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IZOMER PROP-2-IN-1-IL-2-(NITROFENOKSI) ATSETATLAR VA ORTO-BROMFENILAZIDNING KATALITIK HALQALANISHI

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Kalit so'zlar:
monoyodsirka kislotaning propargil efiri, izomer nitrofenollar, 1,2,3-triazollar, halqalanish reaksiyalari, prop-2-in-1-il-2-(2-nitrofenoksi) asetat

Annotatsiya
Monoyodsirka kislotaning propargil efiri monoyodsirka kislotani propargil spirti bilan eterefikatsiyalash orqali sintez qilingan. Olingan monoyodsirka kislota propargil efiri izomer nitrofenollarni alkillash uchun ishlatilgan. Sintez qilingan izomer nitrofenoksisirka kislota propargil efirlarining orto-bromofenil azid bilan 1,3-bipolyar siklodlanish reaksiyasi katalizator ishtirokida amalga oshirilgan. Katalizator sifatida mis (I) galogenidlari ishlatilgan. Natijada 1,2,3-triazol hosilalarining 1,4-izomerlari sintez qilingan. Olingan moddalarning tuzilishi IQ va YaMR spektroskopiya ma’lumotlari bilan tasdiqlangan.

Havola uchun
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Kirish. Hozirgi vaqtda triazol hosilalari asosidagi geterosiklik birikmalar bilan olib borilayotgan tadqiqotlar juda keng tarqalgan. Bu uchta azot atomini o‘z ichiga olgan besh a’zoli triazol birikmalari orasida farmakologik va biologik faollikni ko‘rsatadigan ko‘p miqdordagi moddalar mavjudligi bilan bog'liq. Sintez qilingan moddalar yuqori biologik faolligi va kam zaharliligi bilan organik kimyogarlarni o‘ziga jalb qilmoqda. Ayniqsa, 1,2,3-triazol hosilalarini qishloq xo‘jaligi va tibbiyotda turli kasalliklarga qarshi muvaffaqiyatli qo‘llash muhim masalalardan biridir. Xususan, 1,2,3-triazollar orasida shamollash, mikroblar, saraton, yallig'lanish, leyshmaniya, sil va bezgak kasalliklariga qarshi faolligi yuqori bo‘lgan birikmalar yetakchi o‘rinni egallaydi [1-10]. 1,2,3-triazollar sohasidagi tadqiqotlar ancha oldin boshlangan va hozirgi vaqtda dunyoning ko‘pgina mamlakatlarida ushbu sinf birikmalari asosida tadqiqotlar olib borilmoqda.

Adabiyotlarda 1,2,3-triazollar turli usullar bilan sintez qilingan. Birinchi alkin asetilen 1837 yilda Edmund Devi tomonidan ochilgan bo‘lsa, 1864 yilda Griss organik azidlarni sintez qildi va ularni yangi birikmalar sinfi sifatida tavsifladi. 1,2,3-triazollarni alkinlar va azidlarni o‘zaro halqalash yo‘li bilan olish haqidagi birinchi maqola 19-asr oxirida nashr etilgan. Alkinlar va azidlardan 1,2,3-triazol hosilalari sinteziga bag'ishlangan birinchi maqolada fenil azid va asetilen dikarbon kislota dimetil efirining o‘zaro halqalanish reaksiyasi 8 soat davomida, 100 ° C haroratda, kuchli yorug'lik ampulasi [1] ta'sirida olib borilgan. Bu reaksiyada alkin simmetrik bo‘lganligi sababli bitta izomer

hosil bo‘lgan. 1950-60-yillarning boshlarida Hyusgen alkinlar va organik azidlarning 1,3-bipolyar siklobirikish reaksiyasini umumiy mexanizmini ishlab chiqdi. Keyingi yarim asrda bu reaktsiya faol o‘rganildi [12].

Ammo assimetrik yoki terminal alkinlarning azidlar bilan reaksiyaga kirishishi natijasida ikkita 1,4- va 1,5-izomer triazollar aralashmasi (ko‘pincha bir-biridan farqlash qiyin) hosil bo‘lishi bu reaksiyaning keng rivojlanishiga to‘sqinlik qildi. 21-asr boshlarida, ya’ni 2002-yilda Meldal va Sharpless boshchiligidagi bir guruh olimlar mis (I) tuzi katalizatori ishtirokida terminal alkinlar va organik azidlarning halqalanish reaksiyasi natijasida faqat bitta 1,4 izomer hosil bo‘lishini aniqladilar.

Bu reaksiyada Cu(I) tuzining funksiyasi va reaksiya mexanizmi berilgan va to‘liq asoslab berilgan. Shundan so‘ng alkinlarning azidlar bilan o‘zaro birikish reaksiyasi Hyusgen-Meldal-Sharpless reaktsiyasi deb atala boshlandi. Shundan so‘ng 1,2,3-triazollar kimyosi tez sur’atlarda rivojlandi. Ma’lum vaqtdan keyin ruteniy tuzlari katalizatori bilan reaksiyada faqat 1,5-izomerlar hosil bo‘lishi ham aniqlandi [13-14].

Hozirgi vaqtda butun dunyoda 1,2,3-triazollarning sintez reaktsiyalari va biologik faolligi jadal sur’atlarda o‘rganilmoqda. Buni so‘nggi yillarda nufuzli jurnallarda chop etilgan maqolalardan bilib olish mumkin. O‘zbekistonlik olimlar (Maxsumov A.G. va uning shogirdlari) ham 1,2,3-triazollarni sintez qilib, modifikatsiya qildilar, natijada hosil bo‘lgan ayrim moddalarning yallig‘lanishga qarshi ijobiy ta’sirini aniqladilar [15-16]. Yuqoridagi adabiyotlarni o‘rganish natijalari shuni ko‘rsatadiki, yangi 1,2,3-triazol hosilalari sintezi va biologik faolligini tekshirish bo‘yicha tadqiqotlar dolzarbdir.

Metod va materiallar. Erituvchilardan atsetonitril, etil spirti, geksan, atseton, benzol, toluol va metanol ishlatilgan. Zamonaviy IQ, 1H va 13C YaMR spektroskopiya usullaridan foydalangan holda olingan natijalar asosida birikmalarning tuzilishi ishonchli tahlil qilindi. Reaksiyalarning borishi yupqa qatlamli xromatografiya (YuQX) yordamida kuzatildi. Eluent sifatida benzol: metanol nisbati 10:1 bo‘lgan aralashma ishlatilgan. Sintez qilingan birikmalarning suyuqlanish haroratlari MEL-TEMP asbobi (AQSh) yordamida aniqlandi.

Prop-2-in-1-il-2-(2-nitrofenoksi) asetat sintezi (2)

100 ml sig‘imli bir og’izli yumaloq tubli kolbaga 1.39 g (10 mmol) orto-nitrofenol, 2.46 g (11 mmol) monoyodsirka kislotaning propargil efiri (**1**), 1 g quruq potash, 0.2 g TBAB (tetrabutilammoniy bromid) va 40 ml atsetonitril olindi. Suv hammomida 80 ° C haroratda 6 soat davomida qaynatildi. Reaksiya aralashmasi sovutildi, noorganik qoldiq filtrlanadi va filtrat 100 ml sovuq suvga quyildi. Olingan cho‘kma filtrlandi, suvda yuvildi, quritildi va 1.83 g (78%) mahsulot olindi. Suyuqlanish harorati T_{suyuq}=48-50°C . Rf 0,73 (benzol:metanol - 10:1).**^{1}H YaMR** (400 MHz, $CDCl_3$): 2.53 (1H, t, J=2.47, CH_2-CCH), 4.79 (2H, d, J=2.47 COO-CH_2), 4.82 (2H, s, -OCH_2) 6.98 м.u. (1H, d, J=8.45, H- 6) 7.11 (1H, t, J=7.8, H- 5), 7.51 (1H, м, H- 4) 7.86 (1H, dd, J_1=8.12, J_2=1.75 H-3). **^{13}C YaMR** ($CDCl_3$): 53.04, 66.44, 75.95, 76.66, 115.39, 122.11, 126.05, 134.20, 140.55, 151.16, 167.16. **IQ**-spektr (KBr, ν, $см^{-1}$): 3264 (C≡C-H), 3084 (Ar C-H), 2925 (CH_2), 2134 (-C≡C-), 1768 (>C=O), 1514 (Ar-NO_2), 1204 (C-O-C).

Prop-2-in-1-il 2-(3-nitrofenoksi)atsetat sintezi (3)

Yuqorida keltirilgan usul orqali 1.39 g (10 mmol) meta-nitrofenol, 2.46 g (11 mmol) monoyodsirka kislotaning propargil efiri (**1**), 1 g quruq potash, 0.2 g TBAB (tetrabutilammoniy bromid) va 40 ml atsetonitril olindi. Massasi 2.233 g (95 % unum bilan) mahsulot (**3**) olindi . Tsuyuq=88-90 ºC. Rf 0.48 (sistema benzol : metanol – 10:1). **^{1}H YaMR** (400 MHz, $CDCl_3$): 2.53 (1H, t, J=2.47, CH_2-CCH), 4.76 (2H, s, -OCH_2), 4.81 (2H, d, J=2.47, COO-CH_2), 7.26 (1H, м, H- 6) 7.46 (1H, t, J=8.25, H- 5), 7.71 (1H, t, J=2.34, H- 2), 7.88 (1H, dd, J_1=8.19, J_2=2.14 H-4). **^{13}C YaMR** ($CDCl_3$): 53.05, 65.36, 76.00, 76.64, 109.24, 117.09, 121.88, 130.35, 149.26, 158.20, 167.36. **IQ**-spektr (KBr, ν, $см^{-1}$): 3249 (C≡C-H), 3102 (Ar C-H), 2939 (CH_2), 2132 (-C≡C-), 1753 (>C=O), 1527(Ar-NO_2), 1206 (C-O-C).

Prop-2-in-1-il 2-(4-nitrofenoksi)atsetat sintezi (4)

Yuqorida keltirilgan usul orqali 1.39 g (10 mmol) para-nitrofenol, 2.46 g (11 mmol) monoyodsirka kislotaning propargil efiri (**1**), 1.0 g quruq potash, 0.2 g TBAB (tetrabutilammoniy bromid) va 40 ml atsetonitril olindi. Massasi 1.915 g (81.5% unum bilan) mahsulot (**4**) olindi. Tsuyuq=118-120 ºC. Rf 0.71 (sistema benzol : metanol – 10:1). **^{1}H YaMR** (400 MHz, $CDCl_3$): 2.53 (1H, t, J=2.47, CH_2-CCH), 4.77 (2H, c, -OCH_2), 4.81 (2H, д, J=2.47,COO-CH_2) 6.96 м.u. (2H, d, J=9.22, H- 2, 6) 8.20 (2H, d, J=9.22, H- 3,5). **^{13}C YaMR** ($CDCl_3$): 53.10, 65.24, 76.05, 76.58, 114.81, 126.07, 142.50, 162.46, 167.09. **IQ**-spektr (KBr, ν, $см^{-1}$): 3290 (C≡C-H), 3117 (Ar C-H), 2944 (CH_2), 2134 (-C≡C-), 1758 (>C=O), 1502 (Ar-NO_2), 1203 (C-O-C).

Prop-2-in-1-il 2-(2,4-dinitrofenoksi)atsetat sintezi (5)

Yuqorida keltirilgan usul orqali 1.84g (10 mmol) 2,4-dinitrofenol, 2.46 g (11 mmol) monoyodsirka kislotaning propargil efiri (**1**), 1 g quruq potash, 0.2 g TBAB (tetrabutilammoniy bromid) va 40 ml atsetonitril olindi. Massasi 2.254 g (80.5% unum bilan) mahsulot (**5**) olindi. Tsuyuq=84-86ºC. Rf 0.76 (sistema benzol : metanol – 10:1). **^{1}H YaMR** (400 MHz, $CDCl_3$): 2.53 (1H, t, J=2.47, CH_2-CCH), 4.78 (2H, s, -OCH_2), 4.83 (2H, d, J=2.47,COO-CH_2) 7.18 (1H, d, J=6.81, H- 6), 7.83 (1H, d, J=8.36, H- 5), 8.24 (1H, d, J=5.44, H- 3). **^{13}C YaMR** ($CDCl_3$): 53.31, 65.73, 75.91, 76.46, 116.37, 124.47, 131.14, 134.20, 144.19, 150.32, 167.29. **IQ**-spektr (KBr, ν, $см^{-1}$): 3267 (C≡C-H), 3301 (Ar C-H), 2127 (-C≡C-), 1762 (>C=O), 1524, 1538 (Ar-NO_2), 1211 (C-O-C).

(1-(2-bromofenil)-1H-1,2,3-triazol-4-il) metil 2-(2-nitrofenoksi)atsetat sintezi (6)

100 ml li tubi yumaloq kolbaga 1.0 g (0.005 mol) orto-bromfenilazid, 1.175 g (0.005 mol) prop-2-in-1-il-2-(2-nitrofenoksi)atsetat, 0.10 g (0.32 mmol) mis(I)bromid va 30 ml yangi haydalgan toluol olindi. Kolba moy hammomiga o‘rnatilib, qaytarma sovutgichga ulangan holda, toluolni qaynash haroratida (110º C) 6 soat davomida qizdirildi. Reaksiyani borishi yupqa qavatli xromatografiya orqali tekshirib turildi. Reaksiya aralashmasida vaqt o‘tishi bilan cho‘kma hosil bo‘la boshladi. 6 soatdan so‘ng reaksiya to‘xtatildi va xona haroratida bir kecha qoldirildi. Tushgan cho‘kma filtrlandi, quritildi va etanolda qayta kristallandi. Massasi 1.6887 g (78 % unum) bilan mahsulot (**6**) olindi. Tsuyuq=104-106ºC. Rf 0.68 (sistema benzol : metanol – 10:1). **^{1}H YaMR** (400 MHz, $CDCl_3$): 4.87 (2H, s, -OCH_2), 5.48 (2H, s, COO-CH_2), 6.61 (1H, dd, J_1=8.45, J_2=2.55 Ar-H-6), 7.36 (4H, м, Ar-H- 3’,4’,5’,6’), 7.62 (1H, t, J=8.82 Ar-H- 5), 8.13 (1H, s, triazol-H), 8.21 (1H, dd, J_1=8.81, J_2=2.32 Ar-H- 3), 8.07. **^{13}C YaMR** ($CDCl_3$): 61.46, 64.47, 115.16, 118.20, 120.87, 122.23, 127.34, 128.93, 130.37, 131.12, 133.79, 134.68, 139.23, 140.40, 144.09, 152.78, 169.30. **IQ**-spektr (KBr, ν, sm^{-1}): 3148 (Ar C-H), 3049 (C=C-H), 2944 (CH_2), 1756 (>C=O), 1611 (C=C), 1579(N=N), 1509 (Ar-NO_2), 1378 (C-O-), 1212 (C-N), 1173 (C-O-C), 582 (C-Br).

(1-(2-bromofenil)-1H-1,2,3-triazol-4-il) metil 2-(3-nitrofenoksi)atsetat sintezi (7)

Yuqorida keltirilgan usul orqali 1.0 g (0.005 mol) orto -bromfenilazid, 1.175 g (0.005 mol) prop-2-in-1-il-2-(3-nitrofenoksi)atsetat, 0.10 g (0.32 mmol) mis(I)bromid va 30 ml toluol olindi. Massasi 1.9052 g (88 % unum bilan) mahsulot (**7**) olindi. Tsuyuq=79-80ºC. Rf 0.67 (sistema benzol : metanol – 10:1).**^{1}H YaMR** (400 MHz, $CDCl_3$): 4.92 (2H, s, -OCH_2), 5.43 (2H, s, COO-CH_2) 7.11 (1H, dd, J_1=8.42, J_2=2.41, Ar-H-6), 7.38 (6H, m, Ar-H-2, 5, 3’,4’,5’,6’), 7.77 (1H, dd, J_1=8.86, J_2=2.56, Ar-H-4), 8.11 (1H, s, triazol-H). **^{13}C YaMR** ($CDCl_3$): 61.34, 64.58, 114.68, 116.72, 121.08, 122.43, 126.87, 128.67, 130.28, 131.47, 134.09, 135.07, 138.78, 141.02, 144.19, 153.06, 168.12. **IQ**-spektr (KBr, ν, $см^{-1}$): 3171 (Ar C-H), 3097 (C=C-H), 1741 (>C=O), 1617 (C=C), 1590 (N=N), 1519 (Ar-NO_2), 1355 (C-O-), 1230 (C-N), 1191 (C-O-C), 578 (C-Br).

(1-(2-bromofenil)-1H-1,2,3-triazol-4-il) metil 2-(4-nitrofenoksi)atsetat sintezi (8)

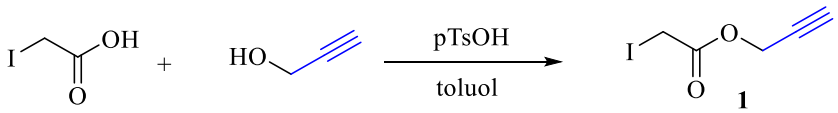
Yuqorida keltirilgan usul orqali 1.0 g (0.005 mol) orto-bromfenilazid, 1.175 g (0.005 mol) prop-2-in-1-il-2-(4-nitrofenoksi)atsetat, 0.10 g (0.32 mmol) mis(I)bromid va 30 ml toluol olindi. Massasi 1.732 g (80 % unum bilan) mahsulot (**8**) olindi. Tsuyuq=84-86ºC. Rf 0.55 (sistema benzol : metanol – 10:1). **^{1}H YaMR** (400 MHz, $CDCl_3$): 4.93 (2H, s, -OCH_2), 5.42 (2H, s, COO-CH_2) 7.07 (2H, d, Ar-H- 2,6), 7.51 (1H, dd, J_1=8.07, J_2=7.15, J_3=2.02, Ar-H-4’), 7.54 (1H, dd, J_1=7.84,

J_2=1.88, Ar-H-3'), 7.57 (1H, dd, J_1=87.11, J_2=1.33, Ar-H-5'), 7.84 (1H, dd, J_1=7.98, J_2=1.19, Ar-H-6'), 8.18 (2H, d, J=9.05, Ar-H-3,5), 8.32 (1H, s, triazol-H). **^{13}C YaMR** ($CDCl_3$): 57.54, 64.93, 114.75, 118.85, 125.41, 126.93, 128.22, 128.62, 131.78, 133.75, 136.35, 142.13, 163.03, 168.24. **IQ**-spektr (KBr, ν, sm^{-1}): 3160 (Ar C-H), 3090 (C=C-H), 2936 (CH_2), 1767 (>C=O), 1610 (C=C), 1592 (N=N), 1510 (Ar-NO_2), 1338 (C-O-), 1201 (C-N), 1170 (C-O-C), 577 (C-Br).

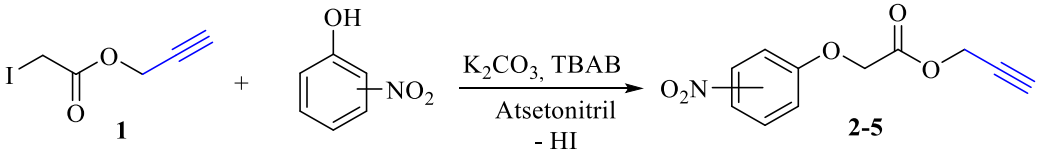
(1-(2-bromofenil)-1H-1,2,3-triazol-4-il) metil 2-(2,4-dinitrofenoksi)atsetat sintezi (9)

Yuqorida keltirilgan usul orqali 1.0 g (0.005 mol) orto-bromfenilazid, 1.4 g (0.005 mol) prop-2-in-1-il-2-(2,4-dinitrofenoksi)atsetat, 0.10 g (0.32 mmol) mis(I)bromid va 30 ml toluol olindi. Massasi 2.0554 g (86 % unum bilan) mahsulot (**9**) olindi. Tsuyuq=110-112^{o}C. Rf 0.51 (sistema benzol : metanol – 10:1). **^{1}H YaMR** (400 MHz, $CDCl_3$): 4.92 (2H, s, -OCH_2), 5.43 (2H, s, COO-CH_2) 7.46 (5H, м, Ar-H-6,3',4',5',6'), 8.12 (1H, dd, J_1=8.36, J_2=2.04, Ar-H-5), 8.21 (1H, s, triazol-H), 8.72 (1H, d, J=8.44, Ar-H-3). **^{13}C YaMR** ($CDCl_3$): 58.24, 66.09, 109.11, 116.85, 122.09, 122.23, 122.540, 122.98, 130.67, 133.22, 136.08, 143.059, 148.78, 157.98, 168.28. **IQ**-spektr (KBr, ν, sm^{-1}): 3146 (Ar C-H), 3088 (C=C-H), 1738 (>C=O), 1602 (C=C), 1527 (N=N), 1483 (Ar-NO_2), 1344 (C-O-), 1221 (C-N), 1157 (C-O-C), 570 (C-Br).

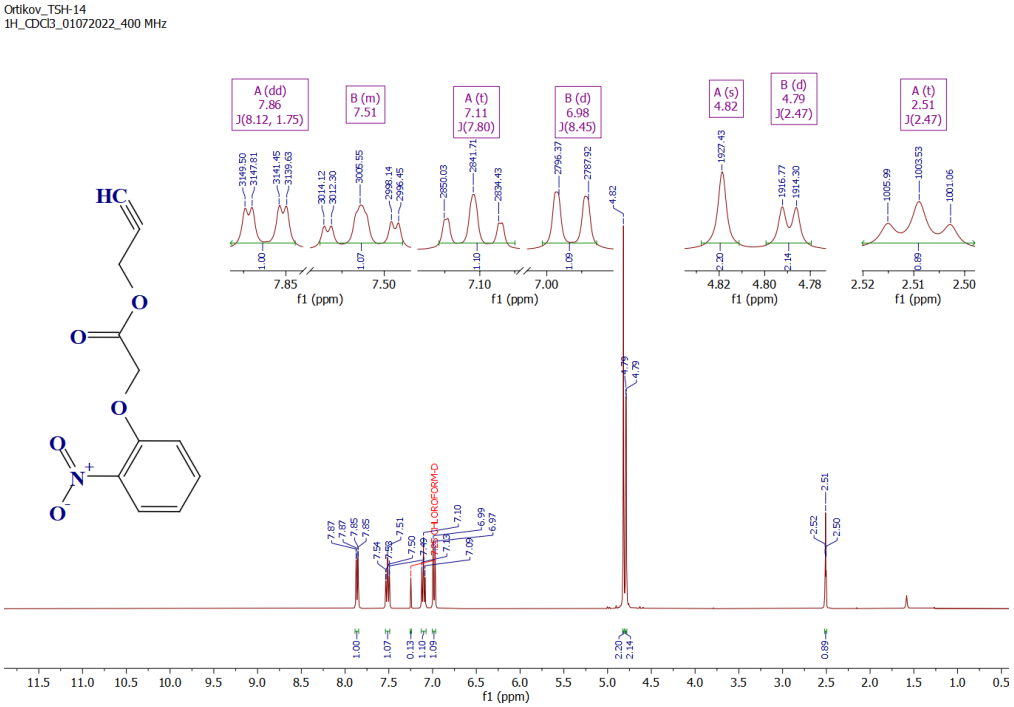
Natijalar va muhokama. Ushbu tadqiqotning asosiy maqsadi izomer nitrofenollar va monoyodsirka kislota propargil efirini o'zaro alkillash natijasida olingan izomer prop-2-in-1-il-2-fenoksi (almashingan) atsetat efirlari bilan orto-bromfenilazidning halqalanish reaksiyasini olib borish va reaksiyaning borishiga ta'sir etuvchi omillarni aniqlashdan iborat edi. Buning uchun biz dastlab ishni, boshlang'ich moddalarni sintez qilishdan boshladik. Dastlab, monoyodsirka kislota propargil efir (**1**) monoyodsirka kislota va propargil spirtining eterifikasiya reaksiyasi orqali sintez qilindi. Reaksiya aralashmasidan suvni olib tashlash uchun para-toluol sulfo kislota (pTsOH) ishlatildi.



Keyin nitrofenollarning (almashingan) monoyodsirka kislotaning propargil efiri bilan alkillanish reaksiyasi amalga oshirildi. Nitrofenol izomerlaridan 2-nitro, 3-nitro, 4-nitro va -2,4-dinitrofenollar ishlatilgan. Reaksiya izomer nitrofenollar va monoyodsirka kislota aralashmasini potash va TBAB katalizatorlari ishtirokida 1:1 mol nisbatda atsetonitril eritmasida qizdirish orqali amalga oshirildi. Natijada, izomer prop-2-in-1-il-2-(nitrofenoksi)asetatlar (**2-5**) yuqori unumlarda ajratib olindi. Moddalar geksanda qayta kristallandi.



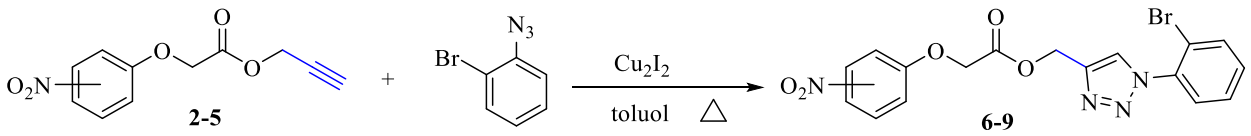
Adabiyotda sintez qilingan propargil efirlari (**2-5**) to'g'risida ma'lumot topa olmaganimiz uchun biz spektral tahlil natijalarini va eksperimental usullarni batafsil keltirishni zarur deb hisobladik. Olingan **2-5** moddalarning tuzilishi IQ va YaMR spektrlari yordamida o'rganildi. Prop-2-in-1-il-2-(2-nitrofenoksi)atsetat (2) ($CDCl_3$) ning ^{1}H YaMR spektri tahlil qilinganda, uch bog' bilan bog'langan terminal alkin protonning kimyoviy siljishi 2,51 m.u. sohada (1H, t, J=2.47) bir protonli triplet shaklida, 4.79 m.u. sohada terminal uchbog' bilan bog'langan metilen guruhi (2H, d, J=2.47) ikki protonli dublet ko'rinishida namoyon bo'ladi, karboksil guruhi va kislorod bilan bog'langan metilen guruhi signali esa 4.82 m.u. sohada (2H, s, -OCH_2) ikki protonli singlet shaklida namoyon bo'ladi (1-rasm). Benzol halqasi molekulasidagi protonlar esa 6.98 m.u. sohada (1H, d, J = 8.45, H - 6) bir protonli dublet holida, 7.11 m.u. sohada (1H, t, J=7.8, H- 5) bir protonli triplet, 7.51 m.u. (1H, m, H-4) va 7.86 m.u. sohalarda multiplet singlet holida va 7.86 m.u. sohada (1H, dd, J_1=8.12, J_2=1.75 H-3) bir protonli dublet-dublet shaklida kimyoviy siljishga ega ekanligini ko'rishimiz mumkin.



1-rasm. Prop-2-in-1-il-2-(2-nitrofenoksi)atsetatning ^{1}H YaMR spektri

2-moddaning IQ spektrida terminal alkin (C≡C-H) funksional guruhining xarakterli yutilish chastotalari 3264 sm^{-1} sohada, aromatik uglerod-vodorod (Ar C-H) bog'i 3084 sm^{-1} sohada, uch bog' saqlagan uglerod-uglerod (- C≡C -) bog'iga tegishli yutilish chastotalari esa 2134 sm^{-1} sohada, karbonil guruhi 1768 sm^{-1} (>C=O) sohada, aromatik halqadagi nitroguruh 1514 sm^{-1} sohada (Ar-NO_2), uglerod-kislorod(-C-O) yutilish sohasi 1204 sm^{-1} kimyoviy siljishga ega. Qolgan efirlarning tuzilishi (**3-5**) ham IQ va YaMR spektrlari yordamida o'rganildi va tahlil qilindi. Olingan spektrlarning natijalari ushbu moddalarning tegishli birikmalarga mos kelishini to'liq isbotlaydi.

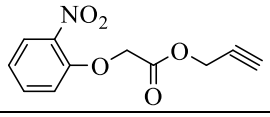
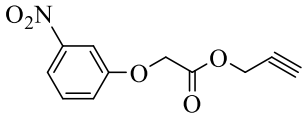
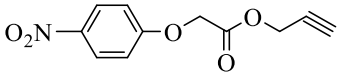
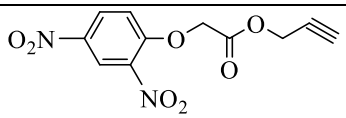
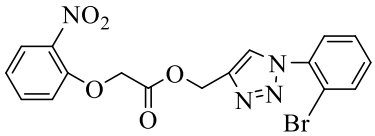
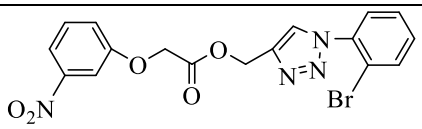
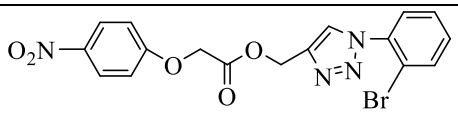
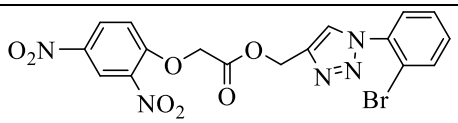
Tadqiqotlarni keyingi bosqichida biz orto-bromofenil azid (**2-5**) bilan izomer prop-2-in-1-il-2-(nitro-fenoksi) asetatlarning katalitik halqalanish reaktsiyalarini olib bordik. Reagentlar aralashmasini 1:1 nisbatda toluol eritmasida mis (I) yodid katalizatori ishtirokida 110°C haroratda (toluolning qaynash harorati) 6 soat davomida qizdirish orqali reaksiya olib borildi.



Reaksiya aralashmasi sovutildi, hosil bo'lgan cho'kma filtrlandi, quritildi va fizik konstantalar o'rganiladi (1-jadval). Natijada 1H-1,2,3-triazollarning (**5-9**) yangi 1,4-izomer hosilalari yuqori unumlar bilan olindi. Aytish mumkinki, oldingi tadqiqotlarimizda biz katalizatorlar va erituvchilarning ushbu halqalanish reaksiyalariga ta'sirini o'rgangan edik [17-18]. Muqobil sharoit sifatida toluol eritmasida mis (I) galogenid katalizatori ishtirokida amalga oshiriladigan usul tanlandi.

1-Jadval. Sintez qilingan moddalarning (2-9) ayrim fizik-kimyoviy kattaliklari

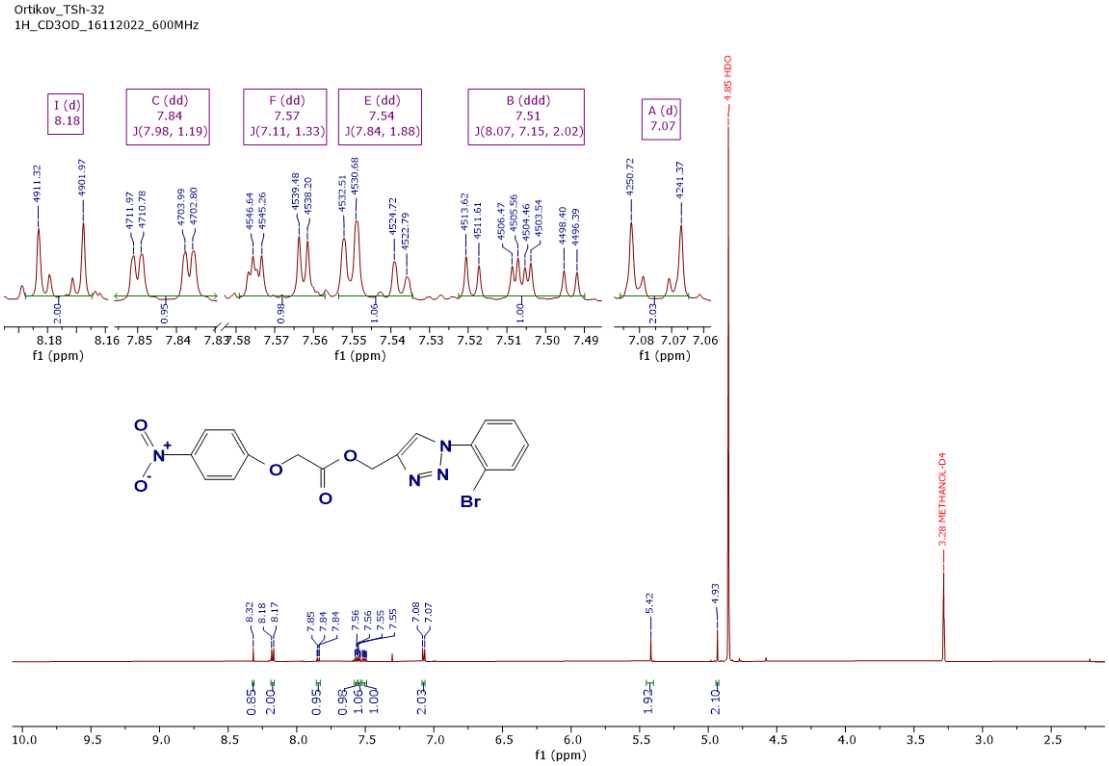
№	Struktura formulasi	Rf (benzol: metanol – 10:1	uq. har., °C	um, %

2		0.73	48-50	78
3		0.48	88-90	95
4		0.71	118-120	82
5		0.76	84-86	81
6		0.73	104-106	78
7		0.48	79-80	88
8		0.55	84-86	80
9		0.51	110-112	86

Olingan triazol hosilasi (1-(2-bromofenil)-1H-1,2,3-triazol-4-il)metil 2-(4-nitrofenoksi)atsetatning (**8**) tuzilishi ^{1}H YaMR va ^{13}C YaMR spektrlari yordamida tahlil qilindi. Uning 1H YaMR-spektrida (CDCl3) karboksil guruh va fenoksi guruh orasidagi metilen guruh 4.93 m.u. da ikki protonli singlet holida tegishli kimyoviy siljishga (2H, s, -OCH_2), triazol halqasini bog‘lab turuvchi metilen guruhi protonlari 5.42 m.u.da ikki protonli singlet holida tegishli kimyoviy siljishga (2H, s, COO-CH_2) ega bo‘lganini ko‘rishimiz mumkin (2-rasm).

Molekuladagi benzol halqasi protonlari 7.07 m.u. (2H, d, J=9.05, Ar-H-2,6) sohada ikki protonli dublet, 7.51 m.u. (1H, ddd, J_1=8.07, J_2=7.15, J_3=2.02, Ar-H-4’) sohada bir protonli dublet-dublet-dublet, 7.54 m.u. (1H, dd, J_1=7.54, J_2=1.88, Ar-H-5’) sohada bir protonli dublet-dublet, 7.57 m.u. (1H, dd, J_1=7.11, J_2=1.33, Ar-H-6’) sohada bir protonli dublet-dublet, 7.84 m.u. (1H, dd, J_1=7.98, J_2=1.19, Ar-H-3’) sohada bir protonli dublet-dublet, 8.18 m.u. (2H, d, J=9.05, Ar-H-3,5) sohada ikki protonli dublet holida kimyoviy siljishga ega. Triazol halqasidagi proton (C-H) bir protonli singlet holida (1H, s) kuchsiz 8.32 m.u. sohada kimyoviy siljishga ega ekanligini ko‘rish mumkin.

8-Moddaning IQ spektrlarini tahlil qilganda, aromatik halqadagi C-H aril bog‘ining yutilish chastotalari 3153 sm^{-1} da, triazol halqasining uglerod-vodorod bog‘i (C=C-H) 3045 sm^{-1} bo‘lgan sohada, karbonil guruhiga tegishli (>C=O) 1760 sm^{-1}da, uglerod-uglerod qo‘sh bog‘ining tebranishlari (C=C) 1610 sm^{-1}, N=N qo’sh bog‘ining tebranishlari 1591 sm^{-1} sohada, aromatik halqadagi nitroguruh (Ar-NO_2) 1201 sm^{-1} sohada signalni namoyon qiladi, 1170 sm^{-1} mintaqadagi uglerod-kislorod-uglerod (C-O-C) bog‘lariga xos yutilish sohalarida valent tebranishlari aniqlandi.



2-rasm. (1-(2-bromfenil)-1H-1,2,3-triazol-4-il)metil,2-(4-nitrofenoksi) atsetatning (8) 1H YaMR spektri

Qolgan 1,2,3-triazol hosilalari (**6-9**) tuzilmalari IQ va YaMR spektroskopiyasi bilan o‘rganildi va tahlil qilindi. Olingan spektral natijalarga asoslanib, ushbu moddalarning strukturaviy muvofiqligi to‘liq isbotlandi. Sintez qilingan triazol hosilalari yangi birikmalar bo‘lib, hozirgi vaqtda bu moddalarning biologik faolligi o‘rganilmoqda.

Xulosa. Yumshoq sharoitda almashingan nitrofenollarni monoyodsirka kislotaning propargil efiri bilan alkillash natijasida izomer prop-2-in-1-il-2-(nitrofenoksi) asetatlar sintez qilingan. Olingan propargil asetat efirlarining orto-bromfenil azid bilan o‘zaro halqalanishi natijasida 1H-1,2,3-triazollarning yangi hosilalari ajratib olingan. Ushbu tadqiqotlar maqsadli sintez reaksiyalarida muvaffaqiyatli qo‘llanilishi mumkin. Ushbu usullarning soddaligi va qulayligi ularning bir qator afzalliklarga ega ekanligini anglatadi.

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