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SYNTHESIS OF QUATERNARY ARYLAMMONIUM SALTS OF PICOLINE ACID

Annotation

Quaternary arylammonium salts were synthesized from the reactions of picolinic acid with aniline, isomeric nitroanilines and aminophenols. The influence of the nature of the solvent on the course of the reactions was studied. Picolinic acid was found to react with aromatic amines in ethanol at room temperature to form quaternary ammonium salts. The physical constants of the synthesized salts were determined, and their structure was studied and confirmed by IR spectroscopy.

Key words: Picolinic acid, anilnie, nitroanilines, aminophenols, aromatic amine, N-protonation, quaternary ammonium salts, organic solvent.

СИНТЕЗ ЧЕТВЕРТИЧНЫХ АРИЛАММОНИЕВЫХ СОЛЕЙ ПИКОЛИНОВОЙ КИСЛОТЫ

Аннотация

Четвертичные ариламмониевые соли синтезированы реакциями пиколиновой кислоты с анилин, изомерными нитроанилинами и аминофенолами. Исследовано влияние природы растворителя на ход реакций. Было обнаружено, что пиколиновая кислота реагирует с ароматическими аминами в этаноле при комнатной температуре с образованием солей четвертичного аммония. Определены физические константы синтезированных солей, изучена их структура и подтверждена данными ИК-спектроскопии.

Ключевые слова: Пиколиновая кислота, анилин, нитроанилины, аминофенолы, ароматический амин, N-протонирование, четвертичные аммониевые соли, органический растворитель.

PIKOLIN KISLOTANING TO‘RTLAMCHI ARILAMMONIY TUZLARI SINTEZI

Annotatsiya

Pikolin kislotasining anilin, izomer nitroanilinlar va aminofenollar bilan reaksiyalaridan to‘rtlamchi arilammoniy tuzlari sintez qilindi. Reaksiyalarning borishiga erituvchi tabiatining ta'siri o‘rganildi. Pikolin kislotasi aromatik aminlar bilan etanolda xona haroratida ta'sirlashib to‘rtlamchi ammoniy tuzlarini hosil qilishi aniqlandi. Sintez qilingan tuzlarning fizik doimiyliklari aniqlandi va tuzilishi IQ- spektroskopiya usulida o‘rganildi va tasdiqlandi.

Kalit so‘zlar: Pikolin kislota, anilin, nitroanilinlar, aminofenollar, aromatik amin, H-protonlanish, to‘rtlamchi ammoniy tuzlari, organik erituvchi.

Kirish. Malumki karbon kislotalarning almashingan alkil- va arilamidlari amaliy ahamiyati va qo‘llanilish sohasining kengligi bilan muhim o‘rin tutadi. Kislota amidlarini sintez qilish aminlarga karbon kislota, kislota angidridi yoki galogenangidridlarini ta'sir ettirish orqali olib boriladi. Kislota amidlarini sintez qilishda ko‘p yillar davomida kislota angidridlari va galogenangidridlaridan foydalanilgan bo‘lib, keyinchalik esa aminlarni kislotalar bilan atsillab kislota amidlarini olishning qulay usullari ishlab chiqilgan. Bu jarayonda kislota bilan aminning ta'sirlashishidan dastlab protonlangan to‘rtlamchi ammoniy tuzlari hosil bo‘lishi ta'kidlab o‘tilgan bo‘lib, ularga oraliq moddalar sifatida qaralib ajratib olinmagan, tuzilishi va hossalari o‘rganilmagan [1]. Biroq, so‘nggi yillarda bu tuzlar sintezi bilan bog‘liq tadqiqotlar kimyogar olimlarda qizig‘ish uyg‘otmoqda.

Mavzuga oid adabiyotlar tahlili. Karbon kislotalarning to‘rtlamchi ammoniy tuzlarini sintez qilish va tuzilishini o‘rganishga oid tadqiqotlar 20 asrning ohirlariga kelib rivojlana boshlagan. O‘tgan asrda germaniyalik olimlar qahrabo kislotasining ammiak bilan reaksiyasidan monoammoniyli tuzni sintez qilishgan va tuzning monokristallarini rentgen tuzilish analizi yordamida o‘rganishgan [5]. Dastlabki tadqiqotlardan biri bo‘lgan yana bir ishda to‘rtlamchi ammoniy tuzlarining analitik kimyoda qo‘llanilishi bilan bog‘liq bo‘lgan ma'lumotlar mavjud. Bu ishda bir qator organik karbon kislotalarning to‘rtlamchi ammoniy tuzlari olingan va ularning analitik hossalari o‘rganilgan hamda ayrim mineral kislotalarning tuzlari bilan taqqoslangan [6].

Karbon kislotalarning birlamchi, ikkilamchi va uchlamchi alkil- va arilaminlar bilan protonlashgan to‘rtlamchi ammoniy tuzlarini hosil qilishi olimlar tomonidan keng o‘rganilgan. Reaksiyalar organik erituvchilarda olib borilgan va olingan barcha tuzlarning fizik doimiyliklari keltirilgan, tuzilishi IQ, YAMR spektroskopiya usullari va rentgen tuzilish analizi yordamida tahlil qilingan [7]. Bundan tashqari adabiyotlarda karbon kislota va aminning tuzilishi, hossalari va reaksiya sharoitiga bog‘liq holda ularning ta'sirlashishidan hosil bo‘ladigan tuzlar supramolekulyar adduktlar ko‘rinishida bo‘lishi mumkinligi ta'kidlangan [10].

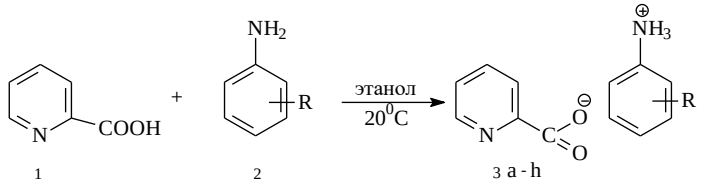
O‘zbekiston Milliy universiteti tadqiqotchilari Q.Ahmedov va uning shogirdlari tomonidan H,H-dietilgidrazinga karbon kislotalar ta'sir ettirib yuqori unumlar bilan protonlangan to‘rtlamchi ammoniy tuzlari sintez qilingan [13].

Kafedra tadqiqotchilari izlanishlarini davom ettirib qator gidraziniy tuzlarini sintez qilishgan hamda bu tuzlarning ayrimlari 1,2-kompleks nisbatdagi ion-molekulyar tarkibli bo‘lishi mumkinligini aniqlashgan [14].

Adabiyotlarda karbon kislotalarning alkil- va arilammoniy tuzlari yuqori biologik faollikni namoyon qilishi hisobiga ulardan halq ho‘jaligining ko‘plab sohalarida turli maqsadlarda foydalanish mumkinligi ta'kidlab o‘tilgan. Hususan, farmasevtika va tibbiyotda olib borilgan sinovlar natijasida turli viruslarga va ular keltirib chiqaradigan saraton, OIV kabi o‘ta havfli kasalliklarga qarshi samara berishi aniqlanmoqda [17]. Shuningdek, tadqiqotlar to‘rtlamchi ammoniy tuzlarini qishloq ho‘jaligida ham qo‘llash mumkinligini ko‘rsatmoqda [20]. So‘nggi yillarda olib borilayotgan izlanishlar natijasida bu birikmalar biotexnologiya va radiofarmasevtika sohalarining rivojlanishiga hissa qo‘shmoqda [21].

Tajriba natijalari va tahlili. To‘rtlamchi ammoniy tuzlari sinteziga oid izlanishlar natijasi avvalgi ishlarda ham bayon qilingan bo‘lib, mazkur tadqiqodlar shu ishlarning davomi hisoblanadi.

Tajribalar uchun pikolin kislota, anilin, izomer nitroanilinlar va aminofenollar tanlab olindi. Pikolin kislotasi va aminlarning qattiq agregat holatdaligini hisobga olib reaksiyalar erituvchilar ishtirokida olib borildi. Aromatik aminlarning H-protonlanish reaksiyalari uchun proton erituvchi - etanol tanlab olindi. Etanol qutbli organik erituvchi bo‘lib, unda pikolin kislota va aminlar xona haroratida eriydi. Shu sababli etanolda reaksiyalar xona haroratida reagentlarning 1:1 mol nisbatida olib borildi. Reaksiyalar quyidagi sxema bo‘yicha boradi:



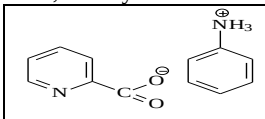
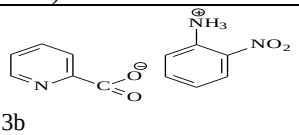
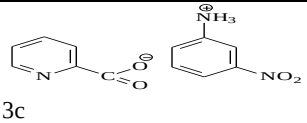
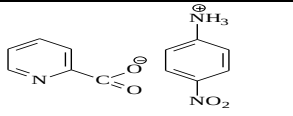
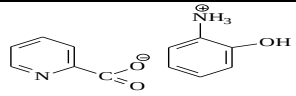
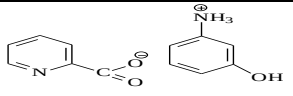
Bu yerda: R = H, 2-NO_2, 3-NO_2, 4-NO_2, 2-OH, 3-OH, 4-OH.

Olib borilgan tajribalarda reaksiya aralashmasi 4-5 kun davomida ochiq idishlarda qoldirildi. Etanol bug‘lanib aralashma ma'lum bir konsentrasiyaga yetganda tuz kristallari tusha boshlaydi va erituvchi uchib ketishi bilan tuz kristallari idish tubiga to‘liq tushadi. Reaksiya mahsuloti benzolda yuvilib qo‘shimchalardan tozalandi.

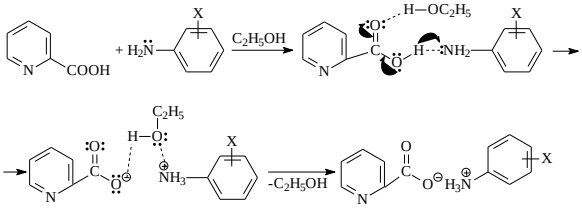
Mazkur usullar asosida pikolin kislotasining anilin va ba'zi almashingan anilinlar bilan reaksiyalari olib borildi va to‘rtlamchi arilammoniy tuzlari sintez qilindi. Tajriba natijalari quyida 1-jadvalda keltirilgan.

1-jadval.

Pikolin kislotasining anilinlar bilan reaksiyalari mahsulotlari
(erituvchi - etanol, reaksiya harorati 20 °C, davomiyligi 4-5 kun.)

 3a	 3b
 3c	 3d
 3e	 3h

Tajriba natijalari pikolin kislotaning anilin, izomer nitroanilinlar va aminofenollar bilan reaksiyalarini spirtda xona haroratida olib borish yuqori unum bilan protonlangan ammoniy tuzlarini olish imkonini berishini ko‘rsatdi. Bu holatni olingan to‘rtlamchi ammoniy tuzlarining hosil bo‘lishida proton erituvchi bo‘lgan etanol spirt protoni bilan hosil bo‘lgan anionni, gidroksil guruhdagi kislorod atomining taqsimlanmagan elektron juftlari hisobiga kationni solvatlashi, buning natijasida esa hosil bo‘lgan tuzning barqarorligini oshirishi bilan izohlash mumkin. Ushbu jarayonni quyidagi reaksiya sxemasi orqali ifodalash mumkin:



Tajribalar qismi. Sintez qilingan birikmalarning IQ-spektri Систем-2000 ФТ-ИР markali spektrofotometrda kaliy bromid bilan tabletka holida 400-4000 sm^{-1} soha oralig‘ida olindi.

Fenilammoniy pikolinat (3a). A) Stakanga 0,615 g (0,005 mol) pikolin kislotaning 7 ml etanoldagi eritmasi, 0,465 g (0,005 mol) anilinning etanoldagi eritmasi solindi, aralashtirildi va xona haroratida hosil bo‘lgan oq iviq cho‘kma filtrlab ajratib olindi. benzolda yuvib tozalandi va $CaCl_2$ li eksikatorda quritildi. Mahsulotning suyuqlanish harorati 117-118^{0}C. IQ-spektri

(sm^{-1}): ν = 2581 sm^{-1} ($^{+}NH_3$), δ = 1548-1585 sm^{-1} ($^{+}NH_3$), ν_{as} = 1609 sm^{-1} (COO^{-}), ν_s = 1460 sm^{-1} (COO^{-}), δ = 834 sm^{-1} (COO^{-}).

2’-Nitrofenilammoniypikolinat (3b). Pikolin kislota va o-nitroanilindan A metodika bo‘yicha sintez qilindi. Suyuqlanish harorati 131-133°C. IQ-spektri (sm^{-1}): ν = 2497 sm^{-1} ($^{+}NH_3$), δ = 1524-1571 sm^{-1} ($^{+}NH_3$), ν_{as} = 1592 sm^{-1} (COO^{-}), ν_s = 1452 sm^{-1} (COO^{-}), δ = 696 sm^{-1} (COO^{-}), ν_{as} = 1698 sm^{-1} (NO_2), ν_s = 1338 sm^{-1} (NO_2), δ = 749 sm^{-1} (NO_2),

3’-Nitrofenilammoniypikolinat (3s). Pikolin kislota va m-nitroanilindan A metodika bo‘yicha sintez qilindi. Suyuqlanish harorati 109°C. IQ-spektri (sm^{-1}): ν = 2667 sm^{-1} ($^{+}NH_3$), δ = 1508-1483 sm^{-1} ($^{+}NH_3$), ν_{as} = 1620 sm^{-1} (COO^{-}), ν_s = 1483 sm^{-1} (COO^{-}), δ = 668 sm^{-1} (COO^{-}), ν_{as} = 1620 sm^{-1} (NO_2), ν_s = 1324 sm^{-1} (NO_2), δ = 734 sm^{-1} (NO_2),

4’- Nitrofenilammoniypikolinat (3d). Pikolin kislota va p-nitroanilindan A metodika bo‘yicha sintez qilindi. Suyuqlanish harorati 116-118°C. IQ-spektri (sm^{-1}): ν = 2699 sm^{-1} ($^{+}NH_3$), δ = 1505-1519 sm^{-1} ($^{+}NH_3$), ν_{as} = 1584 sm^{-1} (COO^{-}), ν_s = 1441 sm^{-1} (COO^{-}), δ = 697 sm^{-1} (COO^{-}), ν_{as} = 1651 sm^{-1} (NO_2), ν_s = 1300 sm^{-1} (NO_2), δ = 762 sm^{-1} (NO_2),

2’- G**idroksofenilammoniypikolinat** (3e). Pikolin kislota va o-aminofenoldan A metodika bo‘yicha sintez qilindi. Suyuqlanish harorati 128-129°C. IQ-spektri (sm^{-1}): ν = 2839 sm^{-1} ($^{+}NH_3$), δ = 1534-1558 sm^{-1} ($^{+}NH_3$), ν_{as} = 1607 sm^{-1} (COO^{-}), ν_s = 1414 sm^{-1} (COO^{-}), δ = 735 sm^{-1} (COO^{-}), ν = 3214 sm^{-1} (OH), δ = 1376 sm^{-1} (OH),

3’- Gidroksofenilammoniypikolinat (3h). Pikolin kislota va m-aminofenoldan A metodika bo‘yicha sintez qilindi. Suyuqlanish harorati 154°C. IQ-spektri (sm^{-1}): ν = 2840 sm^{-1} ($^{+}NH_3$), δ = 1516-1560 sm^{-1} ($^{+}NH_3$), ν_{as} = 1615 sm^{-1} (COO^{-}), ν_s = 1458 sm^{-1} (COO^{-}), δ = 774 sm^{-1} (COO^{-}), ν = 3371 sm^{-1} (OH), δ = 1379 sm^{-1} (OH),

Xulosa. Olingan natijalar asosida shunday xulosaga kelish mumkinki, 2-piridinkarbon kislotaning anilin va almashgan anilinlar bilan reaksiyalari xona haroratida etanolda olib borilganda to‘rtlamchi ammoniy turidagi tuzlarning yuqori unum bilan hosil bo‘ladi va tuzlar suv bilan aziatrop aralashma hosil qiladigan erituvchilarda qizdirilganda esa suv chiqib ketishi natijasida amidga aylanib ketadi. Shuning uchun tuz hosil qilish reaksiyalarni xona hararoratida qutbli erituvchilarda olib borish va mahsulotni qayta kristallamaslik lozim.

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