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β -NAFTOL ASOSIDA AZOBIRIKMALAR SINTEZI

Annotatsiya: Ushbu ishda azobirikmalar sintezi β -naftolning almashingan aminofenollar va nitroanilinlar bilan azobirikish reaksiyasi olib borildi. Olingan moddalarning fizik konstantalari aniqlandi, tuzilishi YuQX, IK, spektroskopiya usullari yordamida tahlil qilindi.

Kalit so'zlar: β -naftol, aminofenol, nitroanilin, azokomponent, diazokomponent, azobirikish

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СИНТЕЗ АЗОСОЕДИНЕНИЙ НА ОСНОВЕ β -НАФТОЛА

Аннотация: В данной работе синтез азосоединений осуществлен реакцией азосочетания β -нафтола с замещенными аминифенолами и нитроанилинами. Определены физические константы полученных веществ и проанализирована их структура методами рентгеновской, ИК-спектроскопии.

Ключевые слова: β -нафтол, аминифенол, нитроанилин, азокомпонент, диазокомпонент, азосоединение.

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SYNTHESIS OF AZO COMPOUNDS BASED ON β -NAPHTHOL

Abstract: *In this work, the synthesis of azo compounds was carried out by azo coupling reaction of β -naphthol with substituted aminophenols and nitroanilines. The physical constants of the obtained substances were determined, and their structure was analyzed using UV, IR, spectroscopy methods.*

Key words: *β -naphthol, aminophenol, nitroaniline, azo component, diazo component, azo compound.*

Kirish

Azobirikmalar bo'yoq va to'qimachilik sanoatida, tibbiyot, biofarmasevtik tadqiqotlar kabi sohalar qo'llaniladi[1].

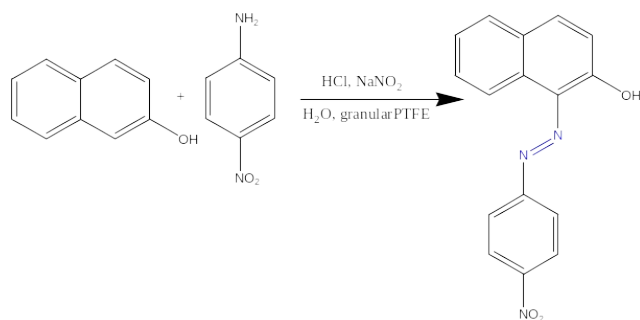
2010 yilda butun dunyo bo'ylab qariyb 560 000 tonna sanoat organik pigmentlari ishlab chiqarilgan va ularning 59% azo pigmentlar bo'lib, qiymati 7 milliard dollardan oshadi. Hisob-kitoblarga ko'ra, bir tonna pigment ishlab chiqarish uchun 120-380 tonna suv sarflanadi va 2010 yilda faqat Xitoyda bu $2,69-8,51 \times 10^7$ tonna oqava suv sarf bo'lishiga olib keldi.

Adabiyotlar tahlili

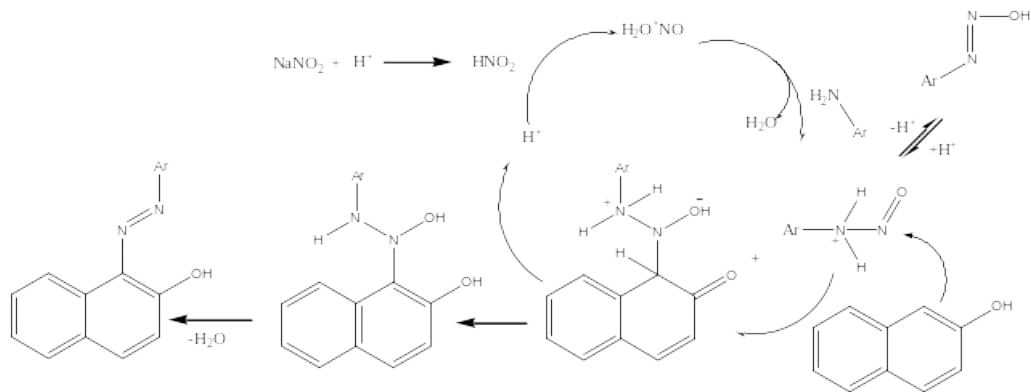
Azo birikmalar sintezi uchun bir necha turdagi reaksiyalar qo'llaniladi [2]. Bular qatoriga azo birikish reaksiyasi [3], Mills reaksiyasi, Valax reaksiyasi[4], azoksibenzollarning qaytarilishi, anilinlarning oksidlanishi, arilgidrazinlarning degidrogenatsiyasi va diazoniy tuzlarining dimerlanish reaksiyalari shular jumlasidandir

[5,6]. Ushbu usullarning barchasi birlashtiruvchi komponentlarni tuzlariga aylantirish uchun 1,0 ekvivalentdan ko'proq asosni talab qiladi va bu asosni keyin neytrallash kerak. Bu ko'p miqdorda chiqindi sho'r suvlar hosil bo'lishiga olib keladi. Ba'zi hollarda eruvchanlikni oshirish uchun sirt faol moddalar ishlatiladi. Shuningdek, organik erituvchi yordamida reaksiyalarni zararsiz(yashil) qilish uchun granula PTFE(politetrafloroetilen) dan foydalangan [7,8].

Granula PTFE(politetraftoretlen) turli xil azo birikmalarini sintez qilish uchun diazokomponent, birlashtiruvchi komponent, HCl va NaNO₂ ning suvli aralashmasiga qo'shiladi va mexanik aralashtirgichda aralashtiriladi. Chiqindi suvlari, granula PTFE va ortiqcha HCl ni 11 marta qayta ishlatish mumkinligi isbotlangan.



Nazariy jihatdan diazotlanish va azobirikish reaksiyalarini amalga oshirish uchun 2 ekvivalentdan ko'proq HCl kerak bo'ladi. Ushbu reaksiya uchun taklif qilingan mexanizm quyida ko'rsatilgan.



(2 ekvivalentdan kam HCl yordamida azopigmentlarni sintez qilish uchun taklif qilingan mexanizm.)

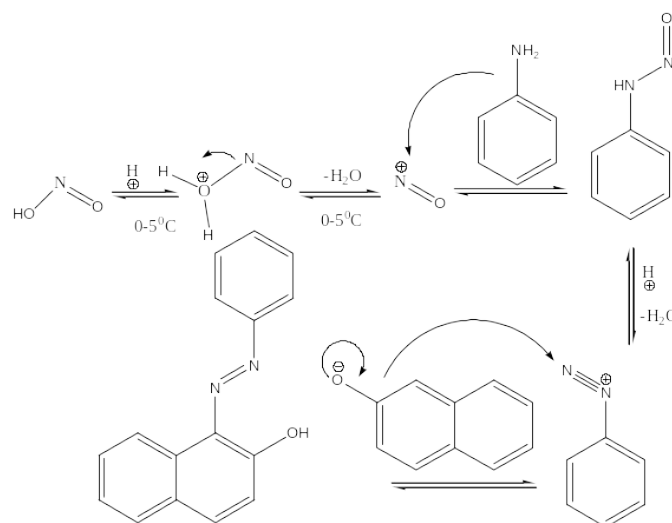
Dastlab NaNO_2 1 ekviv HCl yordamida HNO_2 ga o'tadi. Keyin protonlangan azot kislotasi anilinni nitrozalaydi. 2-naftol hujumidan keyingi mahsulotdan ajralib chiqqan proton azot kislotasini protonlash uchun ishlatiladi. Jarayonda suvning chiqishi bilan mahsulot hosil bo'lishi kuzatilgan va uni oddiy filtrlash orqali yig'ib olingan.

	H_2O sarfi (ml)	HCl sarfi (gr)	NaOH sarfi (gr)	Mahsulot unumi (%)
Yangi ish	15	9.1	0	>99
Amaldagi sanoat usuli	450	27	10.5	93

Shubhasiz, yuqoridagi jadvalga ko'ra bu usul joriy sanoat usulidan har jihatdan ustundir. Sanoat usuli juda ko'p suv, HCl va NaOH sarf qiladi va unumdorligi past bo'ladi. Olingan barcha moddalarning tuzilishi YaMR spektrlari standart sifatida ^1H YaMR uchun 400-MHz, ^{13}C YaMR uchun 101-MHz spektrometrlar bilan tahlil qilinib aniqlangan.

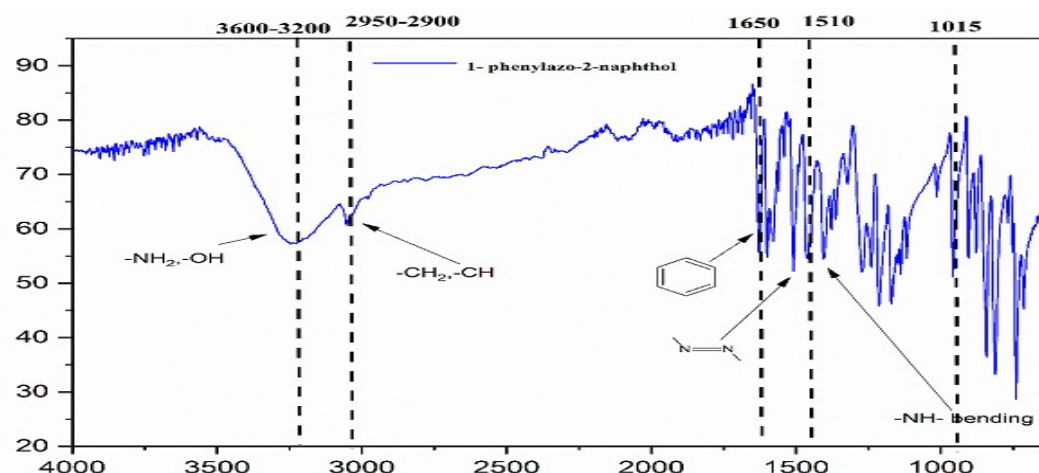
Ushbu ishda 1-fenilazo-2-naftol ($\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}$) fenil diazonium tuzi va b-naftolning sovuq suvda azo birikish reaksiyasi orqali azo-bo'yoq sintez qilindi. Azo birikish halqaning orto holatida sodir bo'ladi, chunki bu holatda zaryad zichligi kuchayadi. Natijalar asosida sintez qilingan birikma 1-fenylazo-2-naftol *Sclerotium rolfsii* ga qarshi antifungal xususiyatga ega emas degan xulosaga kelingan [9, 10].

1-fenilazo-2-naftolning sintezi uchun quyidagicha mexanizm taklif qilingan.



Olingan 1-fenilzo-2-naftolning IQ spektri tahlili keltirildi. 3550- 3215 sm^{-1} bog'lgan sohada intensiv cho'qqi gidroksil ($-\text{OH}$) guruhi mavjudligi ko'rsatdi, 2900-

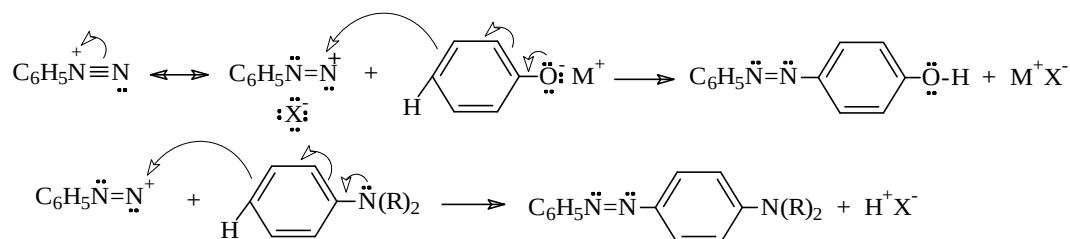
2950 cm^{-1} sohalarda Ph-CH ning sp^2 gibridlangan metin (-CH) guruhlariga mos keladi, shuningdek 1510-1500 cm^{-1} dagi keskin cho'qqi 1- fenilzo-2-dagi azo guruhini (-N=N-) tebranishini ko'rsatadi. Benzol halqasiga tegishli bo'lgan HC=CH bog'lari tebranishlari 1620-1680 cm^{-1} sohalarda kuzatiladi.



Tadqiqot metodologiyasi

Diazotirlash reaksiyasining borishi aromatik aminning tuzilishiga va diazotirlovchi reagentning kuchiga bog'liq. Aromatik amindagi azotning juft elektronlarining harakatchanligi yoki asosiligi halqadagi o'rinbosarlarning xarakteriga bog'liq. Aromatik diazobirikmalar kimyoviy jihatdan juda faol bo'lib, turli xil reaksiyalarga kirishadi. Bular azot chiqishi va diazoniyl guruhning almashinishi bilan boradigan reaksiyalar va azot chiqmasdan boradigan reaksiyalar.

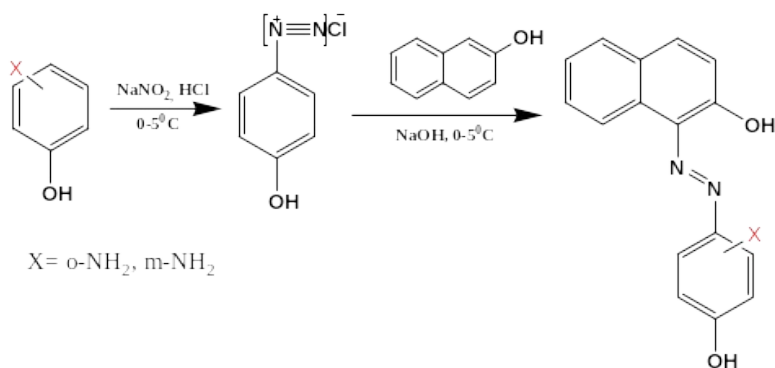
Diazoniyl tuzlarining aromatik aminlar va fenolyatlar bilan reaksiyasida azobirikmalar hosil bo'ladi, reaksiya elektrofil almashinish mexanizmi bo'yicha boradi. Bu turdagi reaksiyalar azobirikish reaksiyalari deb ataladi va sanoatda azobo'yoqlar olishda keng qo'llaniladi. Azobirikish reaksiyasiga kirishayotgan diazobirikma diazokomponent deb, aromatik amin yoki fenol azokomponent deb ataladi:



Azobirikish reaksiyasi quyidagi hollarda oson boradi: diazokomponent tarkibida bitta yoki bir nechta elektronoakseptor o‘rinbosarlar halqaning o-va p-holatlarida bo‘lsa, bunday guruhlar diazoni kationdagi musbat zaryad qiymati va elektrofili xossasini oshiradi. Aksincha, diazokomponentning benzol halqasida birinchi tur o‘rinbosari bo‘lsa, azobirikish reaksiyasini sekinlashtiradi[11].

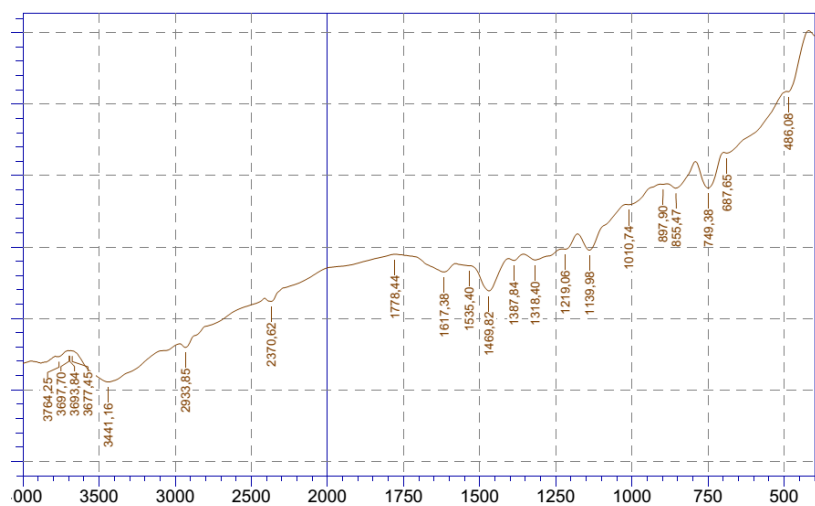
Tahlillar va natijalar

Yuqoridagi usullardan foydalangan holda azobirikmalar sintez qilishga erishildi. Dastlab aminofenol izomerlari so‘ngra nitroanilin izomerlari asosida 2-naftol bilan azobirikish reaksiyalari olib borildi va kutilgan natijalarga erishildi. Reaksiya tenglamalari quyidagicha:

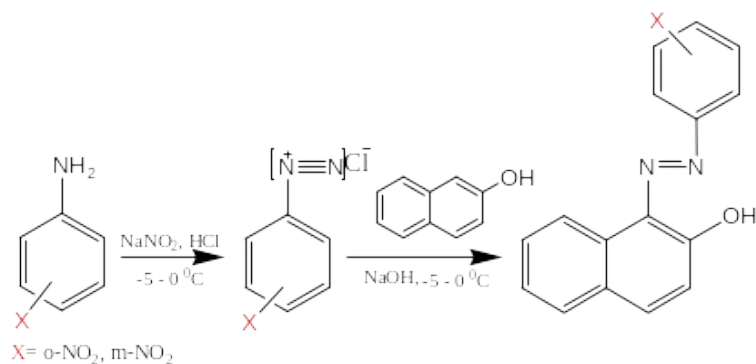


To‘q siyohrangli bo‘yoq(1-(2-gidroksifenilazo)2-naftol) T_{suyuq}=285-290 °C, YuQX da Sistema(EtAc:Petester, 1:3) R_f=(0,42), C%=78, IQ Spektr (v_{max} KBr, sm⁻¹) 3550, 2900, 3019, 1620, 1510,. Brutto formulasi C₁₆H₁₂N₂O₂

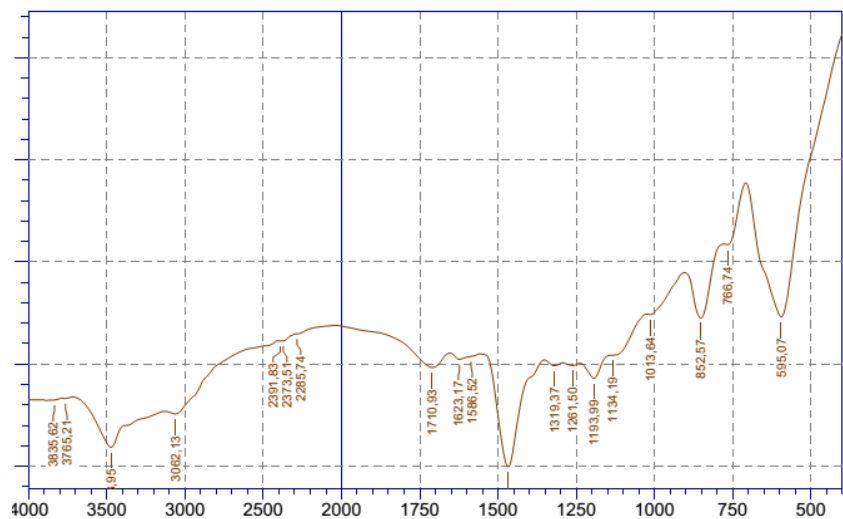
Qora rangli bo‘yoq (1-(3-gidroksifenilazo)2-naftol) T_{suyuq}=235-240°C, YuQX da Sistema(EtAc:Petester, 1:3) R_f=(0,375), C%=84.6% , IQ spektri tahlili keltirildi. 3441sm⁻¹ bog‘lgan sohada intensiv cho‘qqi gidroksil (-OH) guruhi mavjudligi ko‘rsatdi, 2933 sm⁻¹ sohalarda Ph-CH ning



sp^2 gibridlangan metin (-CH) guruhlariga mos keladi, shuningdek 1469 cm^{-1} dagi keskin cho'qqi azo guruhini (-N=N-) tebranishini ko'rsatadi. Benzol halqasiga tegishli bo'lgan HC=CH bog'lari tebranishlari 1617 cm^{-1} sohalarda kuzatiladi. Brutto formulasi $C_{16}H_{12}N_2O_2$

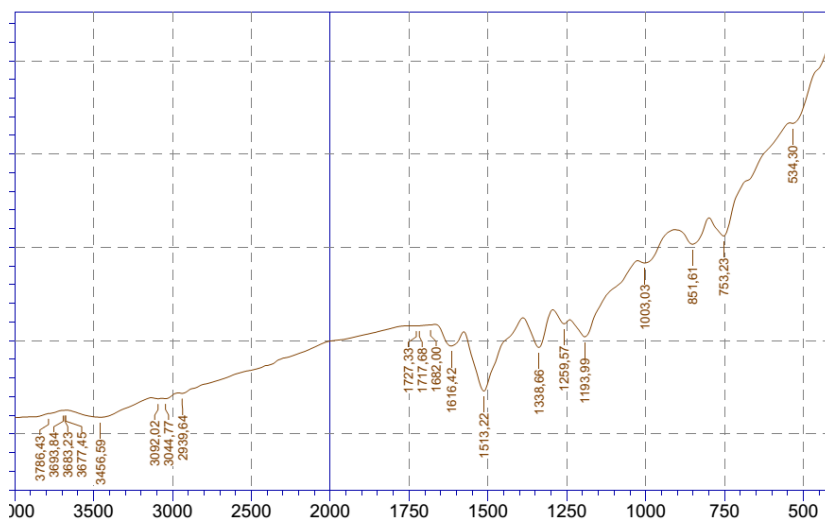


Qizil rang (1-(2-nitrofenilazo)2-naftol) $T_{\text{suyuq}} = 185-187\text{ }^{\circ}\text{C}$, YuQX da Sistema(EtAc:Petester, 1:3) Rf=(0,45), C%=68, Brutto formulasi $C_{16}H_{11}N_3O_3$,



IQ Spektr (vmax KBr, sm⁻¹) IQ-spektr 3062, sm⁻¹ (v_{OH}), 3473 sm⁻¹ yuqori (v_{NH}), 3062 sm⁻¹ (v_{C-H,ArH}), 1586 sm⁻¹ (v_{-N=N-}), 1623,1586, sm⁻¹ (v_{C=C Ar}) 1482 sm⁻¹ (v_{-NO₂})

Och qizil (1-(3-nitrofenilazo)2-naftol) rangli bo'yoq T_{suyuq}=146-148 °C, YuQX da Sistema(EtAc:Petester, 1:3) Rf=(0,55), C%=74.,Brutto formulasi C₁₆H₁₁N₃O₃,



IQ Spektr (vmax KBr, sm⁻¹) IQ-spektrida 3092, sm⁻¹ (v_{OH}), 3456 sm⁻¹ yuqori (v_{NH}), 3044 sm⁻¹ (v_{C-H,ArH}), 1513 sm⁻¹ (v_{-N=N-}), 1616,1682, sm⁻¹ (v_{C=C Ar}) 1482 sm⁻¹ (v_{-NO₂}), 3786, 3677 sm⁻¹ (v_{OH}), 750, sm⁻¹ (v_{C-H Ar})

Xulosa

Xulosa o'rnida shuni aytish mumkinki, bugungi kimyo sanoatida bo'yoqlarga bo'lgan bo'lgan ehtiyoj kundan kunga oshib bormoqda. Azobo'yoqlar sintez qilishning bir necha xil usullari mavjud. Yashik kimyo mezonlariga mos usulni tanlash bugungi kunning dolzarb masalasidir.

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