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ALKYNYLATION OF BENZALDEHYDE AND SOME OF ITS DERIVATIVES WITH 4-ETHYNYL-*p*-AMINOPHENYLACETYLENE

Annotation

In this work, for the first time, a method for the synthesis of acetylenic alcohols containing various substituents in the molecule has been developed based on the reactions of benzaldehyde and some of its homologues with 4-ethynyl-*p*-aminophenylacetylene using a $Rh_2(AcO)_4 \cdot 2H_2O/Et_2O/Et_3N$ complex catalytic system. The influence of the nature of radicals in the aldehyde molecules on the yield and course of the reaction was determined. The effects of the complex catalytic system on the selectivity, activation energy, and thermodynamics of the reaction were studied, and the reaction mechanisms and process scheme were proposed. The physicochemical constants, structure, composition, and quantum chemical calculations of the synthesized compounds were confirmed using modern physicochemical research methods.

Key words: benzaldehyde, 4-ethinyl-p-aminophenylacetylene, acetylene alcohols, catalytic system, solvent nature, reaction mechanism, product yield.

АЛКИНИЛИРОВАНИЕ БЕНЗОЛЬДЕГИДА И НЕКОТОРЫХ ЕГО ПРОИЗВОДНЫХ С УЧАСТИЕМ 4-ЭТИНИЛ-*п*-АМИНОФЕНИЛАЦЕТИЛЕНА

Аннотация

В данной работе впервые разработан метод синтеза ацетиленовых спиртов, содержащих различные заместители в молекуле, на основе реакций бензальдегида и некоторых его гомологов с 4-этинил-*п*-аминофенилацетиленом с использованием комплексной каталитической системы $Rh_2(AcO)_4 \cdot 2H_2O/Et_2O/Et_3N$. Установлено влияние природы радикалов в молекулах альдегидов на выход и течение реакции. Изучено влияние комплексной каталитической системы на селективность реакции, энергию активации и термодинамику, предложены механизм реакции и схема процесса. Физико-химические константы, структура, состав и квантово-химические расчёты синтезированных соединений подтверждены с использованием современных физико-химических методов исследования.

Ключевые слова: бензалдегид, 4-этинил-*p*-аминофенилацетилен, ацетиленовые спирты, каталитической системы, природа растворителя, механизм реакции, выход продукта.

BENZALDEGID VA UNING AYRIM HOSILALARINI 4-ETINIL-*p*-AMINOFENILATSETILEN ISHTIROKIDA ALKINILLASH

Annotatsiya

Ushbu ishda ilk bor $Rh_2(AcO)_4 \cdot 2H_2O/Et_2O/Et_3N$ kompleks katalitik sistemasi yordamida benzaldegid va uning ayrim gomologlarining 4-etinil-*p*-aminofenilatsetilen bilan reaksiyalari asosida molekulasida turli xil o‘rinbosarlar saqlagan atsetilen spirtlarini sintez qilish usuli ishlab chiqilgan. Tanlangan aldegidlar molekulasidagi radikallar tabiatining mahsulot unumi va reaksiya borishiga ta’siri aniqlangan. Kompleks katalitik sistemaning reaksiya selektivligi, faollanish energiyasi va termodinamikasiga ta’siri o‘rganilgan, jarayonning ximizmi va reaksiya mexanizmlari taklif etilgan. Sintez qilingan birikmalarning hususiy konstantalari, tuzilishi, tarkibi va kvant-kimyoviy hisoblashlari zamonaviy fizik-kimyoviy tadqiqot usullari yordamida isbotlangan.

Kalit so‘zlar: benzaldegid, 4-etinil-*p*-aminofenilatsetilen, atsetilen spirtlari, katalitik sistema, erituvchi tabiati, reaksiya mexanizmi, mahsulot unumi.

Kirish. Neft va tabiiy gazni qayta ishlash asosida hosil bo‘ladigan oraliq va ikkilamchi mahsulotlardan maqsadli qo‘llanilishi mumkin bo‘lgan yangi avlod organik moddalarni sintez qilish texnologiyalarini ishlab chiqish dolzarb muammolardan hisoblanadi [1]. Jumladan, dunyoda turli xil organik birikmalarning atsetilen uglevodorodlari bilan reaksiyalari yordamida kimyo, farmatsevtika, elektrotexnika va to‘qimachilik sanoati uchun resurs tejamkor, ekologik toza va arzon kimyoviy preparatlarga bo‘lgan ehtiyoj ortib bormoqda [2, 3]. Mamlakatimizda mahalliy mineral xom ashyo resurslarini chuqur qayta ishlash, sohaga xorijiy investitsiya va zamonaviy texnologiyalarni jalb etish, qurilish materiallari, farmatsevtika, to‘qimachilik, mashinasozlik kabi tarmoqlar uchun zarur bo‘lgan polimerlar, katalizatorlar, reagentlar va sintetik tolalar ishlab chiqarish, mahsulot hajmi va turini ko‘paytirish, sohaning eksport salohiyatini oshirish kabi muhim va ustuvor vazifalar belgilab berilgan [4, 5].

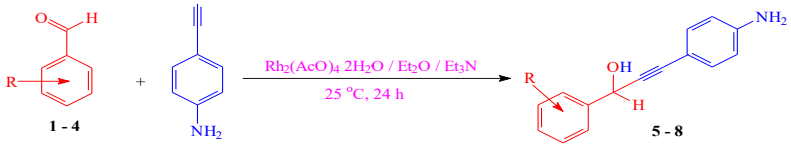
Mavzuga oid adabiyotlar tahlili. Ohirgi yillarda atsetilen birikmalar kimyosi, jumladan turli hil tabiatga ega bo‘lgan atsetilen spirtlarini sintez qilish ustida ilmiy tadqiqotlar rivojlanmoqda. Jumladan, aromatik alkinlarni 100 ºC haroratda Rongalit ishtirokida ishqoriy muhitda gidroliz qilish orqali 62-83% unum bilan atsetilen spirtlari sintez qilingan. Jarayon Rongalit molekulasidagi uglerod atomiga terminal alkinlarning to‘g‘ridan-to‘g‘ri nukleofil hujumi ta’sirida borishi bilan klassik usullardan keskin farq qilishi keltirilgan [6]. Bifunksional kompleks katalitik sistema $InBr_3$/BINOL/Cy_2NMe/CH_2Cl_2 ishtirokida alifatik, aromatik va siklik aldegidlarni assimetrik alkinillash orqali atsetilen spirtlari sintez qilingan. Ushbu katalizator substrat va reagentni bir vaqtda katalitik faollashtirishi bilan boshqa usullarga nisbatan samarali hisoblangan [7]. Bir qator α, β to‘yinmagan alifatik aldegidlarga 1,3-diinlarni toluol eritmasida ruh alkilatlar va aminokislotalar asosida tayyorlangan katalitik sistemalr yordamida alkinillash reaksiyalari bo‘yicha diatsetilen spirtlari olingan [8]. Misning kompleks tuzlari yordamida alkinil bromidlarga In, Sb, Pb, Ti, Cr, Ga, Sn, Zn metallarini ta’sir ettirish orqali olingan atsetilenidlarning Mn tuzlari katalizatori ishtirokida molekulasida aril va geteril o‘rinbosarlar bo‘lgan aldegidlar bilan transformatsiyalash orqali alkinil va allenil spirtlari olingan [9].

Tadqiqot metodologiyasi. Atsetilen spirtlarini sintez qilish reaksiyasi haroratga bardoshli maxsus tayyorlangan 50 ml bo‘lgan flakonda amalga oshirildi. Dastlab flakonda 0,88 mg rodiy (II) atsetat (0,002 mmol) va 21,2 mg benzaldegid (**1**) (0,2 mmol) shlenka trubkasi orqali solindi va suspenziya tayyorlab olindi. So‘ngra ushbu suspenziyaga 0,4 ml dietilefir, 4,08 mg trietilamin (0,04 mmol) va 70,2 mg 4-etinil-*p*-aminofenilatsetilen (0,6 mmol) shprits orqali yuborildi. Barcha reagentlar flakonga solingandan keyin xona haroratida 24 soat davomida o‘zaro aralashtirildi. Flakonda hosil bo‘lgan aralashma 3 ml dixlormetan bilan suyultirildi va unga 150 mg silikagel qo‘shildi. Aralashma tarkibidan erituvchi dietilefir past bosimda haydash orqali ajratib olindi va qoldiq massa, ya’ni organik qatlam tarkibidan mahsulotni tozalab olish uchun silikagel 60 kolonkali xromatografiyada elyuentlardan (geksan/EtOAc 20:1) o‘tkazildi. Natijada 37 mg, (0,17 mmol) 3-(4-aminofenil)-1-fenilpropin-2-ol-1 (**5**) 83% unum bilan (R_f=0.47, T_q= 107-108 ºC, sariq rangli suyuqlik) ajratib olindi.

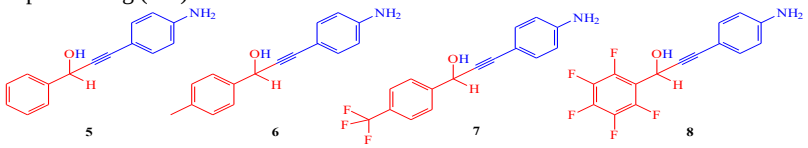
Ushbu usul bo‘yicha 4-metilbenzaldegid (**2**), 4-(triftormetil)-benzaldegid (**3**) va 2,3,4,5,6-pentaftorbenzaldegid (**4**) ni 4-etinil-*p*-aminofenilatsetilen bilan alkinillash reaksiyasi orqali quyidagi atsetilen spirtlari– 80% unum bilan 3-(4-aminofenil)-1-(*p*-tolil)propin-2-ol-1 (**6**, R_f=0.52, T_q= 121-122 ºC, och sariq rangli suyuqlik), 89% unum bilan 3-(4-aminofenil)-1-(3-(triftormetil)fenil)propin-2-ol-1 (**7**, R_f=0.48, T_q= 156-157 ºC, och jigarrang, moysimon suyuqlik) va 74% unum bilan 3-(4-aminofenil)-1-(perftorfenil)propin-2-ol-1 (**8**, R_f=0.45, T_q= 123-124 ºC, sariq rangli suyuqlik) sintez qilindi [10-12].

Tahlil va natijalar. Ushbu ishda ilk bor benzaldegid va uning ayrim gomologlari, jumladan, 4-metilbenzaldegid, 4-(triftormetil)-benzaldegid va 2,3,4,5,6-pentaftorbenzaldegidning $Rh_2(AcO)_4{\cdot}2H_2O$/Et_2O/Et_3N kompleks katalitik sistemasida 4-etinil-*p*-aminofenilatsetilen bilan alkinillash reaksiyalari bo‘yicha bir qancha reaksion faol markazlarga ega bo‘lgan atsetilen spirtlari sintezi o‘rganilgan.

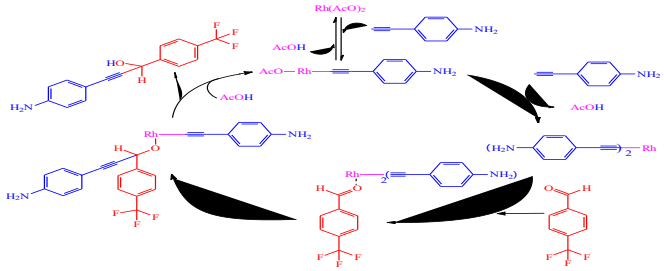
Adabiyot manbalari asosida 4-etinil-*p*-aminofenilatsetilen ishtirokida tanlangan aldegidlarni alkinillash reaksiyasi sxemasi quyidagicha taklif qilindi [13, 14].



Sintez qilingan atsetilen spirtlarining (**5-8**) tuzilish formulalari.



Reaksiya mexanizmi: Jarayonda dastlab katalizator sifatida tanlangan rodiy (II) atsetat kristallogidrati dietilefir eritmasida alkinillovchi agent 4-etinil-*p*-aminofenilatsetilen bilan ta’sirlashib, sistemada stabilligi yuqori bo‘lgan oraliq katalitik komponent (aminoalkinilrodiyatsetat) hamda katalizator molekulasidan ajralgan bir molekula atsetat ioni va alkinning harakatchan vodorod o‘zaro ta’sirlashib AcOH hosil qiladi. So‘ngra oraliq katalitik komponent koordinatsiyaga uchrab, ya’ni uning molekulasidan atsetat ionini alkinillovchi agent siqib chiqarishi natijasida to‘yinmagan oraliq kompleks (bisaminoalkinilrodiy) sistemada barqaror holatga keladi. Jarayonning keyingi bosqichida oraliq kompleksga reaksion qobiliyati yuqori bo‘lgan 4-(triftormetil)benzaldegid ta’sir qilishi mumkin. Bunda aldegid molekulasida elektronlar nisbiy elektormanfiyligi yuqori bo‘lgan kislorod atomi tomon siljiganligi sababli kislorodda elektron zichlikning yuqori bo‘lishi hisobiga uning nukleofillik xossasining oshishi hamda karbonil guruhining qutblanishi ortishi natijasida oraliq kompleksga kuchli ta’sir qilib, dastlab murakkab modifikatsiyali oraliq katalitik fragmentga, so‘ngra diaminoalkinilrodiyalkoksidni hosil qilishi mumkin. Sistemada hosil bo‘lgan alkoksid trietilamin yordamida sirka kislotaning ta’siri natijasida 3-(4-aminofenil)-1-(3-(triftormetil)fenil)propin-2-ol-1 va aminoalkinilrodiyatsetatga aylanishi mumkinligi to‘g‘risida taklif kiritildi [15-17].



Tadqiqot natijalari asosida $Rh_2(AcO)_4{\cdot}2H_2O$/Et_2O/Et_3N kompleks katalitik sistemasi yordamida atsetilen spirtlarini sintez qilishda erituvchi roli, katalitik faol markaz va molekulalarni hosil bo‘lishi, benzaldegid va uning R-almashgan hosilalari tabiati,

molekula tuzilishi, massasi, radikallarning fazoviy ta’siri, simmetrik yoki nosimmetrik holati, elektron bulutlar zichligi va joylashuvi, reaksiyada karbokation va karboanionlar hosil bo‘lish davri kabi omillar ta’siri tizimli ravishda o‘rganildi.

$Rh_2(AcO)_4 \cdot 2H_2O/Et_2O/Et_3N$ katalitik sistemasida 4-etinil-*p*-aminofenilatsetilen va tanlangan aldegidlar asosida atsetilen spirtlarini sintez qilish jarayonining eng muqobil sharoiti topildi. Unga ko‘ra benzaldegid va uning R-almashgan hosilalarining 4-etinil-*p*-aminofenilatsetilen bilan nukleofil birikish reaksiyalari dietilefir eritmasida, 24 soat davomida, 25 ^oC haroratda, boshlang‘ich moddalar (aldegid:alkin) 1:3 mol nisbatda hamda $Rh_2(AcO)_4 \cdot 2H_2O/Et_3N$ komponentlari 1:20 mol miqdorda olinganda atsetilen spirtlarini maksimum unum bilan sintez qilindi.

Sintez qilingan birikmalarning tuzilishi fizik-kimyoviy tadqiqot usullari yordamida tahlil qilindi.

5– ^{1}H YaMR (400 MHz, $CDCl_3$) δ 7.50 - 7.09 (m, 7H), 6.60 - 6.27 (m, 2H), 5.70 (dd, *J* = 29.9, 6.6 Hz, 2H), 4.81 (s, 2H).

^{13}C YaMR (125 MHz, $CDCl_3$) δ 150.27 (C), 139.45 (C), 132.97 (C), 129.15 (C), 129.09 (C), 129.03 (C), 128.71 (C), 127.22 (C), 114.05 (C), 113.99 (C), 111.57 (C), 108.55 (C), 90.64 (C), 89.60 (C), 65.70 (C).

6– ^{1}H YaMR (400 MHz, $CDCl_3$) δ 7.41 - 7.22 (m, 4H), 7.15 (s, 2H), 6.56 (s, 2H), 5.70 (s, 1H), 5.47 (s, 1H), 4.91 (d, *J* = 5.7 Hz, 2H), 2.34 (s, 3H).

^{13}C YaMR (125 MHz, $CDCl_3$) δ 148.19 (C), 137.59 (C), 134.36 (C), 132.98 (C), 130.36 (C), 129.37 (C), 127.16 (C), 124.06 (C), 120.14 (C), 114.01 (C), 111.65 (C), 105.24 (C), 96.70 (C), 90.70 (C), 88.52 (C), 68.15 (C).

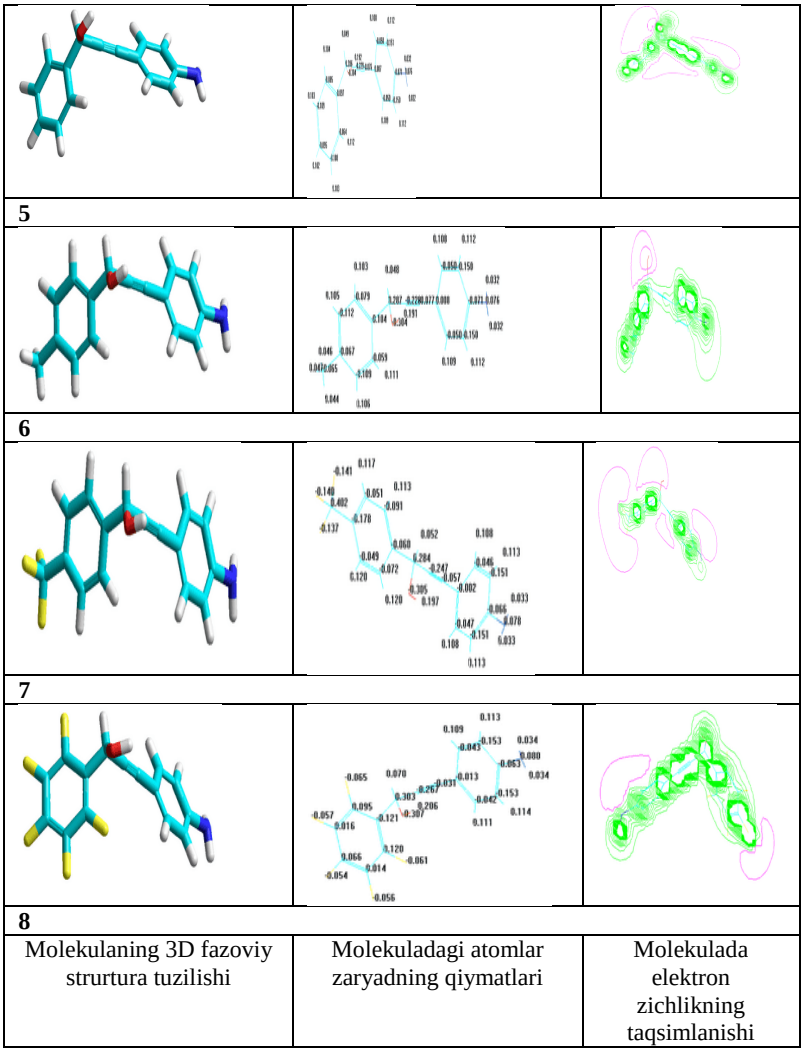
7– ^{1}H YaMR (400 MHz, $CDCl_3$) δ 7.75 - 7.65 (m, 2H), 7.51 - 7.37 (m, 2H), 7.38 - 7.22 (m, 2H), 6.54 - 6.39 (m, 2H), 5.85 (d, *J* = 6.5 Hz, 1H), 5.48 (d, *J* = 6.2 Hz, 1H), 4.90 (s, 2H).

^{13}C YaMR (125 MHz, $CDCl_3$) δ 155.71 (C), 147.71 (C), 142.55 (C), 139.42 (C), 132.98 (C), 131.56 (C), 128.47 (C), 125.24 (C), 123.10 (C), 114.57 (C), 111.54 (C), 107.46 (C), 94.75 (C), 88.52 (C), 78.02 (C).

8– ^{1}H YaMR (400 MHz, $CDCl_3$) δ 7.40 - 7.16 (m, 2H), 6.53 - 6.39 (m, 2H), 6.13 (d, *J* = 6.8 Hz, 1H), 5.36 (d, *J* = 6.7 Hz, 1H), 4.91 (s, 2H).

^{13}C YaMR (125 MHz, $CDCl_3$) δ 156.09 (C), 147.67 (C), 145.70 (C), 143.66 (C), 141.06 (C), 139.98 (C), 136.87 (C), 132.96 (C), 113.58 (C), 111.61 (C), 107.14 (C), 101.12 (C), 92.28 (C), 90.53 (C), 90.49, 89,14 (C), 61.59 (C).

Sintez qilingan atsetilen spirtlarining kinetik o‘zgarishlari, molekulalarining fazoviy tuzilishi, molekulalarda zaryadlar va elektron zichlikning taqsimlanishi hamda kvant-kimyoviy ko‘rsatkichlari zamonaviy dasturlar asosida hisoblandi.



1-Rasm. Atsetilen spirtlarining ayrim fazoviy tuzilishlari

Xulosa va takliflar. Benzaldegid va uning R-almashgan hosilalarining 4-etinil-*p*-aminofenilatsetilen bilan reaksiyasi asosida 3-(4-aminofenil)-1-fenilpropin-2-ol-1, 3-(4-aminofenil)-1-(*p*-tolil)propin-2-ol-1, 3-(4-aminofenil)-1-(3-(triftormetil)fenil)-propin-2-ol-1 va 3-(4-aminofenil)-1-(perftorfenil)propin-2-ol-1 kabi yangi avlod atsetilen spirtlari sintez qilindi.

Ilk bor $Rh_2(AcO)_4 \cdot 2H_2O/Et_2O/Et_3N$ katalitik sistemasi yordamida aldegidlarning alkinlar bilan nukleofil birikish reaksiyasi amalga oshirildi.

Tanlangan aldegidlar tabiatining mahsulot unumi va reaksiya borishiga ta’siri asosida atsetilen spirtlarini sintez qilishning samaradorlik qatori ishlab chiqildi.

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