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**REACTIONS OF AMIDES OF 4-CARBOXYPYRIDINE WITH p-ANIZIDINE, p-BROMANILINE, 2,6-XYLIDINE, 2,4-DICHLORANILINES**

Annotation

Corresponding amides were synthesized from reactions of 4-carboxypyridic acid with p-anisidine, p-bromaniline, 2,6-xylidine, 2,4-dichloroanilines. The influence of the nature of the solvent on the course of the reactions was studied, and the results obtained from the reactions carried out in different solvents were compared. It was found that 4-carboxypyridine acid reacts with some aromatic amines to form amides when heated in non-polar solvents. The physical constants of the synthesized amides were determined. The structure of the reaction products was analyzed using IR- and 1N and 13S NMR spectroscopy methods.
**Key words:** 4-carboxypyridic p-anisidine, p-bromoaniline, 2,6-xylidine, 2,4-dichloroaniline amide, organic solvent.

**п- АНИЗИДИН, п- БРОМАНИЛИН 4-КАРБОКСИПИРИДИНА, РЕАКЦИИ 2,6-КСИЛИДИНА, 2,4-ДИХЛОРАНИЛИНОВ С АМИДАМИ**

Аннотация

Соответствующие амиды синтезированы реакциям 4-карбоксипиридина с п-анизидином, п-броманилином, 2,6-ксилидином, 2,4-дихлоранилинами. Изучено влияние природы растворителя на ход реакций и сопоставлены результаты, полученные в реакциях, проведенных в различных растворителях. Установлено, что 4-карбоксипиридин реагирует с некоторыми ароматическими аминами с образованием амидов при нагревании в неполярных растворителях. Определены физические константы синтезированных амидов. Строение продуктов реакции анализировали методами ИК- и ЯМР-спектроскопии 1Н и 13С.
**Ключевые слова:** п-анизидин4-карбоксипиридиновой, п-броманилин, 2,6-ксилидин, амид 2,4-дихлоранилина, органический растворитель**.**

**4-KARBOKSIPIRIDINNING p- ANIZIDIN, p- BROMANILIN, 2,6 –KSILIDIN, 2,4-DIXLORANILINLAR BILAN AMIDLARINI OLISH REAKSIYALARI**

Annotatsiya

4-Karboksipiridinning p-anizidin, p-bromanilin, 2,6-ksilidin, 2,4-dixloranilinlar bilan reaksiyalaridan tegishli amidlar sintez qilindi. Reaksiyalarning borishiga erituvchi tabiatining ta’siri o‘rganildi, turli erituvchilarda olib borilgan reaksiyalardan olingan natijalar taqqoslandi. 4-Karboksipiridinning ba’zi aromatik aminlar bilan reaksiyalaridan amidlarini hosil qilishi qutbsiz erituvchilarda qizdirilganda borishi aniqlandi. Sintez qilingan amidlarning fizik doimiyliklari aniqlandi. Reaksiya mahsulotlarining tuzilishi IQ- va $^{1}$H va $^{13}$C YAMR spektroskopiya usullari yordamida tahlil qilindi.
**Kalit so’zlar:** 4-Karboksipiridinovaya p-anizidin, p-bromanilin, 2,6-ksilidin, 2,4-dixloranilin, amid, organicheskiyrastvoritel.

**Kirish.** Aminlarni, xususan aromatik aminlarni karbon kislotalarning angidridlari va galogenangidridlari bilan N-asillash (benzoillash) reaksiyalaridan yuqori unumlar bilan kislota amidlarini olish mumkinligi adabiyot ma’lumotlaridan malum. Ammo, bugungi kunda har qanday organik moddani kam bosqichli reaksiyalar orqali, tayyor reagentlardan foydalangan holda sintez qilish yo‘llarini topish kimyogarlar oldidagi muhim vazifalardan biri hisoblanadi. Ta’kidlash kerakki, kislota amidlarining sintezida ham mazkur jihatlarga alohida e’tibor qaratilmoqda. Natijada amidlar sintezida asillovchi agentlar sifatida karbon kislotalarni to‘g‘ridan-to‘g‘ri qo‘llash orqali yuqori unum bilan mahsulot sintez qilishning samarali usullari ishlab chiqilmoqda va buni quyidagi muhim adabiyot ma’lumotlaridan ko’rish mumkin.

Karbon kislotalarning aminlar bilan reaksiyalarini o‘rganish bilan bog‘liq izlanishlarning natijalari reaksiyalarning oraliq protonlangan to‘rtlamchi ammoniy tuzlari hosil bo‘lishi bilan borishi, ma’lum sharoitda qizdirilganda kondensatlanishi natijasida kislota amidlari hosil bo‘lishini ko‘rsatadi [4-8, 1; 371-379 b., 2; 194-197 b., 3].

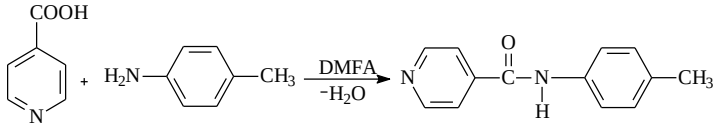
Adabiyotda ba’zi almashingan anilinlarning DMFA va DMSO bilan reaksiyasidan arilamidlar hosil bo‘lishi ta’kidlab o‘tilgan. Reaksiyalar HCl katalizatorligida yuqori unumlar bilan borishi aniqlangan [4; 114-119 b.].

Adabiyot ma’lumotlarida alifatik, aromatik, geterosiklik, birlamchi va ikkilamchi aminlarni DMFA bilan formillash nikel (II) xinazolon ishtirokida yuqori unum bilan borishi keltirib o‘tilgan va reaksiyaning mexanizmi katalitik sikl bilan borishi ko‘rsatib berilgan [5; 2078-2081 b.].

Almashingan fenilsirka kislotalarning benzilamin hosilalari bilan reaksiyasi turli nikel birikmalari ishtirokida olib borilganda quyidagicha katalitik faollik qatori aniqlangan: $NiCl_2$>$(CH_3COO)_2Ni$ >$Ni(asos)_2$>$NiCl_2(PPh_3)_2$>$NiCl_2{\cdot}6H_2O$

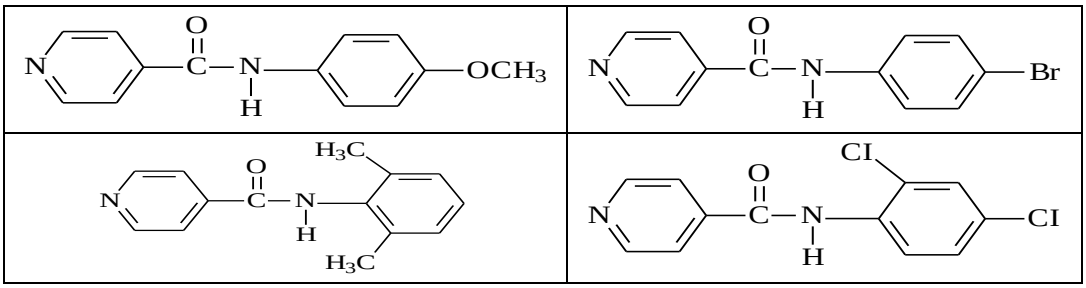
>katalizatorsiz. Bu jarayonda erituvchilar- dietil efiri, TGF, toluol, ftorbenzol, asetonitril, DMFA va DMSO ishlatilgan va toluolda eng yuqori unum (10 soatda 80%, 20 soatda 99,2%) ga erishilgan [80].

**Tajriba natijalari va tahlili.** Tajribalar uchun 4-karboksipiridinning, p-anizidin, p-bromanilin, 2,6-ksilidin, 2,4-dixloranilinlar tanlab olindi. Dastlab 4-Karboksipiridin kislotaning p-anizidin bilan reaksiyasini o‘rganishga bag‘ishlangan. 4-Karboksipiridin p-anizidin bilan reaksiyasini teskari sovutgich bilan jihozlangan kolbada DMFAning qaynash temperaturasida magnitliy aralashtirgichda katalizatorsiz 15 soatda olib borildi. Shu sababli DMFAda reaksiyalar yuqori haroratida reagentlarning 1:1 mol nisbatida olib borildi. Xuddi shu sharoitda DMFAda HCl katalizatorligida yuqori haroratida reagentlarning 1:1 mol nisbatida 7 soatda tegishli amidlarni sintez qilishga erishildi. Reaksiya quyidagi sxema bo‘yicha boradi.




Olingan mahsulotni 40% li etanol-suv aralashmasidan qayta kristallandi, kalsiy xloridli eksikatorda quritildi. Suyuqlanish harorati aniqlandi, IQ va YAMR spektri olindi hamda tozaligi YUQX usuli yordamida tekshirildi.

Mazkur usullar asosida 4-karboksipiridinning p-anizidin, p-bromanilin, 2,6-ksilidin, 2,4-dixloranilinlar bilan reaksiyalari olib borildi va amidlar olindi. Quyida sintez qilingan amidlarning tuzilishi keltirilgan:




**Tajriba natijalari quyida 1-jadvalda keltirilgan**.

| Boshlang‘ich amin | Mol nisbatlar* | Vaqt, soat | mahsulot unumi, % | | | Reaksiya mahsuloti | |
|---|---|---|---|---|---|---|---|
| | | | DMFA (153 °C) | Vaqt, soat | DMFA HCI | $T_c$, °C | $R_f$ |
| p-anizidin | 1:1,1:0,5 | 14 | **33** | **7** | **35** | **74-76** | **0,68** |
| p-bromanilin | 1:1,1:0,5 | 14 | **50** | **7** | **53** | **94-96** | **0,68** |
| 2,6-ksilidin | 1:1,1:0,5 | 14 | **34** | **7** | **36** | **158-160** | **0,62** |
| 2,4-dixloranilin | 1:1,1:0,5 | 14 | **40** | **7** | **43** | **146-148** | **0,52** |

Tajriba natijalari 4-Karboksipiridinning p-anizidin, p-bromanilin, 2,6-ksilidin, 2,4-dixloranilinlar bilan borgan ushbu reaksiyalarida mahsulotlar hosil bo‘lishi tezligi va unimi kislota hamda asosning kuchiga bog‘liq bo‘ladi. va natijalar nazariy xulosalarga mos keladi.

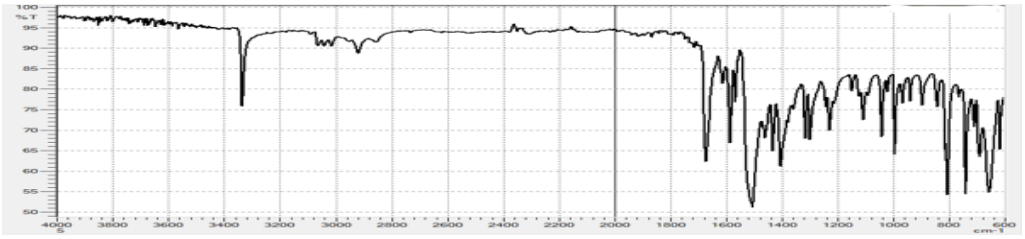
**Sintez qilingan birikmalarning tuzilishini o‘rganish.** Sintez qilib olingan amidlarning individualligi yupqa qatlamli xromatografiya (YuQX) usulida «Sorbfil» (Rossiya), «Whatman® UV-254» UV lampasida, Aluminum TLC plate F-254 (MFR: Qingdao Seeking Technology Co.,Ltd) plastinkalarida tekshirildi, elyuentlar sifatida esa benzol:atseton=3:1 nisbat-da ishlatildi. Sitez qilingan birikmalarning IQ spektrlari ATR tizimi yordamida FT-IR/NIR Spectrum 3 spektrometrida (Perkin Elmer, Shveytsariya) qayd etildi.$^1$H va $^{13}$C NMR spektrlari JNM-ECZ400R spektrometrida (JEOL, Yaponiya) CCl3D eritmalarida $^1$H uchun 400 MGts ish chastotasida qayd etilgan. TMS (0 ppm) $^1$H NMR spektrlarida ichki standart sifatida ishlatilgan. $^{13}$C NMR spektrlarida erituvchining kimyoviy silji-shi ($CCl_3D$, TMSga nisbatan 49,00 ppm) ichki standart sifatida ishlatilgan. Birikmalarning suyuqlanish haroratiBMP-1C modelida 220V/50Hz da (Xitoy) asbobida o’lchandi.

***N-(4-metoksifenil)-izonikotinamid***: 0,615 gr (0,005 mol) 4-karboksipiridin va 0,615 gr (0,005 mol) p-anizidin 0,365 gr (0,01 mol) HCI katalizator ishtirokida sintez qilindi. $R_f$=0,68, suyqlanish harorati $T_s$=74-76ºC. IQ spektr (KBr $sm^{-1}$) ν=3243 (-NH), δ=1545 (-NH), ν=1651(-CO-). $^1$H NMR (400 MHz, METHANOL-*D*$_4$) δ 8.19 (s, 1H), 7.51 – 7.43 (m, 2H), 7.10 (s, 0H), 6.88 (d, *J* = 22.5 Hz, 0H), 4.87 (s, 3H), 3.76 (s, 2H).$^{13}$C NMR (101 MHz, METHANOL-*D*$_4$) δ 165.28, 161.31, 158.85, 158.07, 132.23, 122.97, 122.02, 115.79, 115.04, 55.91.

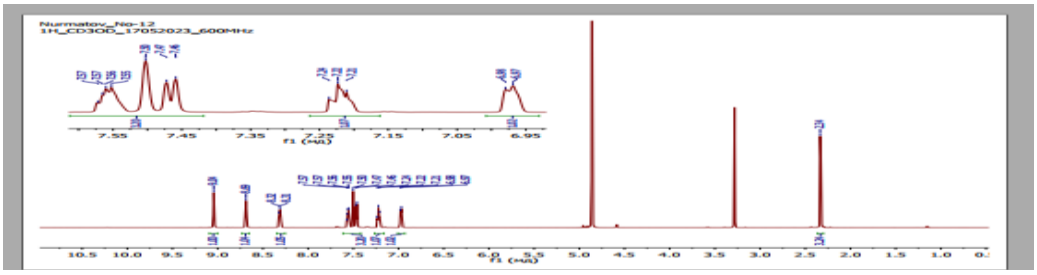
***N-(4-bromfenil)-izonikotinamid***: 0,615 gr (0,005 mol) 4-karboksipiridin va 0,86 gr (0,005 mol) p-bromanilin 0,365 gr (0,01 mol) HCI katalizator ishtirokida sintez qilindi. $R_f$=0,68, suyqlanish harorati $T_s$=94-96ºC. IQ spektr (KBr $sm^{-1}$) ν=3255 (-NH), δ=1532 (-NH), ν=1667(-CO-). $^1$H NMR (400 MHz, METHANOL-*D*$_4$) δ 8.70 (s, 1H), 8.27 (s, 3H), 7.94 (s, 1H), 7.57 – 7.40 (m, 13H), 7.10 (s, 0H), 1.28 (s, 1H), 0.99 – 0.83 (m, 2H).$^{13}$C NMR (101 MHz, METHANOL-*D*$_4$) δ 168.28, 161.61, 151.02, 138.29, 132.75, 124.77, 122.65, 117.79.

***N-(2,4-Dixlorfenil)-izonikotinamid*:** 0,615 gr (0,005 mol) 4-Karboksipiridin va 0,81 gr (0,005 mol) 2,4-dixloranilin 0,365 gr (0,01 mol) HCI katalizator ishtirokida sintez qilindi. $R_f$ = 0,52, suyqlanish harorati $T_s$=146-148°C. IQ spektr (KBr $sm^{-1}$) ν=3240 (-NH), δ=1518 (-NH), ν=1661 (-CO-).$^1$H NMR (400 MHz, METHANOL-*D*$_4$) δ 9.13 (s, 0H), 8.78 (s, 0H), 8.39 (s, 0H), 7.75 (s, 0H), 7.65 – 7.56 (m, 1H), 7.41 (dd, *J* = 8.7, 2.3 Hz, 1H).$^{13}$C NMR (101 MHz, METHANOL-*D*$_4$) δ 165.21, 162.07, 134.43, 131.07, 130.17, 129.31, 126.08, 125.27

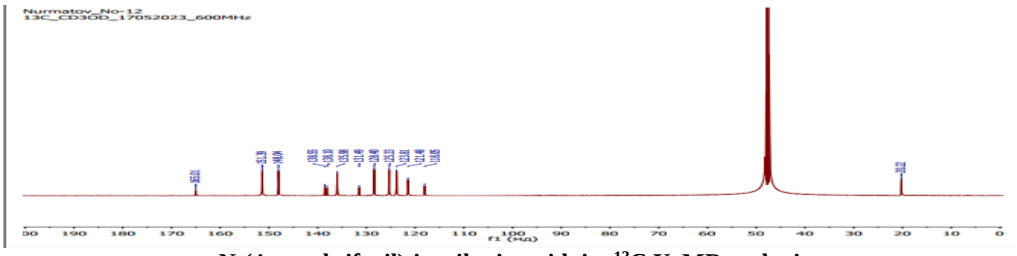
***N-(2,6-Ksilidinfenil)- izonikotinamid*:** 0,615 gr (0,005 mol) 4-karboksipiridin va 0,605gr (0,005 mol) *2,6-ksilidin* 0,365 gr (0,01 mol) HCI katalizator ishtirokida sintez qilindi. $R_f$ = 0,62, suyqlanish harorati $T_s$=158-160°C. IQ spektr (KBr $sm^{-1}$) ν=3232 (-NH), δ=1520 (-NH), ν=1653 (-CO-).$^1$H NMR (400 MHz, METHANOL-*D*$_4$) δ 9.15 (s, 1H), 8.77 (s, 0H), 8.41 (d, *J* = 9.7 Hz, 1H), 7.61 (s, 0H), 7.20 – 7.10 (m, 10H), 4.95 – 4.90 (m, 22H), 2.27 (d, *J* = 0.7 Hz, 19H).$^{13}$C NMR (101 MHz, METHANOL-*D*$_4$) δ 201.28, 166.64, 153.00, 149.35, 137.34, 135.40, 131.91, 129.75, 129.22, 128.71, 125.32, 122.62, 22.69



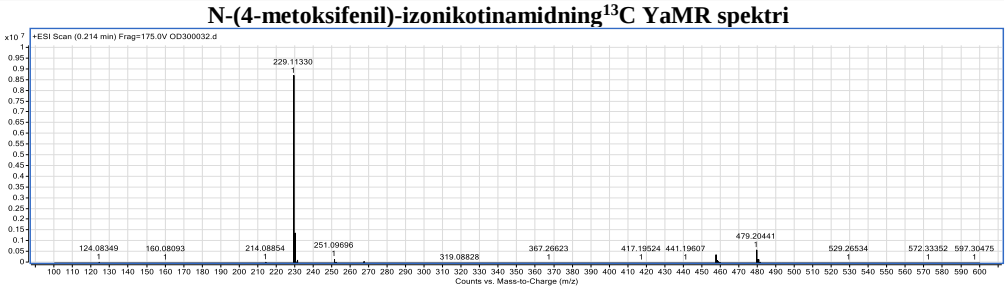
**N-(4-metoksifenil)-izonikotinamidning IQ spektri**



**N-(4-metoksifenil)-izonikotinamidning1H YaMR spektri**



**N-(4-metoksifenil)-izonikotinamidning$^{13}$C YaMR spektri**



**N-(4-metoksifenil)-izonikotinamidning MASS spektri**

**ADABIYOTLAR**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