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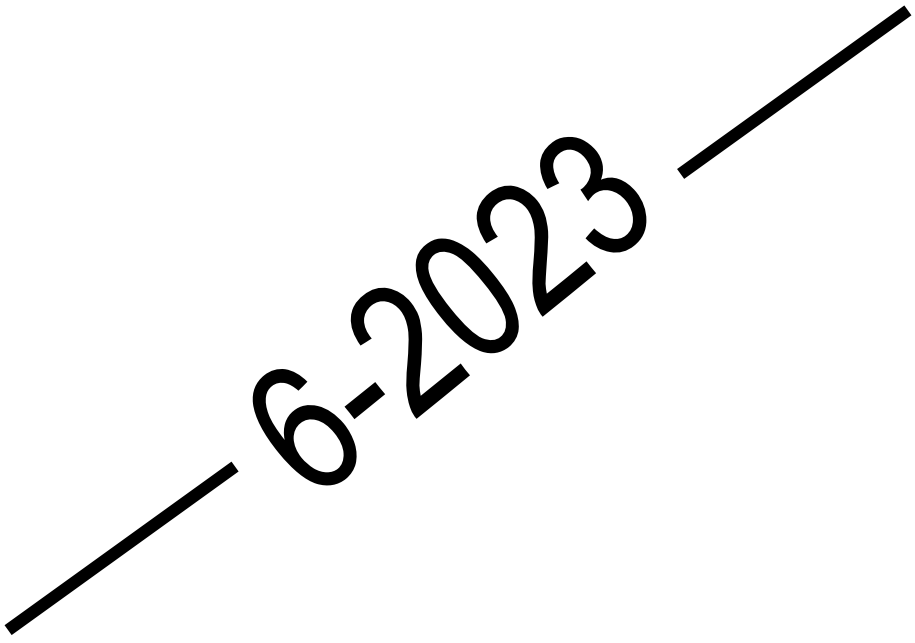

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AYRIM GETEROATOMLI ALDEGIDLARNI $InBr_3/Et_3N/Et_2O$ KATALITIK SISTEMASIDA ALKINILLASH JARAYONI

ПРОЦЕСС АЛКИНИЛИРОВАНИЯ НЕКОТОРЫХ ГЕТЕРОАТОМНЫХ АЛЬДЕГИДОВ С АЛКИНАМИ В ПРИСУСТВИИ КАТАЛИТИЧЕСКОЙ СИСТЕМЫ $InBr_3/Et_3N/Et_2O$

THE PROCESS OF ALKYNYLATION OF SOME HETEROATOMIC ALDEHYDES WITH ALKYNES IN THE PRESENCE OF THE $InBr_3/Et_3N/Et_2O$ CATALYTIC SYSTEM

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Annotatsiya

Molekulasida geteroatom o‘rinbosarlar saqlagan quyidagi aldegidlar– tiofen-2-karbaldegid, 3-metiltiofen-2-karbaldegid, furan-2-karbaldegid, piridin-3-karbaldegid, xinolin-2-karbaldegid va 3-brom-4-piridinkarbaldegidlarning atsetilen, fenilatsetilen, geksin-1 va oktin-1 bilan ilk bor $InBr_3/Et_3N/Et_2O$ katalitik sistemasida atsetilen spirtlari sintez qilingan. Mahsulot unumiga boshlang‘ich moddalar mol miqdori nisbatlari, reaksiya davomiyligi, harorat, katalizator va erituvchilar tabiati ta’siri tizimli ravishda o‘rganilgan. Sintez qilingan yangi avlod atsetilen spirtlarining tarkibi, tozaligi va tuzilishi zamonaviy fizik-kimyoviy usullarda isbotlangan.

Аннотация

Альдегиды, содержащие в своей молекуле гетероатом– тиофен-2-карбальдегид, 3-метилтиофен-2-карбальдегид, фуран-2-карбальдегид, пиридин-3-карбальдегид, хинолин-2-карбальдегид и 3-бром-4 пиридинкарбальдегидов с ацетилен, фенилацетилен, гексин-1, октином-1 впервые были синтезированы ацетиленовые спирты с использованием каталитической системы $InBr_3/Et_3N/Et_2O$. Систематически изучалось влияние молярных количественных соотношений исходных веществ, длительности реакции, температуры, природы катализатора и растворителей на выход продукта. Состав, чистота и структура синтезированных ацетиленовых спиртов нового поколения доказаны современными физико-химическими методами.

Abstract

Aldehydes containing in their molecule heteroatom– thiophene-2-carbaldehyde, 3-methylthiophene-2-carbaldehyde, furan-2 carbaldehyde, pyridine-3-carbaldehyde, quinoline-2-carbaldehyde and 3-bromine-4 pyridine carbaldehyde with acetylene, phenylacetylene, hexin-1, octin-1 were synthesized for the first time acetylene alcohols using the $InBr_3/Et_3N/Et_2O$ catalytic system. The influence of molar quantitative ratios of starting substances, reaction duration, temperature, nature of the catalyst and solvents on the yield of the product was systematically studied. The composition, frequency and structure of synthesized acetylene alcohols of a new generation have been proven by modern physicochemical methods.

Kalit so‘zlar: *aldegidlar, alkinlar, indiy (III) bromid, trietilamin, alkinillash, atsetilen spirtlari, reaksiya mexanizmi, mahsulot unumi.*

Ключевые слова: *альдегиды, алкины, бромид индия (III), триэтиламин, алкинилирование, ацетиленовые спирты, механизм реакции, выход продукта.*

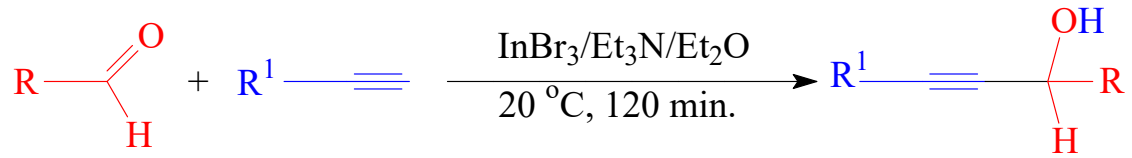
Key words: *aldehydes, alkynes, indium (III) bromide, triethylamine, alkynylation, acetylene alcohols, reaction mechanism, product yield.*

KIRISH

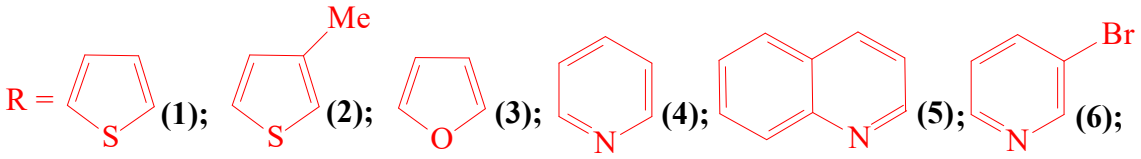
Oxirgi yillarda molekulasida bir nechta faol markazlar saqlagan atsetilen spirtlarini yuqori unum bilan sintez qilish uchun yangi turdagi katalitik sistemalar ishlab chiqilmoqda [1-3]. Jumladan 2-gidroksi-2-(1-metil-1N-indol-3-il)-1-feniletanon asosida -45 °C harorarda tetragidrofuran eritmasida 1-(1-metil-1N-indol-3-il)-2-fenilbut-3-in-1,2-diol sintez qilish jarayoni o'rganilgan [4]. Xitoy olimlari alifatik aldegidlarning dietilruxning ksilol va benzol aralashmasidan tayyorlangan katalitik sistemada fenilatsetilen bilan alkinillanish reaksiya -20 °C haroratda olib borilgan va 51-84% unum bilan aromatik atsetilen spirtlari sintez qilingan [5]. NaOH, KOH yoki CsOH/KO^{tr}Bu/DMSO komponenti bilan ketonlar va aldegidlarni alkinillash jarayoni amalga oshirilgan [6, 7]. Benzaldegidni 24 soat davomida, 0 °C haroratda assimmetrik alkinillanish reaksiyasi uchun katalizator Ti(O^{i}Pr)$_4$/Et$_2$Zn va ligand 1-(4-fenilxinazolin-2-il)etanoldan foydalanib amalga oshirilgan [8]. Rux ва allil bromid katalizatorlarining tetragidrofuran eritmasida, xona haroratida aromatik, alifatik va vinil aldegidlarlarn fenilatsetilen va geksin-1 bilan alkinillash asosida 1-(3-xlorfenil)-3-fenilpropin-2-ol-1, 1-(2,4-xlorfenil)-3-fenilpropin-2-ol-1 sintez qilingan [9]. KOH/EtOH/H$_2$O/DMSO katalitik sistemasi yordamida esa alkil, aril va geteroatomli ketonlarni atsetilen bilan reaksiyasi 10-15 °C haroratda, 2 soat davomida olib borilganda uchlamchi atsetilen spirtlari olingan [10]. Bu$_4$NOH/H$_2$O/DMSO katalitik sistemasi yordamida ketonlarni alifatik, aromatik, siklik terminal alkinlar bilan enantioselektiv alkinillash jarayoni amalga oshirilgan va 72-93% unum bilan atsetilen spirtlari sintez qilingan [11]. Ko'chib o'tuvchi elektronga ega bo'lgan metall kationli (Cu, In, Ga, Pd va Ag singari) katalizatorlar ishtirokida atsetilen dikarbon kislotalariga keton yoki aldegidlar ta'sir ettirib birlamchi atsetilen spirtlari sintez qilingan [12, 13]. Ayrim aldegidlarni ZnEt$_2$/Ti(O^{i}Pr)$_4$ kompleks katalitik sistemasi ishtirokida fenilatsetilen bilan enantioselektiv alkinillash reaksiyalari bo'yicha atsetilen spirtlari olingan [14-17].

NATIJALAR VA MUHOKAMA

Ushbu ishda ayrim geteroatomli aldegidlar- tiofen-2-karbaldegid, 3-metiltiofen-2-karbaldegid, furan-2-karbaldegid, piridin-3-karbaldegid, xinolin-2-karbaldegid va 3-brom-4-piridinkarbaldegidni ilk bor InBr$_3$/Et$_3$N/Et$_2$O katalitik sistemasida terminal alkinlar- atsetilen, fenilatsetilen, geksin-1 va oktin-1 bilan alkinillash reaksiyasi asosida yangi turdagi atsetilen spirtlari sintezi o'tganilgan. Reaksiya sxemasi adabiyot manbaalari asosida quyidagicha taklif etildi [18].

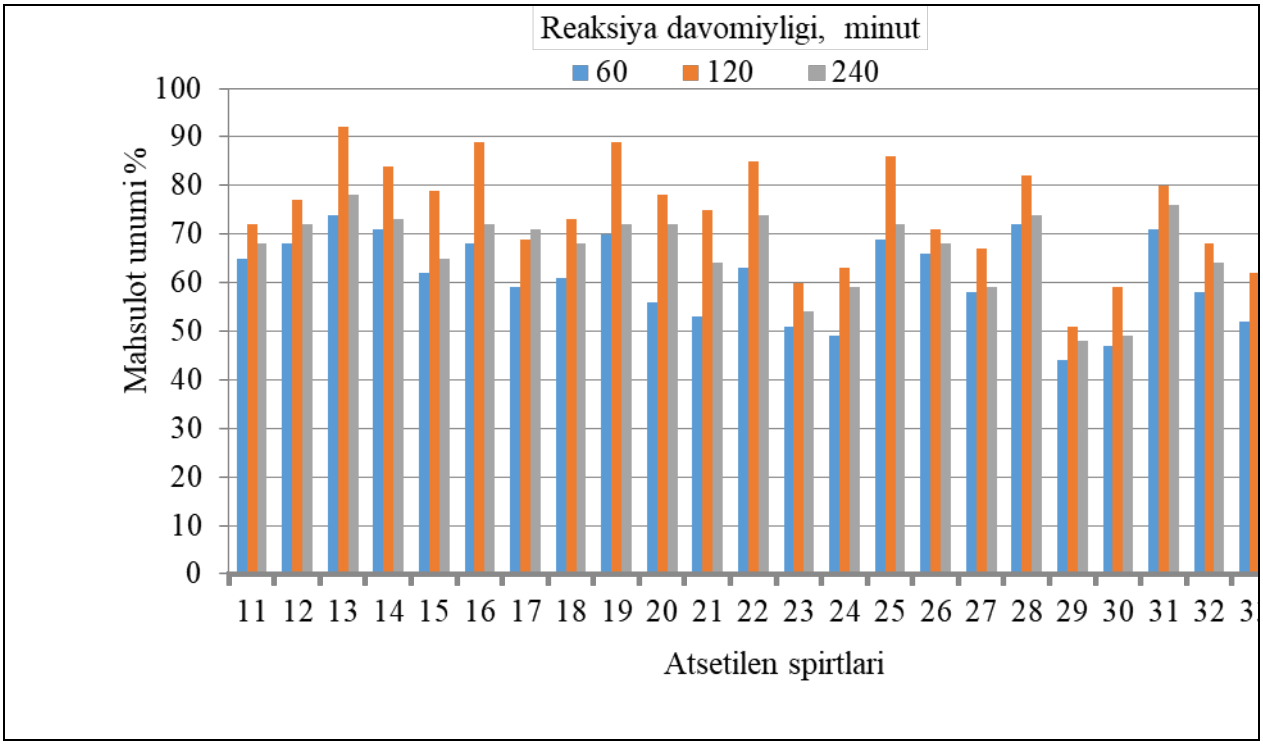


1-6 **7-10** **11-34**



R^1 = H (**7**); C$_6$H$_5$ (**8**); C$_4$H$_9$ (**9**); C$_6$H$_{13}$(**10**)

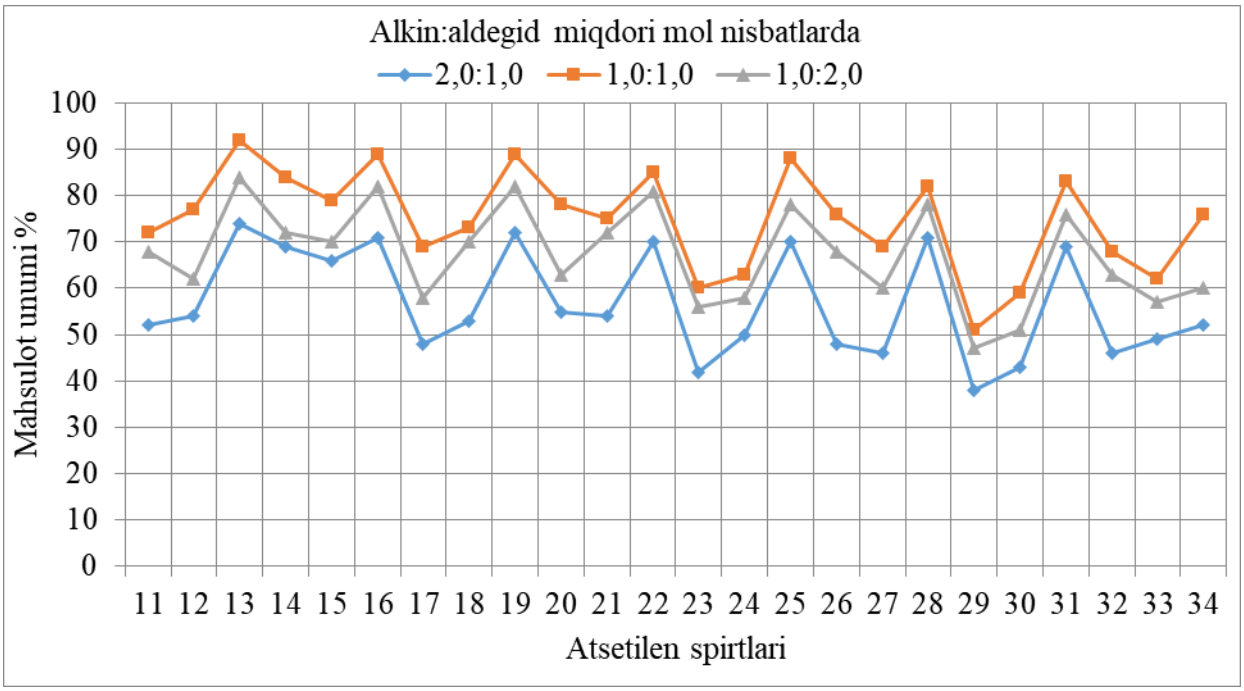
Atsetilen spirtlar unumiga turli omillar ya'ni boshlang'ich moddalar mol miqdori, reaksiya davomiyligi, harorat, erituvchilar tabiatining ta'siri tizimli tahlil qilindi. Bunda dastlab reaksiya davomiyligini o'rganish maqsadida jarayonlar 60÷240 minut interval oralig'ida olib borildi (1-Rasm). Reaksiya 60 minutda olib borilganda aralashmada boshlang'ich moddalar molekula va ionlarning to'liq to'qnashuvi uchun yetarli vaqt bo'lmaganligi sababli mahsulot unumi past chiqdi.



1-Rasm. Atsetilen spirtlari unumiga reaksiya davomiyligining ta'siri (harorat 20 °C, boshlang'ich moddalar mol miqdori 1:1 nisbatda)

Reaksiya davomiyligini 120 minutga oshirilganda esa sistemada oraliq mahsulotning unumdorligi oshishi kuzatildi va muvozanat atsetilen spirtlar hosil bo'lish tomonga siljishi aniqlandi. Ammo jarayonlar 240 minutda olib borilganda asosiy mahsulot unumdorligi pasayganligi, sintez qilingan atsetilen spirtlarining degidratlanishi, qo'shimcha mahsulot sifatida efirlar hosil bo'lishi sababli jarayon selektivligining kamayishiga olib keldi.

Tadqiqotlar asosida atsetilen spirtlari unumiga substrat (aldegid) va reagent (alkin) miqdori mol nisbatlarda ta'siri o'rganildi (2-Rasm). Jarayonda alkinlar miqdori aldegidlarga nisbatan ko'p olinganda, sistemadagi atsetilen diollari bilan vinillanish reaksiyasi sodir bo'lib, vinilefirlar hosil bo'ladi. Boshlang'ich moddalar miqdori teng nisbatlarda olinganda, sistemada kation va anionlarto'qnashuvlar soni maksimum o'tishi aniqlandi. Aksincha aldegidlar miqdori alkinlarga nisbatan ko'p olinganda esa atsetilen spirtlar bilan ta'sirlashishidan uning diollari hosil bo'lishi hisobiga mahsulot unumining kamayish kuzatildi.



2-Rasm. Atsetilen spirtlari unumiga boshlang‘ich moddalar mol nisbati ta’siri (harorat 20 °C, reaksiya davomiyligi 120 minut)

Atsetilen spirtlari unumiga qutbli proton va aproton erituvchilar- dietilefir (Et_2O) atsetonitril (MeCN), tetragidrofuran (TGF) va metanol (MeOH) tabiati ta’siri tizimli ravishda tadqiq qilindi (1-Jadval). Jadvaldan ko‘rinib turibdiki, terminal alkinlarning geteroatomli aldegidlar bilan nukleofil birikish reaksiyasi uchun eng muqobil erituvchi dietilefir bo‘lib, uning $InBr_3/Et_3N$ katalitik sistemasida qisman asoslilik xossasini namoyon qilishi, ya’ni molekulasi tarkibidagi rislarod atomini bog‘ hosil qilishda ishtirok etmagan juft elektronlari hisobiga sistemadagi H^+ bilan donor-akseptor bog‘ hosil qilishi natijasida ishqoriy muhit konsentratsiyasini oshirishi hisobiga jarayonning borishini tezlashtirdi va atsetilen spirtlarining unumi oshishiga sabab bo‘ldi. Atsetonitril ishtirokida aldegidlarning alkinillanish jarayoni olib borilganda, uning molekulasi tarkibidagi $^-C{\equiv}N$ nukleofil reagent ta’sirida karbonil guruhi bilan yondosh reaksiya borishi natijasida sianospirtlar hosil bo‘lishi hisobiga atsetilen spirtlarning unumdorligini pasaytirdi.

Metanol esa qutbli proton erituvchi sifatida indiy metallini o‘ziga tortib olishi natijasida barqaror, eruvchanligi qiyinroq bo‘lgan alkogolyatga aylanadi. Bu esa mahsulot unumi kamayishiga va qo‘shimcha moddalarning paydo bo‘lishiga olib keldi. Erituvchi tetragidrofuran alkinillanish jarayoni uchun mos kelsada, uning dipol momenti (1,75 D) va dielektrik o‘tkazuvchanlik konstantasi (ε= 7,6) pastligi sababli, mahsulot unumi boshqa erituvchilarga nisbatan past bo‘lishi kuzatildi. Tadqiqot natijasida erituvchilarning reaksiya tezligiga va selektivligiga ta’siri ketma ketligi quyidagicha: metanol < atsetonitril < tetragidrofuran < dietilefir ekanligi aniqlandi.

1-Jadval

Atsetilen spirtlar unumiga erituvchilar tabiati ta’siri (harorat 20 °C, boshlang‘ich moddalar miqdori 1:1 mol nisbatda, reaksiya davomiyligi 120 minut, katalizator $InBr_3/Et_3N$ miqdori 0,5:0,5 mol nisbatda)

Atsetilen spirtlari	Mahsulot unumi, %			
	DEE	MeCN	TGF	MeOH
11	72	53	64	32
12	77	56	66	38
13	92	58	69	52
14	84	52	61	48
15	79	48	52	34

16	89	56	64	49
17	69	44	54	28
18	73	55	67	34
19	89	57	63	48
20	78	46	50	32
21	75	57	68	34
22	85	54	61	49
23	60	28	48	21
24	63	30	51	38
25	88	55	63	51
26	76	52	58	32
27	69	29	34	32
28	82	32	39	43
29	51	22	30	21
30	59	24	42	29
31	83	37	48	39
32	68	32	35	22
33	62	28	32	30
34	76	37	43	34

Aldegidlarni alkinillash jarayonida mahsulot unumiga harorat ta’siri ham o‘rganildi. Reaksiya jarayoni 0÷40 °C harorat oralig‘ida olib borildi (2-Jadval). Reaksiya 0 °C haroratda olib borilganda katalizatorning eruvchanligi va faolligi juda past namoyon qilganligi, boshlang‘ich moddalarning dissotsiyalanish darajasining yetarli emasligi sababli, jarayonning haroratini 20 °C gacha oshirildi. Natijada mahsulot unumining oshishi aniqlandi. Haroratning yana oshirilishi esa sistemada reaksiyaning faollanish energiyasi ortishi hisobiga qaytar jarayonning ro‘y berishi orqali asosiy mahsulot unumining pasayishiga sabab bo‘ldi.

2-Jadval

Atsetilen spirtlari unumiga harorat ta’siri (boshlang‘ich moddalar miqdori 1:1 mol nisbatda, reaksiya davomiyligi 120 minut)

Atsetilen spirtlari	**Mahsulot unumi %**		
	0 °C	**20 °C**	**40 °C**
11	63	72	64
12	68	77	70
13	83	92	86
14	74	84	79
15	71	79	68
16	79	89	80
17	60	69	58
18	62	73	67
19	81	89	84
20	68	78	72
21	66	75	69
22	78	85	81
23	51	60	56
24	52	63	58
25	77	88	80
26	63	76	67
27	58	69	62
28	74	82	76
29	44	51	46
30	49	59	53
31	71	83	77

32	56	68	63
33	54	62	54
34	64	76	71

Sintez qilingan atsetilen spirtlari tarkibi, tozaligi va tuzilishi ^{1}H, ^{13}C YaMR spektrlari (Bruker Avance 400 va 100 MHz markali, 20-25 ^{o}C haroratda, $CDCl_3$ va C_6D_6 erituvchilari ishtirokida) yordamida tahlil qilindi.

1-(2-Tiofenil)propin-2-ol-1 (**11**) – R_f= 0.68; (72%), ^{1}H YaMR: δ 7.33 (dd, 1H, $H_{5,Th}$), 7.19 (dd, 1H, $H_{4,Th}$), 6,92 (m, 1H, $H_{3,Th}$), 5.61 (s, 1H), 2.64 (s, 1H, C≡CH), 2.38 (d, 1H, OH); ^{13}C YaMR: δ 145.7, 127.8, 127.3, 126.8, 85.6, 70.1, 61.5.

1-(3-Metil-2-tiofenil)propin-2-ol-1 (**12**) – R_f= 0.57; (77%), ^{1}H YaMR: δ 7.64 (dd, 1H, $H_{4,Th}$), 7.22 (dd, 1H, $H_{3,Th}$), 5.43 (d, 1H), 2.71 (s, 1H, C≡CH), 2.29 (d, 1H, OH), 1.86 (s, 3H, CH_3); ^{13}C YaMR: δ 141.7, 132.8, 127.4, 124.6, 84.3, 72.6, 65.7, 12.8.

1-(2-Furanil)propin-2-ol-1 (**13**) – R_f= 0.68; (92%), ^{1}H YaMR: δ 6.92 (m, 1H, CH_{Fur}), 6.14 (m, 1H, CH_{Fur}), 5.87 (m, 1H, CH_{Fur}), 5.08 (s, 1H), 2.36 (m, 1H, C≡CH), 2.02 (m, 1H, OH); ^{13}C YaMR: δ 152.7, 142.6, 113.5, 106.8, 81.9, 71.4, 57.6.

1-(3-Piridinil)propin-2-ol-1 (**14**) – R_f= 0.47; (84%), ^{1}H: δ 8.44 (d, 2H, $2CH_{Pir}$), 7.64 (m, 1H, CH_{Pir}), 7.52 (s, 1H, CH_{Pir}), 5.16 (s, 1H), 2.45 (s, 1H, C≡CH), 2.09 (d, 1H, OH); ^{13}C YaMR: δ 155.6, 149.9, 137.2, 136.8, 121.7, 87.4, 72.6, 63.3.

1-(2-Xinolinil)propin-2-ol-1 (**15**) – R_f= 0.47; (79%), ^{1}H YaMR: δ 8.27 (d, 1H, CH_{Xin}), 8.15 (d, 1H, CH_{Xin}), 7.96 (m, 1H, CH_{Xin}), 7.48 (m, 2H, $2CH_{Xin}$), 7,25 (m, 1H, CH_{Xin}), 5,63 (m, 1H), 2.93 (s, 1H, C≡CH), 2.26 (d, 1H, OH); ^{13}C YaMR: δ 159.7, 146.4, 136.2, 128.3, 127.4, 126.5, 124.9, 121.8, 83.7, 70.9, 66.9.

1-(3-Bromo-4-piridinil)propin-2-ol-1 (**16**) – R_f= 0.57; (89%), ^{1}H YaMR: δ 8.34 (s, 1H, CH_{Pir}), 8.17 (m, 1H, CH_{Xin}), 7.48 (d, 1H, CH_{Pir}), 5,56 (m, 1H), 2.94 (s, 1H, C≡CH), 2.15 (s, 1H, OH); ^{13}C YaMR: δ 149.5, 147.6, 144.2, 127.3, 123.1, 84.7, 70.6, 61.8.

3-Fenil-1-(tiofenil-2)propin-2-ol-1 (**17**) – R_f= 0.33; (69%), ^{1}H YaMR: δ 8.12 (m, 2H, $2CH_{Th}$), 7.57 (m, 5H, $5CH_{Ph}$), 7.24 (m, 1H, CH_{Th}), 5,89 (d, 1H), 2.34 (d, 1H, OH); ^{13}C YaMR: δ 149.3, 129.6, 128.1, 127.0, 126.3, 121.5, 88.9, 84.7, 64.9.

1-(3-metil-2-tiofenil)-3-fenilpropin-2-ol-1 (**18**) – R_f= 0.37; (73%), ^{1}H YaMR: δ 7.69 (m, 2H, $2CH_{Ph}$), 7.35 (m, 5H, $3CH_{Ph,}$ $2CH_{Th}$), 5.62 (d, 1H), 2.23 (d, 1H, OH), 1.96 (s, 3H, CH_3); ^{13}C YaMR: δ 142.7, 131.3, 128.3, 127.2, 125.9, 122.1, 89.6, 85.8, 63.2.

1-(2-Furanil)-3-fenilpropin-2-ol-1 (**19**) – R_f= 0.41; (89%), ^{1}H YaMR: δ 7.46 (m, 3H, $3CH_{Ph}$), 7.25 (m, 3H, $2CH_{Ph,}$ CH_F), 6.42 (m, 1H, CH_F), 6.29 (m, 1H, CH_F), 5.26 (d, 1H), 1.97 (d, 1H, OH); ^{13}C YaMR: δ 154.2, 144.3, 129.6, 127.8, 121.7, 112.2, 107.5, 89.6, 84.4, 66.9.

3-Fenil-1-(3-piridinil)propin-2-ol-1 (**20**) – R_f= 0.33; (78%), ^{1}H YaMR: δ 8.44 (m, 2H, $2CH_{Pir}$), 7.59 (m, 2H, $2CH_{Pir}$), 7.41 (m, 2H, $2CH_{Ph}$), 7.33 (m, 3H, $3CH_{Ph}$), 5.74 (d, 1H), 2.86 (d, 1H, OH); ^{13}C YaMR: δ 152.6, 146.7, 134.2, 132.1, 129.8, 127.3, 121.5, 86.9, 83.7, 60.4.

3-Fenil-1-(2-xinolinil)propin-2-ol-1 (**21**) – R_f= 0.47; (75%), ^{1}H YaMR: δ 8.27 (d, 1H, CH_{Naphth}), 8.16 (m, 3H, $3CH_{Naphth}$), 7.68 (m, 2H, $2CH_{Naphth}$), 7.37 (m, 2H, $2CH_{Ph}$), 7.18 (m, 3H, $3CH_{Ph}$), 5.44 (d, 1H), 2.69 (d, 1H, OH); ^{13}C YaMR: δ 159.4, 148.7, 136.5, 129.4, 127.9, 126.3, 121.6, 89.8, 84.6, 65.3.

1-(3-Bromopiridinil-4)-3-fenilpropin-2-ol-1 (**22**) – R_f= 0.31; (85%), ^{1}H YaMR: δ 8.52 (m, 2H, CH_{Pir}), 7.76 (s, 1H, CH_{Pir}), 7.46 (m, 2H, $2CH_{Ph}$), 7.14 (m, 3H, $3CH_{Ph}$), 5.23 (d, 1H), 2.18 (d, 1H, OH); ^{13}C YaMR: δ 152.6, 147.5, 127.8, 126.2, 121.8, 120.4, 88.3, 85.6, 57.4.

1-(2-Tiofenil)geptin-2-ol-1 (**23**) – R_f= 0.66; (60%), ^{1}H YaMR: δ 7.96 (m, 1H, CH_{Th}), 7.42 (m, 2H, $2CH_{Th}$), 5.94 (d, 1H), 2.48 (d, 1H, OH), 1.92 (t, 2H, CH_2), 1.45-1.30 (m, 4H, $2CH_2$), 0.89 (t, 3H, CH_3); ^{13}C YaMR: δ 146.0, 129.4, 127.5, 125.9, 86.4, 70.8, 67.3, 33.6, 21.9, 20.2, 13.4.

1-(3-Metil-2-tiofenil)geptin-2-ol-1 (**24**) – R_f= 0.57; (63%), ^{1}H YaMR: δ 7.85 (d, 1H, CH_{Th}), 7.74 (d, 1H, CH_{Th}), 5.84 (d, 1H), 2.52 (d, 1H, OH), 2.18 (s, 3H, CH_3), 1.93 (t, 2H, CH_2), 1.47-1.31 (m, 4H, $2CH_2$), 0.92 (t, 3H, CH_3); ^{13}C YaMR: δ 142.8, 134.3, 120.9, 85.6, 70.7, 65.4, 32.8, 22.6, 19.5, 13.7.

1-(2-Furanil)geptin-2-ol-1 (**25**) – R_f= 0.66; (88%), ^{1}H YaMR: δ 8.14 (d, 1H, CH_{Fur}), 7.78 (m, 2H, $2CH_{Fur}$), 5.77 (d, 1H), 2.22 (d, 1H, OH), 1.90 (t, 2H, CH_2), 1.52-1.43 (m, 4H, $2CH_2$), 0.94 (t, 3H, CH_3); ^{13}C YaMR: δ 157.2, 146.6, 111.4, 107.6, 85.9, 70.3, 59.4, 34.2, 22.6, 18.2, 14.7.

1-(3-Piridinil)geptin-2-ol-1 (**26**) – R_f= 0.43; (76%), ^{1}H YaMR: δ 8.46 (m, 2H, $2CH_{Pir}$), 7.68 (m, 2H, $2CH_{Pir}$), 5.32 (d, 1H), 3.12 (d, 1H, OH), 2.14 (t, 2H, CH_2), 1.62-1.54 (m, 4H, $2CH_2$), 1.02 (t, 3H, CH_3); ^{13}C YaMR: δ 153.4, 145.8, 136.4, 132.0, 122.9, 87.5, 71.3, 62.2, 32.6, 21.5, 18.4, 15.2.

1-(2-Xinolinil)geptin-2-ol-1 (**27**) – R_f= 0.37; (69%): ^{1}H YaMR (400 MHz, $CDCl_3$): δ 8.34 (d, 1H, CH_{Naphth}), 8.19 (m, 3H, $3CH_{Naphth}$), 7.44 (m, 2H, $2CH_{Naphth}$), 5.39 (d, 1H), 3.02 (d, 1H, OH), 2.10 (t, 2H, CH_2), 1.59-1.41 (m, 4H, $2CH_2$), 0.95 (t, 3H, CH_3); ^{13}C YaMR: δ 158.3, 146.7, 134.9, 129.1, 127.5, 126.0, 121.2, 86.5, 72.1, 62.6, 33.1, 22.8, 21.4, 13.9.

1-(3-Brom-4-piridinil)geptin-2-ol-1 (**28**) – R_f= 0.46; (82%), ^{1}H YaMR: δ 8.27 (m, 2H, $2CH_{Pir}$), 7.84 (s, 1H, CH_{Pir}), 5.96 (d, 1H), 2.98 (d, 1H, OH), 1.83 (t, 2H, CH_2), 1.68-1.53 (m, 4H, $2CH_2$), 1.16 (t, 3H, CH_3); ^{13}C YaMR: δ 149.0, 145.7, 127.3, 120.5, 84.4, 72.2, 57.6, 42.6, 31.5, 20.5, 15.7.

1-(2-Tiofenil)nonin-2-ol-1 (**29**) – R_f= 0.67; (51%), ^{1}H YaMR: δ 7.52 (m, 1H, CH_{Th}), 6.97 (m, 2H, $2CH_{Th}$), 5.66 (d, 1H), 2.19 (d, 1H, OH), 1.89 (t, 2H, CH_2), 1.49-1.29 (m, 8H, $4CH_2$), 0.87 (t, 3H, CH_3); ^{13}C YaMR: δ 149.6, 129.9, 127.2, 86.5, 72.3, 66.4, 32.7, 27.8, 21.7, 18.6, 14.5.

1-(3-Metil-2-tiofenil)nonin-2-ol-1 (**30**) – R_f= 0.43; (59%), ^{1}H YaMR: δ 7.76 (m, 2H, $2CH_{Th}$), 5.59 (d, 1H), 2.17 (d, 1H, OH), 2.01 (s, 3H, CH_3), 1.88 (t, 2H, CH_2), 1.64-1.47 (m, 8H, $4CH_2$), 0.89 (t, 3H, CH_3); ^{13}C YaMR: δ 142.8, 133.1, 127.2, 126.5, 121.6, 87.3, 71.3, 62.9, 32.4, 28.4, 21.3, 18.8, 15.8, 11.7.

1-(2-Furanil)nonin-2-ol-1 (**31**) – R_f= 0.67; (83%), ^{1}H YaMR: δ 8.21 (m, 2H, $2CH_{Fur}$), 7.72 (d, 1H, CH_{Fur}), 5.43 (d, 1H), 2.94 (d, 1H, OH), 2.15 (t, 2H, CH_2), 1.54-1.35 (m, 8H, $4CH_2$), 1.12 (t, 3H, CH_3); ^{13}C YaMR: δ 155.4, 147.7, 119.8, 108.6, 86.3, 70.2, 65.7, 32.4, 29.3, 27.1, 16.7.

1-(3-Piridinil)nonin-2-ol-1 (**32**) – R_f= 0.60; (68%), ^{1}H YaMR: δ 8.41 (d, 1H, CH_{Pir}), 8.27 (m, 2H, 2CH), 7.79 (d, 1H, CH), 7.28 (s, 1H, CH), 5.92 (d, 1H), 2.19 (d, 1H, OH), 1.87 (t, 3H, CH_3), 1.60-1.42 (m, 8H, $4CH_2$), 0.87 (t, 3H, CH_3); ^{13}C YaMR: δ 148.7, 143.6, 134.0, 131.6, 121.3, 89.2, 71.6, 31.4, 29.5, 27.4, 21.7, 16.9.

1-(2-Xinolinil)nonin-2-ol-1 (**33**) – R_f= 0.33; (62%), ^{1}H YaMR: δ 8.49 (m, H, $2CH_{Naphth}$), 8.21 (m, 2H, $2CH_{Naphth}$), 7.34 (m, 2H, $2CH_{Naphth}$), 5.69 (d, 1H), 2.21 (d, 1H, OH), 1.96 (t, 2H, CH_2), 1.64-1.41 (m, 8H, $4CH_2$), 1.09 (t, 3H, CH_3); ^{13}C YaMR: δ 159.7, 146.7, 134.7, 129.6, 127.8, 122.3, 87.2, 71.9, 33.7, 29.2, 27.9, 22.4, 19.5, 15.2.

1-(3-Brom-4-pirinil)nonin-2-ol-1 (**34**) – R_f= 0.43; (76%), ^{1}H YaMR: δ 8.44 (d, 1H, CH_{Pir}), 7.96 (d, 1H, CH_{Pir}), 7.14 (s, 1H, CH_{Pir}), 5.33 (d, 1H), 2.25 (d, 1H, OH), 1.83 (t, 2H, CH_2), 1.56-1.34 (m, 8H, $4CH_2$), 1.06 (t, 3H, CH_3); ^{13}C YaMR: δ 149.8, 144.3, 128.6, 121.4, 88.9, 70.4, 30.8, 29.2, 27.4, 21.9, 14.2.

XULOSA

Ilk bor $InBr_3/Et_3N/Et_2O$ katalitik sistemasida atsetilen spirtlari **11**-72%, **12**-77%, **13**-92%, **14**-84%, **15**-79%, **16**-89%, **17**-69%, **18**-73%, **19**-89%, **20**-78%, **21**-75%, **22**-85%, **23**-60%, **24**-63%, **25**-88%, **26**-76%, **27**-69%, **28**-82%, **29**-51%, **30**-59%, **31**-83%, **32**-68%, **33**-62% va **34**-76% unum bilan sintez qilindi.

Atsetilen spirtlarining hosil bo‘lish unumining oshishiga muvofiq reaksiya jarayonining eng muqobil sharoiti topildi, jumladan harorat 20 °C, reaksiya davomiyligi 120 minut, alkin:aldegid:$InBr_3$:Et_3N miqdori mos ravishda 1:1:0,5:0,5 mol nisbatlarda, erituvchi sifatida dietilefir olinganda mahsuloy unumi maksimum chiqishi aniqlandi.

Aldegidlar molekulasida geteroatom element saqlagan o‘rinbosarlar tabiati, ularning fazoviy joylashuvi va ta’sir etish xususiyatiga ko‘ra nukleofil birikish reaksiyasiga moyillik qatori quyidagicha tiofen-2-karbaldegid < 3-metiltiofen-2-karbaldegid < xinolin-2-karbaldegid < piridin-3-karbaldegid < 3-brom-4-piridinkarbaldegid < furan-2-karbaldegid ortib borishi aniqlandi.

ADABIYOTLAR RO‘YXATI

1. A.R. Pandev, D.K. Tiwari, A. Prakhar, D.P. Mishra, S.K. Sharma A review towards synthesis of heterocycles using propargyl alcohols and propargyl amines // Monatsh Chemistry, 2022, Volume 153, pp. 383-407.

2. Surendra Puri Oxygen as a heteroatom in propargylic Alcohols: Reactivity, Selectivity and applications // Organic and Supramolecular chemistry, 2020, Volume 5, Issue 31, pp. 9866-9877.

3. Nikolai A. Sitte, Francesca Ghiringhelli, Grigory A. Shevchenko, Frank Rominger, A. Stephen K. Hashmi, Thomas Schaub Copper-Catalysed Synthesis of Propargyl Alcohol and Derivatives from Acetylene and other Terminal alkynes // Advanced Synthesis and Catalysis, 2022, Volume 364, Issue 13, pp. 2227-2234.

4. Fernando Martínez-Lara, Anisley Suárez, Noelia Velasco, Samuel Suárez-Pantiga, Roberto Sanz Gold-Catalyzed Reactions of 2-Alkynyl-1-indolyl-1,2-diols with Thiols: Stereoselective Synthesis of (*Z*)-α-Indol-3-yl α-(2-Thioalkenyl) Ketones // Advanced Synthesis and Catalysis, 2022, Volume 364, pp. 132-138.

5. En Gao, Qiao Li, Lili Duan, Lin Li, Yue-Ming Li Isosterically designed chiral catalysts: Rationale, optimization and their application in enantioselective nucleophilic addition to aldehydes // Tetrahedron, 2020, Volume 76, pp. 1316-1324.

6. Nadezhda M. Vitkovskaya, Vladimir B. Orel, Vladimir B. Kobychev, Alexander S. Bobkov, Elena Yu. Larionova, Boris A. Trofimov Exploring acetylene chemistry in superbasic media: A theoretical study of the effect of water on vinylation and ethynylation reactions with acetylene in KOH/DMSO and NaOH/DMSO systems // Journal of Physical Organic Chemistry, 2017, Volume 30, Issue 8, pp. 3669-3682.

7. Shoko Nagahata, Seiya Takei, Satoshi Ueno One-Pot Synthesis of Multiarylated Benzophenonnes via [3+2+1] Benzannulation of Ketones, Alkynes and α,β-Unsaturated Carbonyls // Journal Organic Chemistry, 2022, Volume 87, Issue 15, pp. 10377-10384.

8. Idris Karakaya, Semistan Karabuga, Ramazan Altundas, Sabri Ulukanli Synthesis of quinazoline based chiral ligands and application in the enantioselective addition of phenylacetylene to aldehydes // Tetrahedron, 2014, Volume 70, pp. 8385-8388.

9. Ji-Cai, Zhou Lei Zhao, Yuan Li, Ding-Qiang Fu, Zi-Cheng Li, Wen-Cai Huang. Alkynylation of aldehydes mediated by zinc and allyl bromide: a practical synthesis of propargylic alcohols // Research on Chemical Intermediates, 2017, Volume 43, pp. 4283-4294.

10. E. Yu. Shmidt, I. A. Bidusenko, N. I. Protsuk, A. I. Mikhaleva, and B. A. Trofimov Improved Synthesis of Tertiary Propargyl Alcohols by the Favorskii Reaction of Alkyl Aryl (Hetaryl) Ketones with Acetylene // Russian Journal of Organic Chemistry, 2013, Volume 49, Issue 1, pp. 8-17.

11. Elena Yu. Schmidt, Natalia A. Cherimichkina, Ivan A. Bidusenko, Nadezhda I. Protzuk, Boris, A. Trofimov Alkynylation of Aldehydes and Ketones Using the Bu_4NOH/H_2O/DMSO Catalytic Composition: A Wide-Scope Methodology // European Journal of Organic Chemistry, 2014, Volume 2014, Issue 21, pp. 4663-4670.

12. Francis Mariaraj Irudayanathan, Jimin Kim, Kwang Ho Song, Sunwoo Lee Transition-Metal-Free Decarboxylative Coupling Reactions for the Synthesis of Propargyl Alcohols // Asian Journal of Organic Chemistry, 2016, Volume 5, pp. 1148-1154.

13. Nadezhda M. Vitkovskaya, Vladimir B. Orel, Vladimir B. Kobychev, Alexander S. Bobkov, Damir Z. Absalyamov, Boris A. Trofimov Quantum-chemical models of KOH($KOBu^t$)/DMSO superbasic systems and mechanisms of base-promoted acetylene reactions // International Journal Quantum Chemistry, 2020, Volume 120, Isuue 26158, pp. 12-23.

14. Abduraxmanova Saida, Ziyadullaev Odiljon, Ikramov Abduvahob, Saliyeva Muyassar Synthesis of aromatic acetylene alcohols on the basis of various aldehydes in the catalytic system $ZnEt_2/Tl(OiPr)_4$ // Journal of Critical Reviews, 2020, Volume 7, Issue 19, pp. 1488-1499.

15. Ablakulov Lochinbek Kuchkorovich, Ikramov Abduvaxab, Ziyadullaev Odiljon Egamberdievich, Otaqo'ziev Dilshod Do'ltaxo'ja o'g'li. Magniy organik birikmalar asosida aromatik atsetilen spirtlari sintezi // FarDU. Ilmiy habarlar, 2021, №6, 26-32 b.

16. Kang Y.F., Yang W.J. The use of bifunctional catalyst systems in the asymmetric addition of alkynylzinc to aldehydes// Abstract Journal Chemistry, 2005, Volume 48, pp. 112-119.

17. Lin Pu Asymmetric alkynylzinc additions to aldehydes and ketones // Tetrahedron, 2003, Volume 59, pp. 9873–9886.

18. Ryo Takita, Kenichiro Yakura, Takashi Ohshima, Masakatsu Shibasaki Asymmetric Alkynylation of Aldehydes Catalyzed by an In(III)/BINOL Complex // Journal of the American Chemical Society, 2005, Volume 127, Issue 40, pp. 13760-13761.