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P-HOLATDA TURLI O'RINBOSARLAR BO'LGAN AMINLAR ASOSIDA 2-NAFTOL BILAN AZOBIRIKMALAR SINTEZI

Annotatsiya

Mazkur maqolada p-holatda turli xil o‘rinbosarlarga ega bo‘lgan aromatik aminlar asosida 2-naftol bilan azobirikmalar sintezi o‘rganildi. Reaksiya sharoitlari, azo birikmalarning fizik-kimyoviy xossalari va hosil bo‘lgan mahsulotlarning tuzilishi spektroskopik usullar orqali aniqlandi. Olingan natijalar asosida o‘rinbosarlarning mahsulot unumlariga ta’siri o’rganildi

Kalit so‘zlar: 2-naftol, almashingan aromatik aminlar, IK spektr.

СИНТЕЗ АЗОСОЕДИНЕНИЙ НА ОСНОВЕ АМИНОВ С РАЗЛИЧНЫМИ ЗАМЕСТИТЕЛЯМИ В ПАРА-ПОЛОЖЕНИИ И 2-НАФТОЛА

Аннотация

В данной статье изучен синтез азосоединений на основе ароматических аминов с различными заместителями в пара-положении и 2-нафтола. Были рассмотрены условия реакции, физико-химические свойства азосоединений и структура полученных продуктов, определённая с помощью спектроскопических методов. На основе полученных результатов исследовано влияние заместителей на выход продуктов реакции.

Ключевые слова: 2-нафтол, замещённые ароматические амины, ИК-спектр.

SYNTHESIS OF AZO COMPOUNDS BASED ON AMINES WITH VARIOUS SUBSTITUENTS IN THE PARA-POSITION AND 2-NAPHTHOL

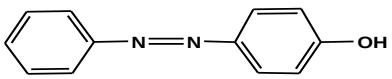
Annotation

This article presents the synthesis of azo compounds based on aromatic amines with various substituents in the para-position and 2-naphthol. The reaction conditions, physicochemical properties of the azo compounds, and the structures of the obtained products were studied using spectroscopic methods. Based on the results obtained, the effect of substituents on the reaction yields was investigated.

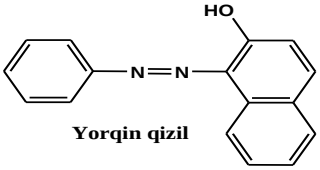
Key words: 2-naphthol, substituted aromatic amines, IR spectrum.

Kirish. Azo birikmalar kimyo sanoatida, ayniqsa bo‘yoq moddalari va biologik faol birikmalar sintezida keng qo‘llaniladi. Bu birikmalarni sintez qilishda 2-naftol fenollarga nisbatan yuqori faollikka ega ekanligini hisobga olib turli xil azobirikmalar olindi. Hozirgi kunda sintetik azo birikmalar ko’plab sohalarda, jumladan tibbiyot, kosmetika, oziq-ovqat sanoati, bo’yoqlar, plastmassa, kemasozlik, avtomobil sanoati, kabel ishlab chiqarish hamda analitik kimyoda keng qo’llanilmoqda. Azo birikmalarning biologik ahamiyati ularning antineoplastik, antidiabetik, antiseptik, yallig‘lanishga qarshi va boshqa foydali kimyoviy terapevtik vositalar sifatida qo’llanilishi bilan ajralib turadi.

Adabiyotlar tahlili va metodlar. Azo bo’yoqlar xromofor sifatida azot va azot qo’sh bog‘iga ega. Ushbu bo’yoqlar diazoniy tuzini olish va uni kuchli faollashtirilgan aromatik halqaga bog’lash orqali hosil bo’ladi[1].

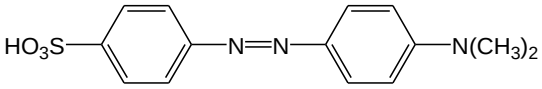


Sariq

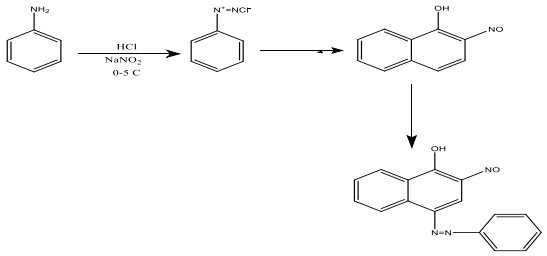


Yorqin qizil

Azo bo‘yoqlar odatda diazonium tuzlarini fenollar yoki aromatik aminlar bilan reaksiyaga kirishish orqali olinadi - azo birikish reaksiyasi. Azo bo‘yoqlar - intensiv rangga ega bo‘lgan birikmalar. Analitik kimyoda ishlatiladigan ko‘plab ko‘rsatkichlar ham azo bo‘yoqlardir.
Masalan:



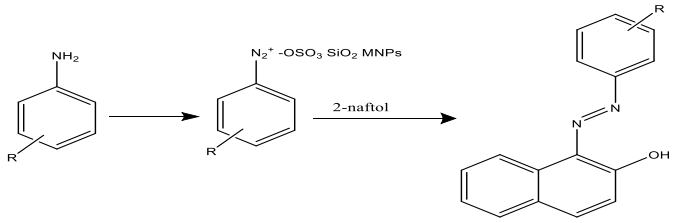
Turli diazoniy tuzlarini biriktirish orqali ko’plab turli azo birikmalar hosil bo’lishi mumkin. [2,3,4] Ushbu ishda ikki xil mono azobirikma sintez qilingan va o’rganilgan: Bunda 2-nitrozo-1-naftol, 1-nitrozo-2-naftol hosil qilingan ikkita mono azo bo’yoqning sintezi haqida so’z boradi.



Qisqacha aytganda, ushbu ishda yangi sintez qilingan azo bo’yoqlarning quyosh elementlarida ishlatilish potentsialini o’rganishga bag'ishlangan bo’lib, ularning elektron o’tishlari, energiya xususiyatlari va yorug‘likni yig‘ish samaradorligi kabi jihatlari nazariy va eksperimental usullar bilan tahlil qilingan[5].

10-aril almashtirilgan azo bo’yoqlar sintezi 2-naftol, katexol va xinolni turli aromatik aminlar bilan azobirikish orqali sintez qilindi. Sintetik birikmalar in vitro mikroblarga qarshi, antioksidant va yallig'lanishga qarshi faolligi uchun tekshirildi. Ushbu tadqiqotga 2-naftol, xinol va katexol *azo birikish reaksiyasiga* turli o’rinbosarlarga ega (-NO_2,-COOH, -$COCH_3$) birlamchi aromatik aminlar tanlab olingan. Keyin diazotirlangan birikmalar NaOH (2,5 M, 200 ml, 98%) ishtirokida b-naftol, katexol va xinol bilan muz hammomida aralashtirib, mahsulot hosil bo’ldi. [6].

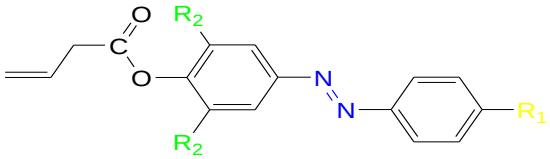
Azo bo’yoqlarni sintez qilishning erituvchisiz, samarali va ekologik toza usuli aromatik aminlarning β-naftol bilan sulfokislota funksionallangan magnit Fe_3O_4 nanozarrachalar (Fe_3O_4@SiO_2-SO_3H) ishtirokida xona haroratida maydalash usuli orqali diazo birikish reaktsiyalari yordamida ishlab chiqildi. Ushbu yashil metod avval aniqlangan usullarning kamchiliklari va nuqsonlarini, masalan, past harorat, kislotalar, ishqorlar va zaharli erituvchilardan foydalanish, diazoniy tuzlarining xona haroratida beqarorligi, o’rtacha unum va uzoq reaksiya vaqtlarini bartaraf etishga qaratilgan. Bundan tashqari, jarayonning afzalliklari orasida mukammal konversiya bilan yumshoq sharoitlar, mahsulotni oddiy ajratish jarayoni, arzon usul va magnit katalizatorning qayta ishlatilishining mavjudligi.



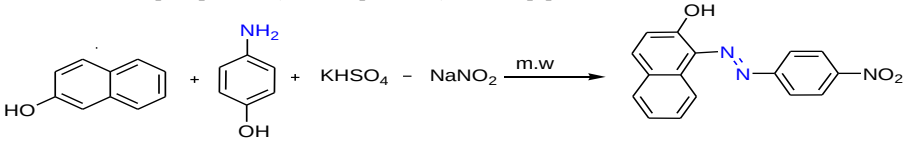
Magnetit Fe_3O_4 nanokompozitlari Massart usuli bo’yicha tayyorlangan , Fe_3O_4@SiO_2 nanokompozitlari esa Stöber usuli bo’yicha tayyorlangan. Naftollarning ariltriazenlar bilan Bronsted kislotali suyuqlik (IS) katalizatorligida diazo biriktirish reaktsiyasi orqali azo bo’yoqlarni sintez qilishning samarali va ekologik toza usuli ishlab chiqildi. Reaksiya diazotirlovchi agentlar sifatida ariltriazenlar, katalizator sifatida Bronsted kislotali suyuqliklar va yashil erituvchi sifatida suv ishtirokida xona haroratida va ishqorsiz sharoitlarda olib borildi. Keyingi tadqiqotlar shuni ko’rsatdiki, erituvchisiz sharoitlarda faqat oz miqdorda mahsulot hosil bo’lgan, bu substratlar va katalizatorning erimasligi bilan bog'liq bo’lishi mumkin[7].

Azo bo’yoq polimerlari naftol asosidagi azo bo’yoqlarning oksidlanish polikondensatsiyasi reaksiyasi orqali sintez qilingan bo’lib, bu jarayon NaOCl oksidlovchi moddasi yordamida suvli muhitda amalga oshirilgan. Natijalarga ko’ra, azo bo’yoq monomerlarining chidamlilik xususiyatlari polimerlarga qaraganda yaxshiroq ekanligi, chunki monomerlarning mato bilan bog‘lanish qobiliyati, yuqori molekulyar og‘irlikka ega bo’lgan uzun zanjirli polimerlarga qaraganda yaxshiroq bo’lganligi aniqlangan[8].

Quyidagi ishda polimerizatsiya qilinadigan akriloiloksi guruhiga ega bo'lgan yangi sintezlangan azo-efir birikmalarining sintezi haqida ma’lumot berilgan[9].

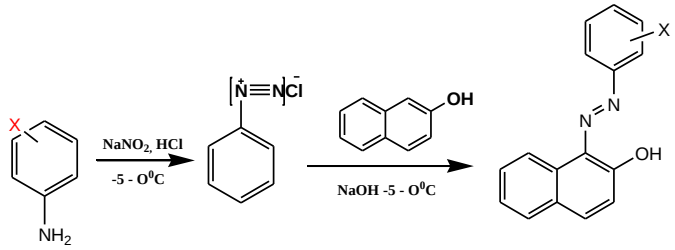


Sintezlangan azo-efir bo'yoqning xarakteristikasi IR, UV, H NMR, 13C NMR spektroskopik usullari va elementar tahlillar bilan tavsiflangan[10] Oddiy tajribada p-nitroanilin, natriy nitrit, kaliy gidrosulfat va 2-naftolning ekvimolyar aralashmasi mayda kukunga aylantirildi va mikroto‘lqinli pechda (138 Vt quvvatda) ikki daqiqa davomida nurlantirildi [11].



t/r	Yangi usul(mikroto’lqinli metod)			Eski usul		
	vaqt	W	Unum	vaqt	harorat	unum
1	2 min	138	100%	>1 soat	<10C°	<80%
2	1 min	138	100%	>1 soat	<10C°	<80%
4	1 min	138	85%	>1 soat	<10C°	<80%
5	30 s	138	80%	>1 soat	<10C°	<80%

Ushbu tadqiqotda ishlatilgan barcha reagentlar va erituvchilar BDH chemicals kompaniyasidan analitik yoki texnik darajada olingan. Reaksiya jarayoni yupqa qatlam xromatografiyasi yordamida kuzatildi, [12].



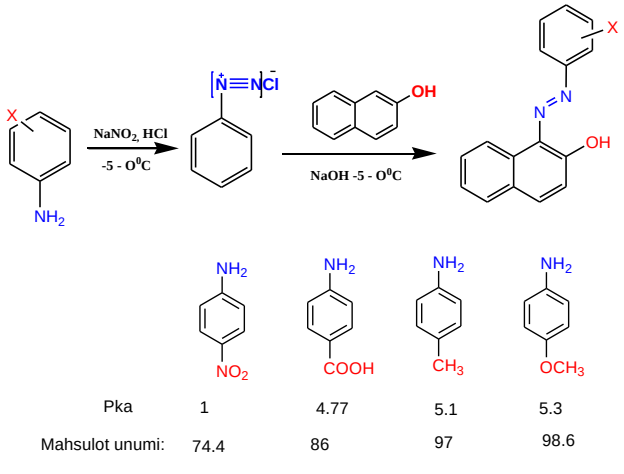
Ushbu tadqiqotda turli aromatik aminlarning diazotirlanishi va so’ngra 2-naftol bilan azobirikish reaksiyasi orqali yuqori unum bilan bir qator azo birikmalar sintez qilindi. Sintez qilingan birikmalar in vitro sharoitda bir qator mikroorganizmlarga qarshi antimikrob xususiyatlarini baholash maqsadida diffuziya usuli bilan sinovdan o’tkazildi. Ba’zi mahsulotlar shu konsentratsiyada ma’lum standart dori vositalari bilan taqqoslanadigan faollikni ko’rsatdi[13].

Tahlil va natijalar. Tajribalar davomida P-holatda turli o’rinbosarlar bo’lgan aromatic aminlar(p-toluidin, p-nitroanilin, p-bromanilin, p-aminoazobenzol, p-anizidin, p-aminobenzoy k-ta, p-amino salitsil k-ta, p-aminofenol)lar tanlab olindi. Azobirikma sintezi azobirikish reaksiyasi orqali olib borildi. Azobirikish reaksiyasi elektrofil mexanizmda 2 bosqichda boradi. Dastlab diazotirlash reaksiyasi, unda diazoniy tuzi hosil bo’ladi. Ikkinchi bosqichda esa diazoniy tuzi bilan 2-naftolning kuchsiz ishqoriy eritmasi azobirikish reaksiyasiga kirishadi. Bu jarayonlar -5-0 °C haroratda olib boriladi. Olingan mahsulot suv bilan qayta filtrlab olinadi va ochiq havoda quritiladi. Mahsulotlarning tuzilishi zamonaviy fizik kimyoviy usullar yordamida aniqlandi.

Sintez asosida olingan azobirikmalarning ba’zi fizik-kimyoviy kattaliklari

t/r	Mr	Brutto formulasi	Aromatic amin	Rangi	Mahsulot unumi	Tsuyuq	Rf qiymati
1	293	$C_{16}H_{11}N_3O_3$	p-nitroanilin	Sarg’ish qizil	74,4	248-252	0,63
2	264	$C_{16}H_{12}N_2O_2$	p-aminofenol	To’q siyohrang	84,6	237-239	0,4
3	262	$C_{17}H_{14}N_2O$	p-toluidin	qizil	97,8	131-134	0,72
4	278	$C_{17}H_{14}N_2O_2$	p-anizidn	qizil	98,6	139-142	0,77
5	352	$C_{22}H_{16}N_4O$	p-AAB	qizil	91	158-160	0,75
6	308	$C_{17}H_{12}N_2O_4$	p-aminsalitsil k-ta	To’q qizil	65	278-280	0,365*
7	327	$C_{16}H_{11}N_2OBr$	p-bromanilin	qizil	88	162-164	0,65
8	292	$C_{17}H_{12}N_2O_3$	p-aminobenzoy k-ta	qizil	86	240-242	0,45*

Yupqa qatlam xromotografiyasi yordamida (Sistema: EtAc:Pet.ester(1:3)., geksan:aseton(1:1)*) aniqlab Rf qiymatlar topildi. Reaksiyaning umumiy sxemasi:



Ko‘rinib turibdiki, elektron-donor o‘rinbosarlari (-CH_3, -OCH_3) reaksiyaning samaradorligini oshiradi, aksincha elektron-akseptorlar (-NO_2, -COOH) reaktivlikni pasaytiradi.

Ik spektr natijalari			
1	3455, sm^{-1} (ν_{OH}), 3094 sm^{-1} ($\nu_{=C-H,ArH}$), 1597 sm^{-1} ($\nu_{-N=N-}$), 1328, sm^{-1} ($\nu_{C=C\ Ar}$) 1505 sm^{-1} (ν_{-NO2}) 1717(vC=C)	5	3506 sm^{-1} (ν_{OH}), 2933-3070 sm^{-1} ($\nu_{=C-H,ArH}$), 1499 sm^{-1} ($\nu_{-N=N-}$), 1618, sm^{-1} ($\nu_{C=C\ Ar}$) 1132(vC-O), 845 sm^{-1}=C-O δ
2	3528, sm^{-1} (ν_{OH}), 3039 sm^{-1} ($\nu_{=C-H,ArH}$), 1496 sm^{-1} ($\nu_{-N=N-}$), 1328, sm^{-1} ($\nu_{C=C\ Ar}$)	6	3410 sm^{-1} (ν_{OH}), 3045 sm^{-1} ($\nu_{=C-H,ArH}$), 1492 sm^{-1} ($\nu_{-N=N-}$), 1616 sm^{-1} ($\nu_{C=C\ Ar}$) 1119 sm^{-1} (vC-O), 843 sm^{-1}=C-O δ, 1664 sm^{-1} (V-COOH)
3	3528 sm^{-1} (ν_{OH}), 3039 sm^{-1} ($\nu_{=C-H,ArH}$), 1597 sm^{-1} ($\nu_{-N=N-}$), 1606, sm^{-1} ($\nu_{C=C\ Ar}$) 2934(vC-CH_3)	7	3543 sm^{-1} (ν_{OH}), 3060 sm^{-1} ($\nu_{=C-H,ArH}$), 1496 sm^{-1} ($\nu_{-N=N-}$), 1622 sm^{-1} ($\nu_{C=C\ Ar}$) 1145 sm^{-1} (vC-O), 516 sm^{-1}=C-Br δ
4	3442 sm^{-1} (ν_{OH}), 3084 sm^{-1} ($\nu_{=C-H,ArH}$), 1492 sm^{-1} ($\nu_{-N=N-}$), 1602, sm^{-1} ($\nu_{C=C\ Ar}$) 1241(vC-O), 823 sm^{-1}=C-O δ	8	3421 sm^{-1} (ν_{OH}), 2935 sm^{-1} ($\nu_{=C-H,ArH}$), 1501 sm^{-1} ($\nu_{-N=N-}$), 1617 sm^{-1} ($\nu_{C=C\ Ar}$) 1146 sm^{-1} (vC-O), 845 sm^{-1}=C-O δ, 1664 sm^{-1} (V-COOH)

Xulosa. Ushbu ishda p-holatda turli elektron-ta’sir ko‘rsatuvchi o‘rinbosarlarga ega bo‘lgan aromatik aminlar asosida 2-naftol bilan azobirikmalar sintezi amalga oshirildi. Tadqiqot natijalariga ko‘ra, p-holatdagi o‘rinbosarlarning tabiatiga qarab 2-naftol bilan azobirikish reaksiyasiga kirish qobiliyati aromatic aminning asoslik xossasiga bo‘gliqligi aniqlandi.

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