol-2, 77% unum bilan 2,4-difenilbutin-3-ol-2, 67% unum bilan 2-(naftil-2)-4-fenilbutin-3-ol-2, 75% unum bilan 2-(furanil-2)-4-fenilbutin-3-ol-2 va 71% unum bilan

4-fenil-2-(piridinil-4)butin-3-ol-2 sintez qilindi.

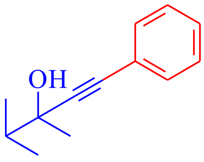
Natijalar va muhokama

Olib borilgan ilmiy tadqiqotlar asosida katalizator sifatida $Pd(OAc)_2$ va yordamchi katalizator sifatida CuCl, ham promotor, ham erituvchi vazifasini bajaruvchi Et_3N va $MeCN/H_2O$ (3:1) erituvchi aralashmasidan tayyorlangan katalitik sistema yordamida terminal atsetilen spirtlar - 3,4-dimetilpentin-1-ol-3, 3,4,4-trimetilpentin-1-ol-3, 1-etinilsiklogeksanol, 2-etiniladamantanol-2, 2-fenilbutin-3-ol-2, 2-(naftil-2)butin-3-ol-2, 2-(furanil-2)butin-3-ol-2 va 2-(piridinil-4)butin-3-ol-2 ning asosli muhitda xlorbenzol bilan olib borilgan reaksiyalari natijasida quyidagi internal aromatik atsetilen spirtlari – 3,4-dimetil-1-fenilpentin-1-ol-3 (1), 3,4,4-trimetil-1-fenilpentin-1-ol-3 (2), 1-(2-feniletinil)siklogeksanol (3), 2-(1-feniletinil)adamantanol-2 (4), 2,4-difenilbutin-3-ol-2 (5), 2-(naftil-2)-4-fenilbutin-3-ol-2 (6), 2-(furanil-2)-4-fenilbutin-3-ol-2 (7) va 4-fenil-2-(piridinil-4)butin-3-ol-2 (8) sintez qilingan. Reaksiya sxemasi quyidagicha taklif etildi [17].



1-8

Bu yerda: R= Me, R'= ^{i}Pr (1); R= Me, R'= ^{t}Bu (2); RR'= $_{c}$Hx (3); RR' = Ad (4); R= Me, R'= Ph (5); R= Me, R'= $_{\beta}$Nh (6); R= Me, R'= Fr (7); R= Me, R'= Py (8)



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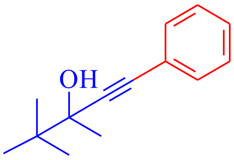

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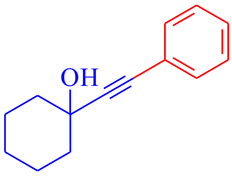

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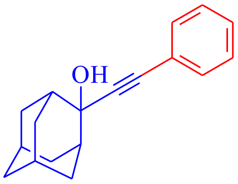

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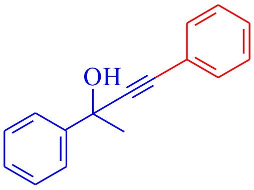

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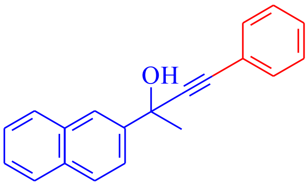

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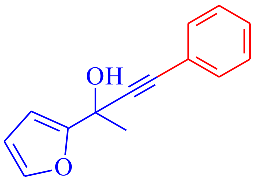

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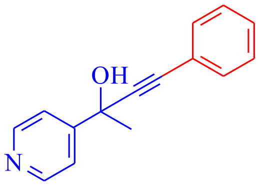

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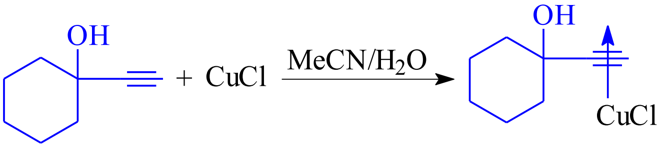
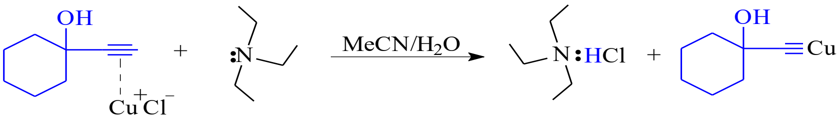
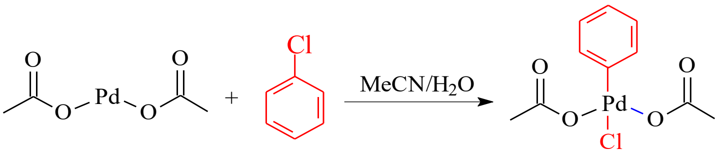
Reaksiya mexanizmi: (Namuna sifatida 3 sintezi keltirilgan) Sonogashira birikish reaksiyasini amalga oshirish uchun qo‘sh katalizatorlar $CuCl/Pd(OAc)_2$ ta’sirida bir paytda ikkita katalitik sikl amalga oshadi. Bunda birinchi katalitik siklda 1-etinilsiklogeksanolning mis (I)-xlorid bilan ta’sirlashuvidan π-kompleksni hosil qiladi. Jarayonda nukleofil erituvchi sifatida MeCN va suv ishtirokida olib borilgan.



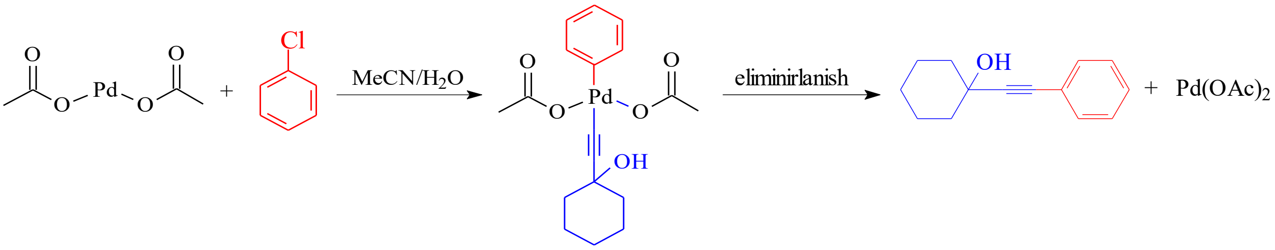
Sistemaga qo‘shilgan trietilamin tarkibidagi azot atomining bog‘ hosil qilishda ishtirok etmagan juft elektronlari hisobiga π-kompleksning vodorod va xlor atomlari bilan donor akseptor bog‘lanish asosida biriktirishi natijasida mis (I)-atsetilenid tuzi olinadi.



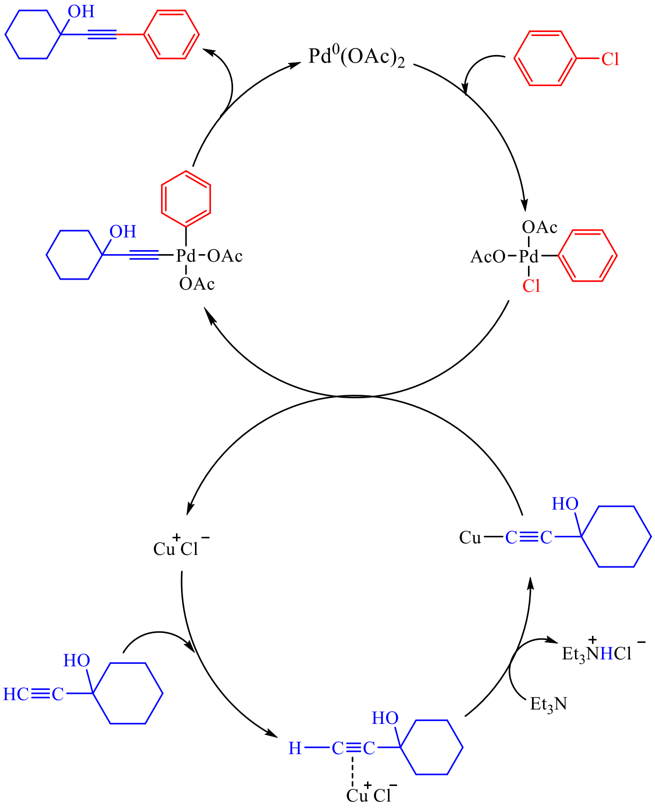
Jarayonda ikkinchi katalitik siklda aril guruh ta'sirida $Pd(OAc)_2$ ning oksidlanishidan Pd atomining +2 oksidlanish darajadan +4 oksidlanish darajaga o'tadi va natijada aril va xlorni o'ziga biriktiradi.



Keyingi bosqichda mis(I)-atsetilenid ta'sirida palladiyning valentligi Pd^0 gacha qaytarilib, so'ngra eliminirlanishidan internal aromatik atsetilen spirti - 1-(feniletinil)siklogeksanol-1 ajralib chiqadi va katalitik sikl yana qayta davom etadi.



Sonogashira kross-birikish reaksiyasi mexanizmini katalitik sikl ko'rinishida tasvirlash taklif etildi.



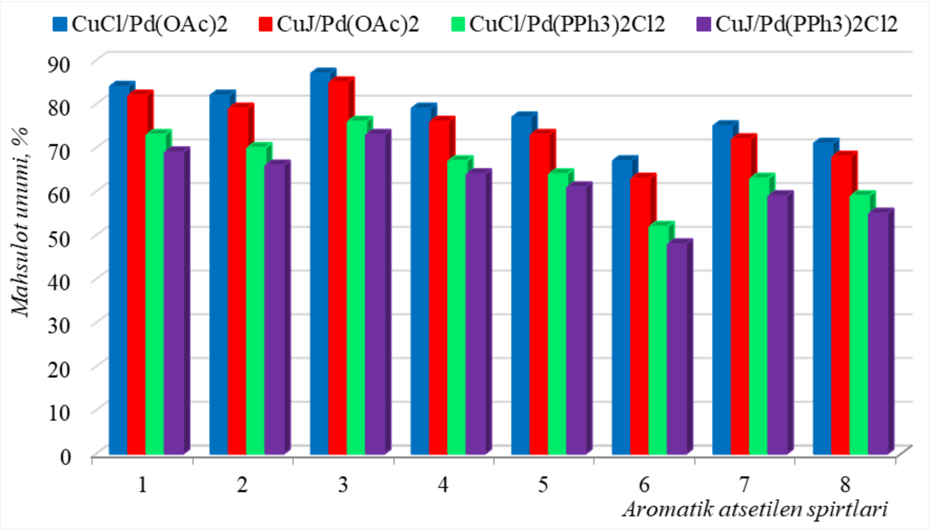
Internal aromatik atsetilen spirtlarining unumiga harorat, reaksiya davomiyligi, erituvchi, katalizator tabiati hamda boshlang'ich moddalar mol nisbatlari ta'siri tizimli tahlil qilindi. Bunda dastlab terminal atsetilen spirtlarning xlorbenzol bilan reaksiyasi uchun $CuJ/Pd(OAc)_2$, $CuCl/Pd(OAc)_2$, $CuCl/Pd(PPh_3)_2Cl_2$, $CuJ/Pd(PPh_3)_2Cl_2$ katalizatorlari ishtirokida ilmiy tadqiqot jarayoni olib borildi (1-rasm).

Rasmdan ko‘rinib turibdiki, tanlangan katalizatorlar ichida mahsulot unumi eng yuqori, qo‘shimcha mahsulotlar miqdori eng kam hosil bo‘lishi reaksiya $CuCl/Pd(OAc)_2$ katalitik sistemada olib borilganda kuzatildi. Bizga ma’lumki, nukleofil birikish reaksiyalarida karbanionni nukleofillinigi oshirish orqali yuqori unumni ta’minlash uchun ishqoriy muhit talab etiladi. Tadqiqotda nisbatan kuchli kislota hisoblangan CuJ dan foydalanilganda muhitning ishqoriyligi pasayishi, oraliq (alkogolyatlar) va qo‘shimcha (kompleks birikmalar) birikmalarning miqdori ortishi hisobiga aromatik atsetilen spirtlari unumi selektivligi pasayishi aniqlandi. Kross-birikish reaksiyasi $CuCl/Pd(PPh_3)_2Cl_2$ katalitik sistemada olib borilganida mahsulot unumi keskin pasayishi (1– 84 dan 73% ga, 2 – 82 dan 70% ga, 3 – 87 dan 76% ga, 4 – 79 dan 67% ga, 5 – 77 dan 64% ga, 6 – 67 dan 52% ga, 7 – 75 dan 63% ga, 8 – 71 dan 59% ga) kuzatildi. Bunga sabab molekuladagi Pd ga birikkan trifenilfosfin hamda xlor radikali hisobiga unga substratni birikishi uchun fazoviy to‘silganligini keltirishimiz mumkin.

Kross-birikish jarayoni uchun erituvchilar ta’siri tahlil qilindi. Qutbli aproton erituvchilar – atsetonitril (MeCN), dixlorometan (CH_2Cl_2), atseton (ASE) hamda tetragidrofuran (TGF) ishtirokida olib borildi va mahsulot unumi samaradorligiga ta’siri o‘rganildi va olingan natijalar 1-jadvalda keltirildi.

Foydalanilgan qutbli aproton erituvchilar S_N2 reaksiyalari uchun qulay sharoitni namoyon qilsada, ammo nisbatan mahsulot unumining $MeCN/H_2O$ da yuqori ekanligi tahlil natijalari asosida aniqlandi. Sistemada erituvchi sifatida suvdan ham foydalanishga sabab katalizatorning erishi va dissotsiyalanish darajasini oshirishga qaratilgan. Natijada katalizator faolligining ortishi, jarayonning borishi uchun yuqori haroratni talab etmasligiga olib keldi. Adabiyot manbaalaridan ma’lumki, Sonogashira reaksiyalari 80-140 °C harorat oralig‘ida amalga oshirilgan. Ushbu jarayon quyidagicha izohlanadi:

-MeCN va TGF bipolyar aproton eritu-



1-Rasm. Internal aromatik atsetilen spirtlari unumiga katalizator tabiati ta’siri (reaksiya davomiyligi 8 soat, harorat 40 °C, erituvchi MeCN).

1-Jadval

Internal aromatik atsetilen spirtlari unumiga erituvchilar tabiatining ta’siri (reaksiya davomiyligi 8 soat, harorat 40 °C, katalizator $CuCl/Pd(OAc)_2$)

Internal atsetilen spirtlari	Mahsulot unumi, %							
	1	2	3	4	5	6	7	8
$MeCN/H_2O$	84	82	87	79	77	67	75	71
CH_2Cl_2/H_2O	67	65	70	57	55	49	54	51
ASE/H_2O	61	59	54	51	49	42	49	45
TGF/H_2O	72	70	75	67	63	53	63	59

vchilar Sonogashira reaksiyalarining borishini osonlashtirdi. Buning boisi o‘rganilganda, har ikkala erituvchilar suv bilan juda yaxshi aralashishi, shuningdek, ham qutbli, ham qutbsiz moddalarni yaxshi erita olishi, sistemadagi protonni o‘ziga biriktirishi orqali, muhitning ishqoriyligi yanada oshirishi natijasida reaksiyaning borishini tezlashtirdi. Ammo MeCN ga nisbatan TGF da qutblilik nisbatan quyi ko‘rsatkich namoyon qilganligi bois mahsulot unumida pasayish kuzatildi.

-Dixlorometan va atsetonda ham MeCN ga nisbatan past mahsulot unumini namoyon qildi. Chunki, ularning mos ravishda trietilamin va terminal atsetilen spirt bilan qo‘shimcha reaksiya borishi aniqlandi.

-MeCN ning boshqa erituvchilarga qaraganda palladiy (II)-tuzlarini juda yaxshi eritib, suspensiya hosil qilishi aniqlandi hamda uning dielektrik konstantasi (ε= 37) va dipol momenti (3,92 D) yuqori bo‘lganligi sababli, internal aromatik atsetilen spirtlar sintez qilishda eng yuqori mahsulot unumini (1 – 84%, 2 – 82%, 3 – 87%, 4 – 79%, 5 – 77%, 6 – 67%, 7 – 75% va 8 – 71%) berdi.

-Atsetonning ko‘pgina ketonlar singari keto va enol tautomeriyasi mavjud bo‘lishi, uning eritmadagi ionlarning fazoviy to‘qnashuvlar sonining kam bo‘lganligi, shuningdek, dipol momenti miqdori ham kichikligi sababli reaksiyada mahsulot unumining pasayishiga olib keladi.

-TGF dielektrik o‘tkazuvchanlik konstantasi past bo‘lganligi (ε= 7,6), alkin ionlarning ketonlar bilan fazoviy to‘qnashuvlar sonining yetarlicha bo‘lmasligi oqibatida unumning pasayishiga sabab bo‘ladi.

Sonogashira reaksiyasi mahsulot unumdorligiga haroratning ta’siri 20÷60 ^{o}C interval oralig‘ida o‘rganildi. (2-jadval).

Reaksiya $CuCl/Pd(OAc)_2/Et_3N$ katalitik sistemasida 40 ^{o}C da 8 soat davomida olib borilganda internal aromatik atsetilen spirtlari yuqori unumda chiqishi kuzatildi. Kuzatilgan reaksiya jarayonlaridan ma’lum bo‘ldiki, jarayon 20 ^{o}C harorat oraliqda olib borilganda reaksiyaga kirishmasdan qolgan boshlang‘ich mahsulotlarni yupqa qatlamli xromatografiyada aniqlandi, bu esa molekulalarning to‘liq ionlarga dissotsiyalanishi amalga oshmaganligi mahsulot unumining yuqori bo‘lmasligiga sabab bo‘lgan.

Jarayon 60 ^{o}C gacha oshirilganda sistemada tanlangan palladiy (II) atsetatning boshlang‘ich reagentlar bilan qo‘shimcha mahsulotlar hosil bo‘lishi, aromatik atsetilen spirtlari o‘zaro birikib yenindiollar hosil qilishi, polimerlanishi natijasida smolasimon mahsulotlarning paydo bo‘lishi mahsulot unumining keskin pasayishiga olib keldi.

Aromatik atsetilen spirtlarining unumiga reaksiya davomiyligining ta’siri 6-10 soat oralig‘ida tahlili amalga oshirildi (2-jadvalda keltirilgan). Bunda harorat 40 ^{o}C, erituvchi atsetonitril muhitida 6 soat davomida olib borilganda, boshlang‘ich reagent (1-etinilsiklogeksanol) va substrat (xlorbenzol) o‘zaro

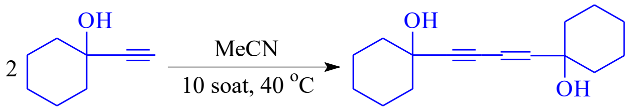
2-Jadval

Internal aromatik atsetilen spirtlari unumiga harorat ta’siri (reaksiya davomiyligi 8 soat, katalizator $CuCl/Pd(OAc)_2$, erituvchi MeCN)

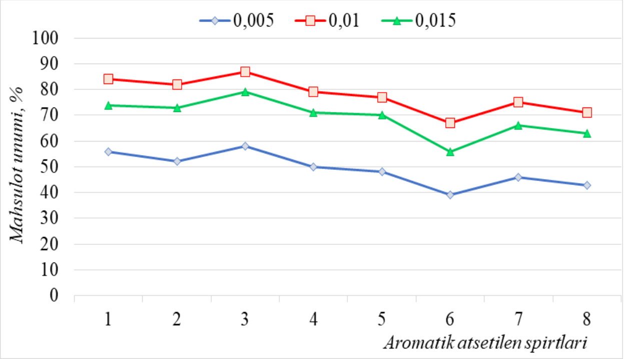
Reaksiya davomiyligi, soat	Harorat, ^{o}C	Mahsulot unumi, %							
		1	2	3	4	5	6	7	8
6	20	61	58	66	56	54	45	54	49
	40	69	66	73	64	62	52	61	57
	60	56	51	59	51	48	38	48	43
8	20	77	74	80	71	69	58	67	63
	40	84	82	87	79	77	67	75	71
	60	71	68	75	66	63	52	62	59
10	20	69	66	72	63	61	52	60	56
	40	76	74	80	71	70	59	68	64
	60	62	61	67	56	54	43	56	51

to‘liq reaksiyaga kirishmasdan qolganligini yupqa qatlamli xromatografiya analizi orqali aniqlandi, shu sababli ham samarali mahsulot unumiga erishilmagan. Reaksiya 8 soat davomida olib borilganida to‘liqroq ohirigacha borganligini fizik-kimyoviy tahlil natijalari ko‘rsatdi, bu esa boshlang‘ich moddalar MeCN da to‘liq erib, yuqori darajada dissotsiyalanishni namoyon qilganligi, xlorbenzol ta’sirida Pd(OAc)$_2$ ning oksidlanishidan Pd atomining +2 oksidlanish darajadan +4 oksidlanish darajaga o‘tishi va natijada aril va xlorni o‘ziga biriktirishi ya’ni “oksidlab birikish” bosqichi uchun hamda chiqib ketuvchi xlor molekulasini mis (I) atsetilenidning karbanion qismiga almashinishi natijasida palladiyning valentligi Pd^0 gacha qaytarilib, so‘ngra eliminirlanishi uchun optimal davr bo‘lganligi, internal aromatik atsetilen spirtlarining unumini ya’ni, 1- 69 dan 84% ga, 2- 66 dan 82% ga, 3- 73 dan 87% ga, 4- 64 dan 79% ga, 5- 62 dan 77% ga, 6- 52 dan 67% ga, 7- 61 dan 75% ga, 8- 57 dan 71% ga o‘shishiga olib kelgan.

Reaksiya davomiyligini 10 soatga oshirganimizda murakkab alkogolyatlar, poliatsetilen spirtlar, enindiollar, smolasimon va polimer mahsulotlar hosil bo‘lishi natijasida aromatik atsetilen spirtlari unumida pasayish kuzatildi. Masalan, sistemadagi 1-etinilsiklogeksanolning o‘zaro birikishi asosida qo‘shimcha mahsulot sifatida 1,1'-(1-buten-3-diil) disiklogeksanol-1) hosil bo‘lishi natijasida asosiy mahsulot unumining pasayishiga olib keladi.



Unga ko‘ra katalizator miqdori 0,005 mol olinganda aromatik atsetilen spirtlari hosil bo‘lish unumining pastligi, bunga katalitik faol markazlarning kam hosil bo‘lishi hamda reaksiyaning faollanish energiyasining yuqoriligi sabab sifatida keltirish mumkin. Katalizator miqdori 0,01 mol olinganda esa eng yuqori unum ko‘rsatkichini hosil qildi, ammo katalizatorning yanada oshirish reaksiya selektivligini pasayishiga sabab bo‘ldi. Ta’kidlab o‘tish joizki, miqdorning oshirilishi sistemada qo‘shimcha reaksiyalarning borishi, ya’ni sintez bo‘lgan internal atsetilen spirtlarining ortiqcha katalizatorlar bilan ta’sirlashib alkogolyatlar hosil qilishi shuningdek, polimer mahsulotlarga aylanishi tahlil natijalari orqali aniqlangan.



2-Rasm. Atsetilen diollari unumiga katalizator miqdori ta’siri (harorat 40 ^{o}C, erituvchi MeCN, reaksiya davomiyligi 8 soat, terminal atsetilen spirt: xlorbenzol 1,5:1 mol nisbatda).

Olib borilgan tadqiqot natijalariga ko‘ra, tanlangan terminal atsetilen spirtlarini xlorbenzol bilan Sonogashira birikish reaksiyasi CuCl/Pd (OAc)$_2$/Et$_3$N katalitik sistema yordamida (CuCl:Pd (OAc)$_2$:Et$_3$N o‘zaro ekvimolyar nisbatda) MeCN eritmasida, 8 soat davomida, 40 ^{o}C haroratda olib borilganda internal aromatik atsetilen spirtlari eng yuqori unum (1- 84%, 2- 82%, 3- 87%, 4- 79%, 5- 77%, 6- 67%, 7- 75%, 8- 71%) bilan sintez qilindi va jarayon uchun muqobil sharoit qilib tanlandi.

Sintez qilingan atsetilen diollarining tozaligi, tarkibi, tuzilishi va xususiy xossalari zamonaviy IQ-, ^{1}H-YAMR, ^{13}C-YAMR spektroskopiya, mass spektrometriya, xromatografik (YUQX, KX), kvant-kimyoviy, biologik va boshqa fizik-kimyoviy tadqiqot usullari yordamida tahlil qilindi. Xususiy konstantalari aniqlandi, energetik va kvant-kimyoviy kattaliklari hisoblandi, molekuladagi atomlar zaryadlari, elektronlar zichligi va optik taqsimlanishi kabi xossalari maxsus dasturlar asosida tadqiq qilindi.

Xulosa

Ilk bor turli xil tabiatga ega bo‘lgan terminal atsetilen spirtlarining xlorbenzol bilan Sonogoshira birikish reaksiyasi asosida internal aromatik atsetilen spirtlari- 3,4-dimetil-1-fenilpentin-1-ol-3, 3,4,4-trimetil-1-fenilpentin-1-ol-3, 1-(2-feniletinil) siklogeksanol, 2-(1-feniletinil)adamantanol-2, 2,4-difenilbutin-3-ol-2, 2-(naftil-2)-4-fenilbutin-3-ol-2, 2 -(furanil-2)-4-fenilbutin-3-ol-2 va 4-fenil-2-(piridinil -4)butin-3-ol-2 sintezi qilingan.

Mahsulot unumiga harorat, reaksiya davomiyligi, erituvchilar, katalizator, reagent va substratlarning tabiati va miqdorlari ta’siri o‘rganilgan. Tadqiqotlar tahlili natijasida jarayon uchun muqobil sharoit topilgan va reaksiya jarayonining mexanizmi ishlab chiqilgan. Sintez qilingan internal aromatik atsetilen spirtlarining tarkibi, tozaligi va tuzilishi zamonaviy fizik-kimyoviy usullarda isbotlangan.

Terminal atsetilen spirtlar molekulasidagi o‘rinbosarlarning tabiati va ularning fazoviy ta’sir etish xossasiga ko‘ra reaksiya borishi va mahsulot unumiga ta’sir etish qonuniyati topildi, unga ko‘ra 2-(naftil-2)butin-3-ol-2 < 2-(piridinil-4)butin-3-ol-2 < 2-(furanil-2)butin-3-ol-2 < 2-fenilbutin-3-ol-2 < 2-etiniladamantanol-2 < 3,4,4-trimetilpentin-1-ol-3 < 3,4-dimetilpentin-1-ol-3< 1-etinilsiklogeksanol bo‘yicha etinillash reaksiyasini samaradorligi oshib borishi aniqlangan.

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