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THE HYDROSILYLATION OF 3-(HEXEN-5-IN-2-ILOXY) PROPIONITRILE

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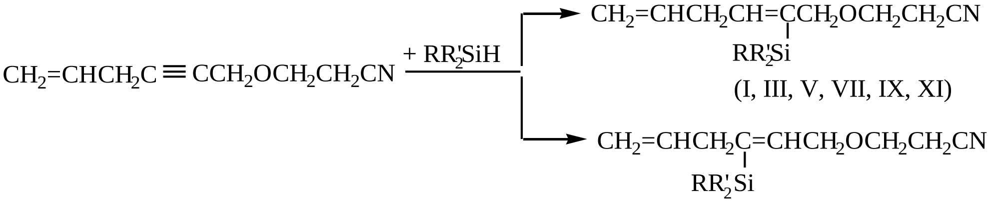
The addition reaction of triorganosilanes to 3-(hexen-5-in-2-iloxy) propionitryle in the presence of acetylacetonate dicarbonyl rhodium catalyst proceeds on triple bonds in two directions obtaining of β(52–65%)- and γ(35–48%)-isomers mixture (relatively oxygen atom) and with advantage of β-yield.

Keywords: *3-(hexen-5-in-2-iloxy) propionitrile, triorganosilanes, acetylacetonate dicarbonyl rhodium, hydrosilylation, β-isomer, γ-isomer.*

Catalytic hydrosilylation reaction in the presence of hexene-5-in-2-ol-1 [1] and its acetate [2] acetylacetonate dicarbonyl rhodium [(acac)Rh(CO)$_2$] has been studied. Hydrosilylation reactions of 3-(hexen-5-in-2-iloxy)propionitrile (HPN) (Figure 1) in the presence of shown catalyst has been carried out and their condensation reactions with polychlorinecyclopentadienes have been studied.

As expected HPN addition reactions of trioorganosilanes proceed on triple bonds and reaction occurs with the formation of β- and γ-isomer mixture in two directions [3]:



$$CH_2{=}CHCH_2C{\equiv}CCH_2OCH_2CH_2CN \xrightarrow{+\,RR'_2SiH} \begin{cases} CH_2{=}CHCH_2CH{=}\underset{RR'_2Si}{C}CH_2OCH_2CH_2CN & \text{(I, III, V, VII, IX, XI)} \\ CH_2{=}CHCH_2\underset{RR'_2Si}{C}{=}CHCH_2OCH_2CH_2CN & \text{(II, IV, VI, VIII, X, XII)} \end{cases}$$

(I, III, V, VII, IX, XI)

(II, IV, VI, VIII, X, XII)

R=CH_3, R'=C_2H_5 (I, II), n-C_3H_7 (III, IV), $-(CH_2)_4-$ (V, VI), C_6H_5 (VII, VIII);

R=R'=C_2H_5 (IX, X), C_2H_5O (XI, XII) .

In (VII, VIII) IR spectrum of mixture (Figure 2) Si–C=CH (1610), C=N (2260) and CH_2=CH (1630, 3025 and 3080 cm^{-1}) fragments absorption lines exist. With TLC and NMR ^{1}H spectroscopy methods it was defined that the synthesized nitriles consist of mixture of two substances (I, II) (Figure 3) protons of CH_2O group were found in 4.12 (s) and 4.06 (d) ppm (I:II=60:40) CH_2=CH fragment of nitrile mixture in I, II NMR ^{1}H spectrum in 4.75–6.00 ppm area that consists of seven group absorption lines belong to protons (compared with =CH (*b*) group the last CH_2= (*a*) was found in stronger area), Si–C=CH (*d*) group proton correspond 5.40–6.00 area. Methylene protons of CH_2–C= (*c*) is situated in 2.70–3.00 ppm range. OCH_2 (*f*) group protons were found out singlet in 4.2 ppm and doublet in 4.06 ppm triplets in 2.52 and 3.56 ppm belongs to (*J*=6 Hz) $CH_2CH_2C{\equiv}N$ group protons. $(C_2H_5)_2Si$ group protons have multyplet signals in 0.30–1.05 ppm area (CH_3Si group protons were found out as singlet in $CDCl_3$ 0.024 and 0.044 ppm [3]).

Corresponding to [4, 5] methods with the preparative chromatographic column (length 800 mm, diameter 21 mm, 1 g subs for 200 g adsorbent, adsorbent – Al_2O_3, eluent – benzene:ether – 5:1, additive – iodine) XI and XII isomers were separated and their composition and structure confirmed by modern research methods. For example, in XI NMR ^{1}H spectrum of 3-(2-triethoxysilylhexadiene-2,5-iloxy) propionitrile all signals of proton fragments were found out (Figure 4). In the spectrum of 3-(3-triethoxysilylhexadiene-2,5-iloxy) propionitrile protons of CH_2O group are observed in 4.10 doublet form (*J*=6 Hz). All chemical replacements are characteristic for all kind of protons of researched compounds.

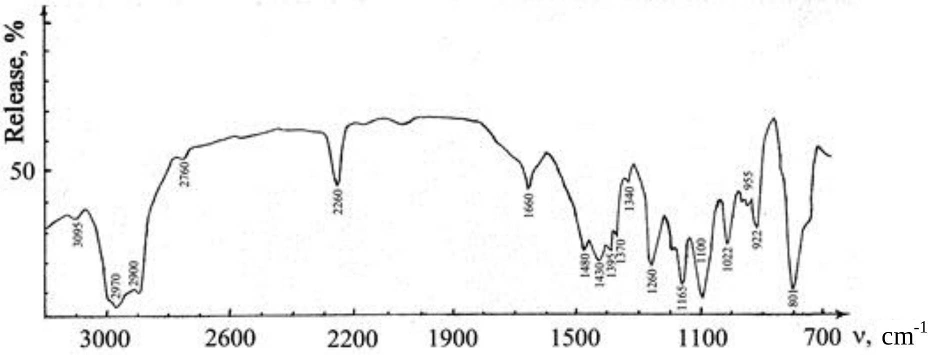


Fig. 1. IR spectrum of 3-(hexene-5-in-2-iloxy)propionitrile.

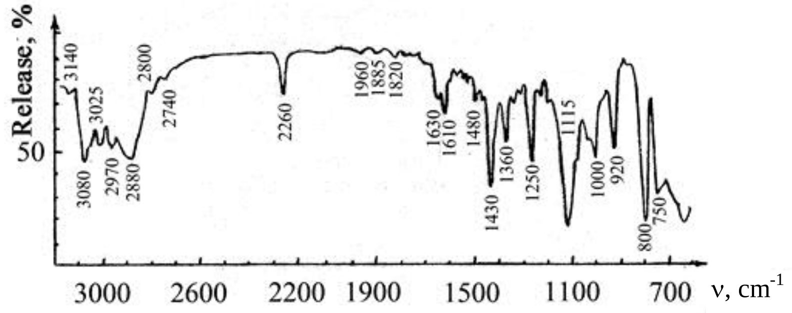


Fig. 2. IR spectrum of 3-(2-metyldiphenilsililhexadiene-2,5-iloxy propionitrile (VII) and 3-(3-methyldiphenilsililhexadiene-2,5-iloxy) propionitrile VIII mixtures.

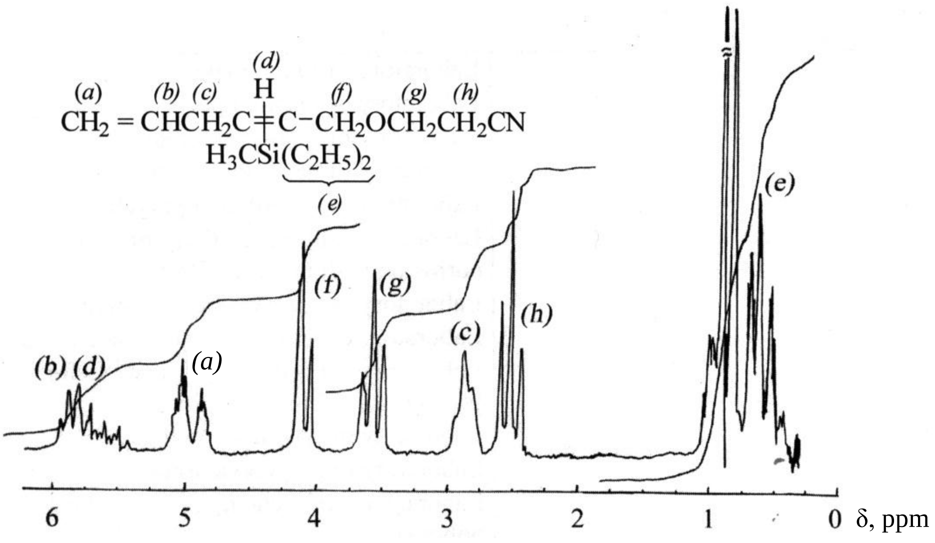


Fig. 3. NMR ^{1}H spectrum of 3-(2-methyldiethylhexadiene-2,5-iloxy) propionitrile (I) and 3-(2-methyldiethylhexadiene-2,5-iloxy) propionitrile II mixtures.

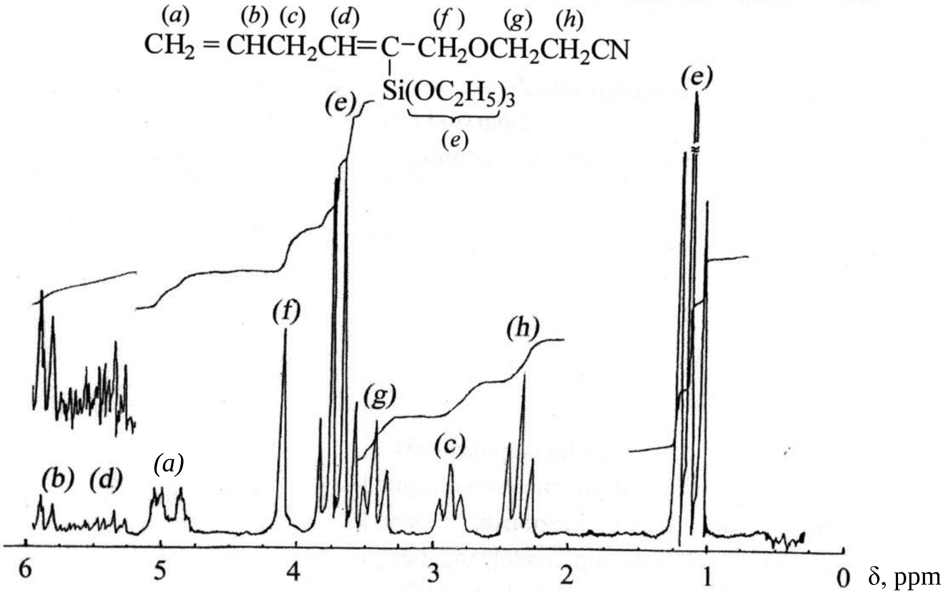


Figure 4. NMR ^{1}H spectrum of 3-(2-triethoxysililhexadiene-2,5-iloxy) propionitrile (XI).

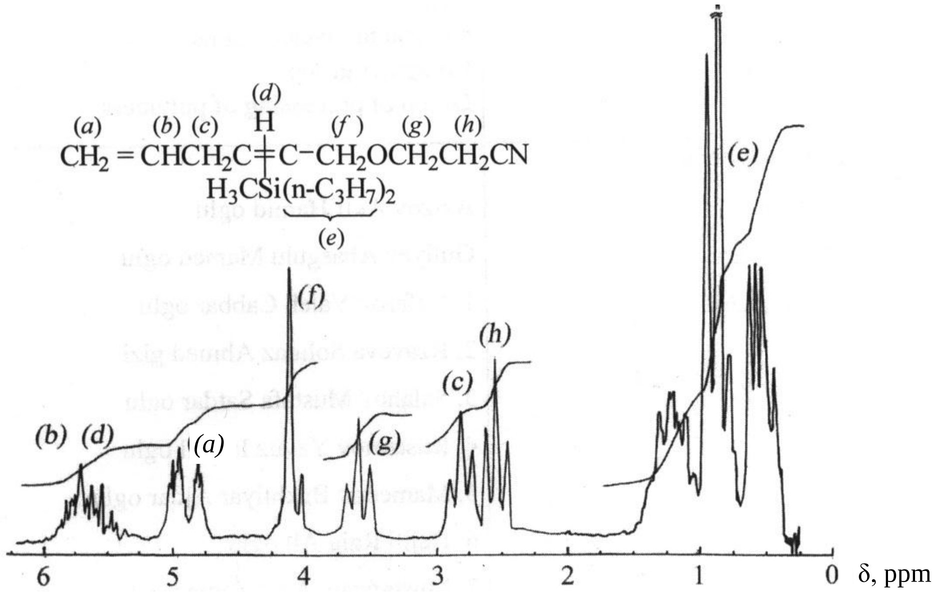
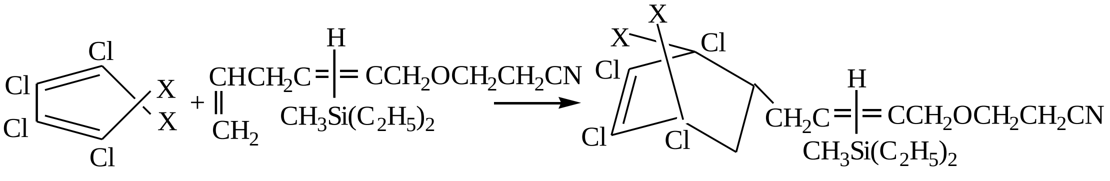


Figure 5. NMR ^{1}H spectrum of 3-(2-methyldi-*n*-propylsililhexadiene-2,5-iloxy) propionitrile (III) and 3-(3-methyldi-*n*-propylsililhexadiene-2,5-iloxy) propionitrile (IV) mixtures (was obtained in the presence of $H_2PtCl_6 \cdot 6H_2O$ catalyst).

As a result of experiments it was defined that the most efficient catalyst for this reaction is (acac)Rh(CO)$_2$, as it gives opportunity to realize the reaction in short time, in soft condition without solvent and with high yield. But, the amount of γ-isomer in isomer mixture increases and sometimes it is 48%. For comparison we can mention the ratio of nitrile synthesized in benzene in the presence of $H_2PtCl_6 \cdot 6H_2O$ is like this III:IV=74:26 (Figure 5).

It was defined that merging yield of triorganosilanes to HPN depends on character of radicals merged to silica atom and decreases in alkoxysilane anhydride case. Thus, methyl tetramethylenesilane reaction with HPN proceeds exothermically and the yield is 82%. High reactivity of methyltetramethylenesilane can be explained only with steric efficiency in silica atom molecule. In alkoxysilaneanhydride case low yield can be explained with the position of ethoxy group in space. Low yield (58%) is connected with disproportion reaction of triethoxysilane that is not reactive in hydrosilylation.

Isomer mixture enter diene synthesis reaction with (I, II) hexachlorine- and 5,5-dimethoxytetrachlorocyclopentadiene in *m*-xylene condition at 125–130^{0}C temperature, with the formation of polychlorine containing bicyclic silica organic nitriles (XI, XII)–(XIII, XIV) by double bond at the end of molecules. The shown adducts, also methyldiethylenesilane are obtained by mutual influence of polychlorine bicyclic nitriles [6]:



XIII, XIV, XV, XVI

X=Cl (XIII, XIV); OCH$_3$ (XV, XVI)

Absorption lines of obtained adducts in IR spectrum CH$_2$=CH (3000–3100 cm^{-1}) and C=C (2190–2260 cm^{-1}) are not found out. Valence vibrations of C=C (2190–2260 cm^{-1}) and C≡N (2220–2260 cm^{-1}) are found out almost in the same area. Absence of C=C bonds in that area is proved by being valence vibration line which is characteristic to Si–C=CH group in IR spectrum 1610 cm^{-1} of (I, II) isomers mixture.

Experimental part

The IR spectra were taken on spectrometer ″UR-20″ [7]. The spectra NMR ^{1}H have been registered on spectrometer ″Tesla BS-487″ (80 MHz) as internal standard, solvent – CCl$_4$ [8]. The purity of synthesized compounds was controlled by means TLC (plates Silufol UV-254, eluent – benzene:ether = 3:1, developer – iodine vapors).

HPN, prepared by the method [6], has the following constants: b.p. 99–100^{0}C (0.067 kPa), n_D^{20} - 1.4720, d_4^{20} - 0.9732. Yield – 90%.

Interaction of HPN with methyldiethylsilane. 4.1 g (0.04 mol) methyldiethylsilane in presence of 0.007 g (acac)Rh(CO)$_2$ is added to 6 g (0.04 mol) HPN with drops and mixing reaction mixture is mixed at 70–80^{0}C temperature for 3 hours. With extracting in vacuum 7.7 g isomer mixture (I, II) are separated. (III, IV–XI, XII) isomer mixture are obtained by analogical method. Constants and analysis of synthesized substances are given in the table.

Reaction of (I, II) isomer mixture with hexachlorocyclopentadiene. 25 g (0.01 mol) (I, II) and 2.1 g (0.01 mol) hexachlorcyclopentadiene mixture in the presence of 0.01g hydroquinone are mixed at 125–130^{0}C temperature in 10 ml *m*-xylene condition for 25 hours. Then, reaction mixture is cooled, solvent and preliminary components that did not enter reaction are extracted in vacuum. By column (column length – 250 mm, diameter – 21 mm, adsorbent – Al_2O_3, eluent benzene:ether =5:1, developer – iodine vapors) chromatography method 4.02 g (87.20%) adduct mixture (XIII, XIV) cleaned from preliminary substances are obtained. By analogical method from condensation reaction of (I, II) isomer mixture with 5,5-dimethoxy-tetrachlorinecyclopentadiene (XV, XVI) adduct mixture were obtained.

Mutual synthesis. 0.51 g (0.005 mol) boiling in 10 ml benzene methyldiethylsilane in the presence of 0.2 ml 0.1 N solution in $H_2PtCl_6 \cdot 6H_2O$ isopropyl alcohol is added to 2.11 g (0.005 mol) 1,2,3,4,7.7-hexachlorine-5-[4-(2-sianoethoxy)butin-2-il])bicyclo[2.2.1]hepten-2 reaction mixture is boiled another 18 hours. After extracting benzene 1.66 g (63.36%) (XIII, XIV) are obtained by colonnade chromatography method. By analogical method from 2.1 g (0.005 mol) 1,2,3,4-tetrachlorine-7,7-dmethoxy-5-[4-(2-sianoethoxy)butin-2-il]bicyclo[2.2.1] hepten-2 and 0.51 g (0.005 mol) methyldiethylesilane 1.76 g (64.00%) (XV, XVI) are obtained.

Constants and analysis of synthesized compounds

No of compaunds	$T_{b.p.}$, ^0C (0.067 kPa)	n_D^{20}	d_4^{20}	Yield, %	MR_D		R_f	Brutto-formule	Found/Calculated, %				IR spectrum, cm^{-1}
					found	calcu-lated			C	H	N	Si	
I, II	121–122	1.4760	0.9299	76.54	76.25	77.05	0.66 0.55	$C_{14}H_{25}ONSi$	$\frac{66.81}{66.87}$	$\frac{9.85}{10.02}$	$\frac{5.66}{5.57}$	$\frac{11.27}{11.17}$	1250 (Si–C), 1610 (SiC=CH), 2260 (C≡N), 3080 (CH_2=CH)
III, IV	130–132	1.4735	0.9118	68.33	86.08	86.55	0.72 0.60	$C_{16}H_{29}ONSi$	$\frac{68.85}{68.76}$	$\frac{10.33}{10.46}$	$\frac{4.87}{5.01}$	$\frac{9.94}{10.05}$	1255 (Si–C), 1610 (SiC=CH), 2260 (C≡N), 3085 (CH_2=CH)
V, VI	125–126	1.4978	0.9546	82.50	76.56	76.16	0.65 0.54	$C_{14}H_{23}ONSi$	$\frac{67.49}{67.42}$	$\frac{9.22}{9.29}$	$\frac{5.51}{5.62}$	$\frac{11.33}{11.26}$	1250 (Si–C), 1610 (SiC=CH), 2260 (C≡N), 3080 (CH_2=CH)
VII, VIII	209–212	1.5630	1.0500	80.00	107.50	107.67	0.78 0.66	$C_{22}H_{25}ONSi$	$\frac{75.92}{76.03}$	$\frac{7.29}{7.25}$	$\frac{3.98}{4.03}$	$\frac{8.15}{8.08}$	1260 (Si–C), 1610 (SiC=CH), 2260 (C≡N), 3085 (CH_2=CH
IX, X	131–133	1.4794	0.9200	72.25	81.80	81.56	0.70 0.59	$C_{15}H_{27}ONSi$	$\frac{67.89}{67.87}$	$\frac{10.18}{10.25}$	$\frac{5.35}{5.28}$	$\frac{10.67}{10.58}$	1255 (Si–C), 1610 (SiC=CH), 2260 (C≡N), 3090 (CH_2=CH)
XI, XII	139–141	1.4552	1.0090	57.90	84.32	84.20	0.73 0.60	$C_{15}H_{27}O_4NSi$	$\frac{57.64}{57.47}$	$\frac{8.61}{8.68}$	$\frac{4.38}{4.47}$	$\frac{9.03}{8.96}$	1250 (Si–C), 1610 (SiC=CH), 2260 (C≡N), 3080 (CH_2=CH)
XIII, XIV	212 decomp	1.5190	1.2780	87.20	124.49	124.96	0.90 0.78	$C_{19}H_{25}ONCl_6Si$	$\frac{43.65}{43.53}$	$\frac{4.88}{4.81}$	$\frac{2.74}{2.67}$	$\frac{5.27}{5.36}$	1255 (Si–C), 1610 (C=C), 2260 (C≡N), 790 (C–Cl)
XV, XVI	209 decopm	1.5086	1.2022	85.60	127.80	128.10	0.88 0.76	$C_{21}H_{31}O_3NCl_4Si$	$\frac{49.07}{48.94}$	$\frac{6.15}{6.06}$	$\frac{2.57}{2.72}$	$\frac{5.39}{5.45}$	1255 (Si–C), 1610 (C=C), 2260 (C≡N), 785 (C–Cl)

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3-(HEKSEN-5-İN-2-İLOKSİ)PROPİONİTRİLİN HİDROSİLİLLƏŞMƏSİ

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3-(Heksen-5-in-2-iloksi)propionitrilə asetilasetonatdikarbonilrodium katalizatorunun iştirakı ilə triorqanosilanların birləşmə reaksiyası, üçqat rabitə üzrə, lakin iki istiqamətdə β(52–65%)- və γ (35–48%)-izomerlər (oksigen atomuna nəzərən) qarışığının alınması və β-məhsulun çıxımının üstünlüyü ilə baş verir.

Açar sözlər: *3-(heksen-5-in-2-iloksi)propionitril, triorqanosilanlar, asetilasetonatdikarbonilrodium, hidrosililləşmə, β-izomer, γ-izomer.*

ГИДРОСИЛИЛИРОВАНИЕ 3-(ГЕКСЕН-5-ИН-2-ИЛОКСИ)ПРОПИОНИТРИЛА

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Реакция присоединения триорганосиланов к 3-(гексен-5-ин-2-илокси)пропионитрилу в присутствии катализатора ацетилацетонатдикарбонила родия протекает по тройной связи, но в двух направлениях с образованием смеси β(35–48%)- и γ(52–65%)-изомеров (относительно атома кислорода) с преимущественным выходом β-продукта.

Ключевые слова: *3-(гексен-5-ин-2-илокси)пропионитрил, триорганосиланы, ацетилацетонатдикарбонил родия, гидросилилирование, β-изомер, γ-изомер.*