

O'ZBEKISTON RESPUBLIKASI  
OLIV TA'LIM, FAN VA INNOVATSIYALAR VAZIRLIGI  
FARG'ONA DAVLAT UNIVERSITETI

**FarDU.  
ILMIY  
XABARLAR-**

1995-yildan nashr etiladi  
Yilda 6 marta chiqadi

3-2023

**НАУЧНЫЙ  
ВЕСТНИК.  
ФерГУ**

Издаётся с 1995 года  
Выходит 6 раз в год

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**TURLI XIL TABIATGA EGA KETONLARNI ENANTIOSELEKTIV ETINILLASH ASOSIDA ATSETILEN SPIRTLARI SINTEZI****СИНТЕЗ АЦЕТИЛЕНОВЫХ СПИРТОВ НА ОСНОВЕ ЭНАНТИОСЕЛЕКТИВНОГО ЭТИНИЛИРОВАНИЯ КЕТОНОВ РАЗЛИЧНОЙ ПРИРОДЫ****SYNTHESIS OF ACETYLENE ALCOHOLS BASED ON ENANTIOSELECTIVE ETHYNYLATION OF KETONES WHICH HAVE VARIOUS NATURE****Tirkasheva Sarvinoz Isoq qizi<sup>1</sup>, Ziyadullayev Odiljon Egamberdiyevich<sup>2</sup>,  
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**Аннотация**

Ilk bor TBAF·3H<sub>2</sub>O/DMSO/H<sub>2</sub>O katalitik sistemasida ayrim ketonlarni kalsiy karbid yordamida enantioselektiv etinillash reaksiyasi bo'yicha terminal atsetilen spirtlari sintez qilingan. Mahsulot unumiga erituvchilar, katalizator, reagent va substratlarning tabiati va miqdorlari ta'siri o'rganilgan. Reaksiyalarni boshqarish va nazorat qilishning eng muqobil sharoitlari aniqlangan. Tanlangan ketonlarning mahsulot hosil bo'lish samaradorlik qatori ishlab chiqilgan. Sintez qilingan terminal atsetilen spirtlari identifikatsiyalangan, tarkibi, tozaligi, tuzilishi va xususiy konstantalari zamonaviy fizik-kimyoviy usullarda isbotlangan.

**Аннотация**

Впервые терминальные ацетиленовые спирты были синтезированы в каталитической системе TBAF·3H<sub>2</sub>O/DMSO/H<sub>2</sub>O по реакции энантиоселективного этинирования некоторых кетонов карбидом кальция. Изучено влияние природы и количества растворителей, катализаторов, реагентов и субстратов на выход продукта. Выявлены наиболее альтернативные условия управления и контроля реакций. Была разработана линия эффективности производства выбранных кетонов. Синтезированные концевые ацетиленовые спирты идентифицированы, их состав, чистота, структура и собственные константы доказаны современными физико-химическими методами.

**Abstract**

For the first time, terminal acetylene alcohols were synthesized by the enantioselective ethynylation reaction of some ketones using calcium carbide in the TBAF·3H<sub>2</sub>O/DMSO/H<sub>2</sub>O catalytic system. The influence of the nature and amounts of solvents, catalysts, reagents and substrates on product yield was studied. The most alternative conditions of control and direction of reactions are determined. The series of product formation efficiency of selected ketones was developed. Synthesized terminal acetylene alcohols were identified, their composition, purity, structure and specific constants were proved by modern physico-chemical methods.

**Kalit so'zlar:** kalsiy karbid, ketonlar, tetra-n-butilammoniy florid, atsetilen spirtlari, asosiy va qo'shimcha mahsulotlar, reaksiya mexanizmi, mahsulot unumi.

**Ключевые слова:** карбид кальция, кетоны, фторид тетра-н-бутиламмония, ацетиленовые спирты, основные и второстепенные продукты, механизм реакции, выход продукты.

**Key words:** calcium carbide, ketones, tetra-n-butylammonium fluoride, acetylene alcohols, major and minor products, reaction mechanism, product yield.

**KIRISH**

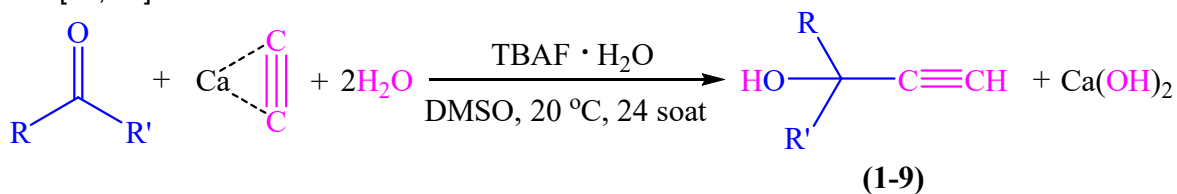
Atsetilen spirtlari farmatsevtika sanoatida ingibitorlar, ionitlar, vitaminlar va antibiotiklar olishda oraliq mahsulot sifatida keng foydalanilmoqda [1-3]. Atsetilen spirtlari molekulasidagi –C≡CH guruhi mavjudligi uchun, ularning nukleofil, elektrofil, radikal va siklobirikish reaksiyalari asosida turli hil organik birikmalar olish imkoniyatini oshiradi [4-6]. Aldegid va ketonlarning

## KIMYO

alkinillash jarayoni kuchli asosli muhitni ta'minlovchi alkil litiy, dialkil rux yoki magniy organik birikmalar ishtirokida amalga oshirilgan [7-9]. Shuningdek Y.N.Sum tomonidan aldegid yoki keton bilan kalsiy karbid reaksiyalari uchun katalizator sifatida  $\text{Cs}_2\text{CO}_3$ , erituvchi dimetilsulfoksid ishtirokida, 60 °C haroratda, 8 soat davomida olib borilgan va 72-98% unum bilan terminal atsetilen spirtlari (TAS) sintez qilingan [10, 11]. Aromatik aldegidlarni kalsiy karbid va suv bilan reaksiyasi 80 °C haroratda 180 minut davomida kuchli ishqoriy muhitda dimetilformamid eritmasida olib borilganda atsetilen spirtlarining izomerlanishi kuzatilgan [12]. Organik sintezda enantiomer birikmalar sintez qilishga qiziqish katta bo'lib, aynan enantiomerlarga boy atsetilen spirtlari ikki xil usulda, propargil ketonlarning xemoselektiv qaytarilishi [13] yoki karbonil birikmalarning alkinillanishi asosida sintez qilish mumkin. Aromatik aldegidlarning enantioselektiv alkinillash reaksiyasi reagent litiyfenilatsetilenid va 3-aminopirrolidin litiyamid yordamida 180 minut davomida -78 °C haroratda olib borilganda xiral konfiguratsion fazoviy tuzilishga ega bo'lgan atsetilen spirtlarining ratsemt aralashmasi (85%) hosil bo'lgan [14]. E.Yu.Schmidt tomonidan atsetilenning alifatik, aromatik, siklik va asiklik ketonlar va aldegidlar bilan  $\text{Bu}_4\text{NOH}/\text{H}_2\text{O}/\text{DMSO}$  katalitik sistemasi yordamida yumshoq sharoitda, 5 °C harorat, 60 minut davomida reaksiyasi olib borilganda 64-93% unumgacha propargil spirtlari sintez qilingan, qo'shimcha mahsulotlar sifatida atsetilen diollari hosil bo'lishi aniqlangan [15]. Umuman olganda tetra-*n*-butilammoniy tuzlaridan oldin ham alkinillash jarayoni uchun  $\text{Bu}_4\text{NBr}/\text{KOH}/\text{PhF}$  [16] katalitik sistemasi foydalanilgan va yuqori samaradorlik bilan atsetilen spirtlari sintez qilingan, ammo  $\text{Bu}_4\text{NCl}$  va  $\text{Bu}_4\text{NJ}$  dan foydalainganda mahsulot unumi nisbatan past chiqishi kuzatilgan [17].

## NATIJALAR VA MUHOKAMA

Adabiyot manbaalari asosida tadqiqot obyekti sifatida tanlangan ketonlar- siklogeksanon, adamantanon, atsetofenon, para-xloroatsetofenon, etilbutilketon, metilgeptilketon, diizopropilketon, etilgeptilketon va 2-metilsiklogeksanonni kalsiy karbid ishtirokida etinillash reaksiyasi quyidagicha taklif qilindi [18, 19].



RR' = -cHx (1); RR' = -Ad (2); R = -Me, R' = -Ph (3); R = -Me, R' = -(4-Cl)Ph (4); R = -Et, R' = -Bu (5); R = -Me, R' = -Hp (6); R = -iPr, R' = -iPr (7); R = -Et, R' = -Hp (8); RR' = -(2-Me)Ph (9)

TBAF organik erituvchilarda ayniqsa, dimetilsulfoksid va atsetonitrildagi eritmalarida barqaror hisoblanib, ftor ionining manbaasi sifatida ishlatiladi [20, 21]. Dastlab TAS unumiga tanlangan katalizator  $\text{TBAF} \cdot 3\text{H}_2\text{O}$  miqdori 0,25 dan 1 molgacha ta'siri o'rganildi (1-Jadval). Jadvaldan ko'rinib turibdiki, 0,25 dan 0,5 molga oshirilganda TAS unumi, ya'ni 1- 84 dan 99% ga, 2-80 dan 92% ga, 3- 68 dan 79% ga, 4- 72 dan 82% ga, 5- 74 dan 86% ga, 6- 59 dan 68% ga, 7 60 dan 71% ga, 8- 44 dan 56% ga va 9- 77 dan 89% gacha ortishi kuzatilgan. Ammo katalizator miqdori 0,75 dan 1 molga oshirilganda esa, sistemadagi ortiqcha olingan TBAF katalitik faolligi ta'sirida TAS larning ketonlar bilan nukleofil birikish reaksiyasi natijasida atsetilen diollar va kalsiy karbid bilan polimerlanishi asosida to'yinmagan viniloksi birikmalar hosil bo'lishi oqibatida TAS unumi kamayishi ro'y berdi. Demak,  $\text{TBAF} \cdot 3\text{H}_2\text{O}$  miqdori 0,5 molda sistemadagi boshlang'ich moddalarning dissotsiyalanish darajasi eng yuqori bo'lishi va ionlarning reaksiyada to'qnashuvlar soni maksimum namoyon qilishi natijasida ketonlarni etinillashda eng yuqori unum bilan TAS sintez qilishga erishildi.

1-jadval

Terminal atsetilen spirtlari unumiga TBAF·3H<sub>2</sub>O miqdori ta'siri (harorat 20 °C, erituvchi DMSO, reaksiya davomiyligi 24 soat)

TAS	Mahsulot unumi, %				R <sub>f</sub> qiymati
	TBAF·3H <sub>2</sub> O miqdori, mol				
	0,25 mol	0,5 mol	0,75 mol	1 mol	
1	84	99	86	77	0,67
2	80	92	79	69	0,78
3	68	79	66	58	0,65
4	72	82	71	62	0,63
5	74	86	74	63	0,57
6	59	68	57	46	0,79
7	60	71	58	49	0,60
8	44	56	44	35	0,55
9	77	89	76	64	0,66

TAS unumiga reaksiya davomiyligi ta'sirini o'rganish uchun jarayon 12 – 48 soat intervallar oralig'ida olib borildi (2-Jadval). Dastlab reaksiya 12 soat davomida olib borilganida, katalizator katalitik faolligini to'liq namoyon qilmaganligi, oraliq birikma kalsiyatsetilenidning yetarli miqdorda hosil bo'lganligi natijasida reaksiya oxirigacha bormaganligi aniqlandi. Jarayon vaqti 24 soatga uzaytirilganda, TBAF ning selektivligi to'liq namoyon bo'lishi, sistemada faol kompleksning hosil bo'lishi bilan faollanish energiyasining kamayishi va reaksiya tezligi ortishi natijasida mahsulot umuni eng yuqori (1- 99%, 2- 92%, 3- 79%, 4- 82%, 5- 86%, 6- 68%, 7- 71%, 8- 56%, 9- 89%) chiqishi kuzatildi. So'ngra, yana reaksiya davomiyligi 30 va 48 soatga oshirilganda esa sistemadan qo'shimcha mahsulot ajratib olingan, ya'ni reaksiyada hosil bo'lgan TAS ning yana qayta keton bilan ta'sirlashib atsetilen diol yoki kalsiy karbid bilan ta'sirlashganda mos ravishda atsetilen spirtning vinil efiri hosil bo'lganligi, hattoki qaytar jarayon ro'y berishi aniqlandi va bu esa kutilgan mahsulot unumining pasayishiga sabab bo'ldi. Jadvaldan ko'rinib turibdiki, kalsiy karbid asosida keton bilan nukleofil birikish reaksiya davomiyligi 24 soat bo'lgan mahsulot unumi maksimum orqali o'tish kuzatilgan.

2-jadval

Terminal atsetilen spirtlar unumiga reaksiya davomiyligi ta'siri (harorat 20 °C, erituvchi DMSO, TBAF·3H<sub>2</sub>O miqdori 0,5 mol)

TAS	Mahsulot unumi, %			
	12 soat	24 soat	30 soat	48 soat
1	66	99	91	65
2	59	92	83	60
3	47	79	71	46
4	49	82	74	51
5	54	86	77	53
6	35	68	60	35
7	40	71	62	38
8	26	56	47	26
9	57	89	78	54

TAS unumiga boshlang'ich moddalar turli mol miqdor nisbatlarda o'rganildi, jumladan jarayonda CaC<sub>2</sub>:RCOR miqdori 1:1 nisbatda olib borilganida kalsiy karbidning sistemaga qo'shilgan suv bilan hosil qilgan oraliq mahsuloti kalsiyatsetilenidning anion miqdori keton bilan to'qnashuvlar soni uchun yetarli emasligi mahsulot unumining past bo'lishiga sabab bo'ldi. Kalsiy karbid miqdori keton miqdoriga nisbatan ikki marta ko'paytirilganida jarayonda hosil bo'ladigan faol kompleks miqdori oshishi natijasida mahsulot unumi ham yuqori bo'lganligi kuzatildi (3-Jadval). Ammo reagent miqdori substrat miqdoriga nisbatan 3 martaga oshirilganida esa sistemada TAC larning ortiqcha miqdordagi atsetilenid bilan vinillash, polimerlanish reaksiyalari natijasida mono va

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poliviniloksi birikmalar hamda ortiqcha kalsiy karbidning ketonlar bilan ta'sirlashishi natijasida to'yinmagan ketonlar (yennonlar) hosil bo'lishi asosiy mahsulot unumining 1- 99 dan 88% ga, 2- 92 dan 81% ga, 3- 79 dan 67% ga, 4- 82 dan 69% ga, 5- 86 dan 75% ga, 6- 68 dan 57% ga, 7- 71 dan 59% ga, 8- 56 dan 46% ga va 9- 89 dan 77% ga pasayishiga olib keldi.

3-jadval

**Terminal atsetilen spirtlari unumiga boshlang'ich moddalar mol miqdori ta'siri (reaksiya davomiyligi 24 soat, harorat 20 °C, erituvchi DMSO, TBAF·3H<sub>2</sub>O miqdori 0,5 mol)**

TAS	Mahsulot unumi, %			
	CaC <sub>2</sub> :RCOR' mol miqdori			
	1:1	2:1	2,7:1	3:1
1	62	74	99	88
2	56	68	92	81
3	43	54	79	67
4	56	58	82	69
5	51	62	86	75
6	35	45	68	57
7	37	48	71	59
8	24	34	56	46
9	55	64	89	77

Ketonlarning kalsiy karbid yordamida etinillash jarayoni uchun harorat 0+40 °C intervallar oralig'ida tahlil qilindi (4-Jadval). Jarayon 0 °C va 10 °C haroratlarda olib borilganida faol molekula va ionlarning to'qnashishlar soni uchun yetarlicha energiyaga ega bo'lmagani bois oraliq mahsulot (kompleks alkogolyat tuz) kam hosil bo'lishi hisobiga TAS unumi pasayishi ro'y berdi. Harorat 0 °C dan 20 °C gacha oshirilganda TAS unumi 1- 68 dan 99% ga, 2- 62 dan 92% ga, 3- 50 dan 79 % ga, 4- 64 dan 82% ga, 5- 66 dan 86% ga, 6- 43 dan 68% ga, 7- 46 dan 71% ga, 8- 38 dan 56% ga va 9- 58 dan 89% ga oshganligi kuzatildi. Ammo harorat yana oshirilgan sari katalizatorida selektivlik pasayishi hisobiga yondosh reaksiyalar ya'ni sikllanish, polimerlanish jarayonlari borishi hisobiga TAS unumi pasayganligi jadvalda keltirildi.

4-jadval

**Terminal atsetilen spirtlar unumiga harorat ta'siri (reaksiya davomiyligi 24 soat, CaC<sub>2</sub>:RCOR' mol miqdori 2,7:1 nisbatda)**

Harorat, °C	Mahsulot unumi, %								
	1	2	3	4	5	6	7	8	9
0	68	62	50	64	66	43	46	38	58
10	89	84	69	71	74	59	60	46	78
20	99	92	79	82	86	68	71	56	89
30	95	88	74	78	82	64	77	52	84
40	86	79	67	69	74	53	68	44	75

Elektrofil karbonil uglerodning nukleofil reagent bilan  $\delta$  bog'lanish amalga oshirish uchun kationlarni yaxshi stabillovchi qutbli aproton erituvchilar qulay hisoblanadi. Shu sababdan ketonlarni etinillash jarayoni uchun DMFA, DMSO, TGF va MeCN kabi erituvchilar tabiatining TAS unumiga ta'sirini o'rganish uchun tanlab olindi (5-Jadval). Ma'lumki qutbli aproton erituvchilar kislotalik xossaga ega vodorod ajrata olmaydi, ammo tarkibida yuqori elektromanfiy atom mavjud bo'lganligi bois vodorod bilan bog' hosil qila oladi va nukleofilarni solvatlamaydi, ya'ni ushbu jarayonda foydalanilgan katalizator tetra-*n*-butilammoniy floridning florid anionini va atsetilenid anionini solvatlamaganligi sababli, u substrat bilan reaksiyaga kirishish uchun erkin bo'ladi. Shuning uchun nukleofil birikish reaksiyalari proton erituvchilarga qaraganda qutbli aproton erituvchilarda sezilarli darajada tezroq boradi. Natijada eng yuqori mahsulot unumdorligi DMSO erituvchisida (1- 99%, 2- 92%, 3- 79%, 4- 82%, 5- 86%, 6- 68%, 7- 71%, 8- 56%, 9- 89%) namoyon bo'ldi. Ushbu jarayon quyidagicha izohlanadi:

- DMFA tarkibida ikkita rezonans markaz (C=O va C-N) mavjud bo'lib, faollik C-N bog'ida ortadi. Natijada azotning bog' hosil qilishda ishtirok etmagan juft elektroni hisobiga vodorod bog' hosil qila oladi. Xona haroratida atsetilen atsetonga nisbatan (27,9 g) DMFA da yaxshi (51 g) eriydi, ammo u kuchli kislotalar va asoslarning ta'siriga chiqamli emas, bu esa gidrolizga olib keladi [22]. Shuning uchun DMSO ga nisbatan TAS unumdorligi past bo'lishi kuzatildi.

- DMSO ning dielektrik o'tkazuvchanligi konstantasi ( $\epsilon = 47$ ) va dipol momenti (3,96 D) boshqa erituvchilarga nisbatan yuqori bo'lib, ion juftni ionlarga ajratish oson bo'ladi [23]. Sistemada qisman asoslilik xossasini namoyon qilishi orqali katalizator bilan birga super ishqoriy muhitni ta'minlaydi va nukleofil reagentning substrat bilan to'qnashuvlar sonining ortishi natijasida TAS selektivligi yuqori bo'lishini taqozo etadi.

- Qutbli aproton erituvchi TGF etinillash jarayoni uchun mos kelsada, uning dipol momenti (1,75 D) va dielektrik o'tkazuvchanlik konstantasi ( $\epsilon = 7,6$ ) pastligi sababli, TAS unumi boshqa erituvchilarga nisbatan past bo'lishi kuzatildi.

- MeCN qisman past qovushqoqligi, yuqori kimyoviy barqarorligi va  $\text{C}\equiv\text{N}$  nukleofil reagent ta'sirida karbonil guruhi bilan yondosh reaksiya borishi [24] natijasida qo'shimcha mahsulotlar (siano spirtlar) hisobiga TAS unumdorligini pasaytirdi.

### 5-jadval

#### Terminal atsetilen spirtlar unumiga erituvchilar tabiati ta'siri (harorat 20 °C, reaksiya davomiyligi 24 soat, $\text{CaC}_2:\text{RCOR}$ mol miqdori 2,7:1 nisbatda)

Erituvchilar	Mahsulot unumi, %								
	1	2	3	4	5	6	7	8	9
DMFA	86	79	66	71	74	57	58	44	76
DMSO	99	92	79	82	86	68	71	56	89
TGF	77	69	58	62	63	46	49	35	64
MeCN	84	80	68	72	74	59	60	44	77

Sintez qilingan TAS tarkibi, tozaligi va tuzilishi  $^1\text{H}$ ,  $^{13}\text{C}$  YaMR spektrlari (Bruker Avance 400 va 101 MHz markali, 20-25 °C haroratda,  $\text{CDCl}_3$ , atseton- $d_6$ ,  $\text{C}_6\text{D}_6$  erituvchilar ishtirokida) yordamida tahlil qilindi.

**1-Etinilsiklogeksanol (1)** – rangsiz suyuqlik,  $R_f$  (dixlorometan-metanol 100:1) = 0.67; (mahsulot unumi 99%):  $^1\text{H}$  YaMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.71 (s, 1H, OH), 2.44 (s, 1H,  $\text{C}\equiv\text{CH}$ ), 1.90-1.83 (m, 2H,  $\text{CH}_2$ ), 1.67-1.62 (m, 2H,  $\text{CH}_2$ ), 1.57-1.46 (m, 5H, 2 $\text{CH}_2$ , CH), 1.22-1.16 (m, 1H, CH);  $^{13}\text{C}$  ЯMP (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  87.3, 71.7, 68.1, 39.3, 24.7, 22.7.

**2-Etiniladamantanol-2 (2)** – oq rangli kukun,  $R_f$  (dixlorometan-metanol 100:1) = 0.78; (mahsulot unumi 92%):  $T_c = 97-99$  °C.  $^1\text{H}$  YaMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.54 (s, 1H,  $\text{C}\equiv\text{CH}$ ), 2.19-2.13 (m, 4H, 2 $\text{CH}_2$ ), 2.02 (s, 1H, OH), 1.97-1.96 (m, 2H, 2CH), 1.83-1.76 (m, 4H, 2 $\text{CH}_2$ ), 1.71-1.69 (m, 2H,  $\text{CH}_2$ ), 1.59-1.54 (m, 2H, 2CH);  $^{13}\text{C}$  YaMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  88.0, 72.7, 38.4, 37.1, 35.1, 31.1, 26.4, 26.3.

**2-Fenilbutin-3-ol-2 (3)** – rangsiz suyuqlik,  $R_f$  (dixlorometan-metanol 100:1) = 0.65; (mahsulot unumi 79%):  $^1\text{H}$  YaMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.80 (s, 3H,  $\text{CH}_3$ ), 2.43 (s, 1H, OH), 2.69 (s, 1H,  $\text{C}\equiv\text{CH}$ ), 7.34-7.31 (m, 1H, CH), 7.41-7.37 (m, 2H, 2CH), 7.69-7.67 (m, 2H, 2CH);  $^{13}\text{C}$  YaMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  144.6, 128.0, 127.5, 124.4, 86.8, 72.7, 69.4, 32.7.

**2-(4-Xlorofenil)butin-3-ol-2 (4)** – sariq moysimon suyuqlik,  $R_f$  (dixlorometan-metanol 100:1) = 0.63; (mahsulot unumi 82%):  $^1\text{H}$  YaMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.76 (s, 3H,  $\text{CH}_3$ ), 2.61 (s, 1H, OH), 2.69 (s, 1H,  $\text{C}\equiv\text{CH}$ ), 7.34-7.32 (d, 2H, 2CH of Ph,  $J=7.5$  Hz), 7.60-7.58 (d, 2H, 2CH of Ph,  $J=7.5$ ).  $^{13}\text{C}$  YaMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.1, 133.3, 128.0, 126.0, 86.4, 73.0, 69.0, 32.8.

**3-Etinilgeptin-1-ol-3 (5)** – rangsiz suyuqlik,  $R_f$  (dixlorometan-metanol 100:1) = 0.57; (mahsulot unumi 86%):  $^1\text{H}$  YaMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.44 (s, 1H,  $\text{C}\equiv\text{CH}$ ), 2.42-2.38 (m, 2H,  $\text{CH}_2$ ), 1.92 (br, s, 1H, OH), 1.74-1.27 (m, 6H, 3 $\text{CH}_2$ ), 1.07-0.89 (m, 6H, 2 $\text{CH}_3$ ).  $^{13}\text{C}$  YaMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  86.3, 71.7, 71.1, 40.7, 34.2, 25.8, 22.4, 8.00.

**3-Metildeklin-1-ol-3 (6)** – sariq rangli suyuqlik,  $R_f$  (dixlorometan-metanol 100:1) = 0.79; (mahsulot unumi 68%):  $^1\text{H}$  YaMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.41 (s, 1H,  $\text{C}\equiv\text{CH}$ ), 2.11 (s, 1H, OH), 1.69-1.59 (m, 2H,  $\text{CH}_2$ ), 1.52-1.42 (m, 5H,  $\text{CH}_2$ ,  $\text{CH}_3$ ), 1.31-1.25 (m, 8H, 4 $\text{CH}_2$ ), 0.88 (t, 3H,  $\text{CH}_3$ ,  $J=7.2$  Hz).  $^{13}\text{C}$  YaMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  87.8, 71.1, 68.1, 43.5, 31.8, 29.64, 29.61, 29.2, 24.5, 22.6, 14.1.

## KIMYO

**3-Izopropil-4-metilpentin-1-ol-3 (7)** – rangsiz suyuqlik,  $R_f$  (dixlorometan-metanol 100:1) = 0.60; (mahsulot unumi 71%):  $^1\text{H}$  YaMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.41 (s, 1H,  $\text{C}\equiv\text{CH}$ ), 1.98-1.92 (m, 1H, OH), 1.41 (m, 2H, 2CH), 1.14-0.99 (dd, 12H, 4 $\text{CH}_3$ ).  $^{13}\text{C}$  YaMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  84.6, 72.9, 33.7, 17.5, 15.7.

**3-Etildekin-1-ol-3 (8)** – rangsiz suyuqlik,  $R_f$  (dixlorometan-metanol 100:1) = 0.55; (mahsulot unumi 56%):  $^1\text{H}$  YaMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.49 (br, s, 1H,  $\text{C}\equiv\text{CH}$ ), 2.02 (br, s, 1H, OH), 1.62-1.56 (m, 4H, 2 $\text{CH}_2$ ), 1.54-1.45 (m, 4H, 2 $\text{CH}_2$ ), 1.31-1.25 (m, 2H,  $\text{CH}_2$ ), 1.18-1.00 (m, 2H,  $\text{CH}_2$ ), 0.97-0.87 (m, 8H, 2 $\text{CH}_3$ ,  $\text{CH}_2$ ).

**1-Etil-2-metilsiklogeksanol (9)**. Sis va trans izomerlarning 1:1 aralashmasi olindi. Rangsiz suyuqlik. Sis izomer uchun  $R_f$  (dixlorometan-metanol 100:1) = 0.66; (mahsulot unumi 89%):  $^1\text{H}$  YaMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.48 (s, 1H,  $\text{C}\equiv\text{CH}$ ), 2.47 (s, 1H,  $\text{C}\equiv\text{CH}$ ), 2.11 (s, 2H, OH), 1.99-1.94 (m, 4H), 1.76-1.22 (m, 14H), 0.92 (d,  $J=6.6$  Hz, 3H), 0.91 (d,  $J=6.0$  Hz, 3H);  $^{13}\text{C}$  YaMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  87.1, 72.2, 68.9, 47.9, 39.3, 29.9, 26.4, 21.5, 15.6. Trans-1-etil-2-metilsiklogeksanol.  $R_f$  (dixlorometan-metanol 100:1) = 0.71; (mahsulot unumi 92%):  $^1\text{H}$  YaMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.49 (d, 1H,  $\text{C}\equiv\text{CH}$ ), 2.13 (s, 1H, OH), 2.01-1.95 (m, 1H), 1.75-1.33 (m, 6H), 1.18-1.05 (m, 2H), 0.92 (d,  $J=6.4$  Hz, 3H);  $^{13}\text{C}$  YaMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  86.9, 72.2, 69.1, 47.9, 39.4, 33.5, 31.9, 23.1, 21.6.

## XULOSA

Ilk bor TBAF·3 $\text{H}_2\text{O}$ /DMSO/ $\text{H}_2\text{O}$  katalitik sistemasida 1-etinilsiklogeksanol-1 (**1**), 2-etiniladamantanol-2 (**2**), 2-fenilbutin-3-ol-2 (**3**), 2-(4-xlorofenil)butin-3-ol-2 (**4**), 3-etilgeptin-1-ol-3 (**5**), 3-metildekin-1-ol-3 (**6**), 3-izopropil-4-metilpentin-1-ol-3 (**7**), 3-etildekin-1-ol-3 (**8**) va (sis va trans (1:1)) 1-etil-2-metilsiklogeksanol (**9**) sintez qilindi.

TAS unumiga asoslanib ketonlar molekulasidagi radikallar va o'rinbosarlar tabiati, joylashuvi va ularning fazoviy ta'sir etish xususiyatiga ko'ra etinillash reaksiyalariga kirishishi bo'yicha quyidagicha nisbiy faollik qatori 3-etildekin-1-ol-3 < 3-metildekin-1-ol-3 < 3-izopropil-4-metilpentin-1-ol-3 < 2-fenilbutin-3-ol-2 < 2-(4-xlorofenil)butin-3-ol-2 < 3-etilgeptin-1-ol-3 < 1-etil-2-metilsiklogeksanol < 2-etiniladamantanol-2 < 1-etinilsiklogeksanol-1 aniqlandi.

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