Synthesis and Properties of Diacetylene Azides

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Abstract—A three-stage method was developed for the synthesis of diacetylene azides from diacetylene alcohols prepared by Cadiot–Chodkiewicz reaction. By their bromination the corresponding diacetylene bromides were obtained whose azidation resulted in the target diacetylene azides. The attempt was performed to prepare azides of triacetylene series, but the low stability of the synthesized triacetylene alcohols prevented their conversion into the corresponding bromides.

The chemistry of acetylene and its derivatives is a well developed field of the industrial organic synthesis [1, 2]. However the employment of compounds with a triple bond in the fine organic synthesis is especially efficient for due to their high reactivity their contribution to the cost of the final product proves to be negligibly small.

Besides the acetylene series compounds possess a high amount of intrinsic energy, and they are the most energy-rich among all open-chain compounds. The ΔH°_{298} value of the acetylene molecule attains 226.3 kJ mol^{-1} and the heat of formation of the diacetylene molecule ΔH°_{298} is 433.5 kJ mol^{-1}. The polyynes as a rule are of low stability that decreased with the number of triple bonds. The stability of polyynes also essentially depended on the substituents at the terminal sp-atoms. For instance, the 2,2,15,15-tetramethylhexadeca-3,5,7,9,11,13-hexayne is stable at heating up to 50°C, the dimethyltetrayne suffers decomposition at 80°C, whereas the terminal dodeca-1,3,5,7,9,11-hexayne explodes even at –10°C.
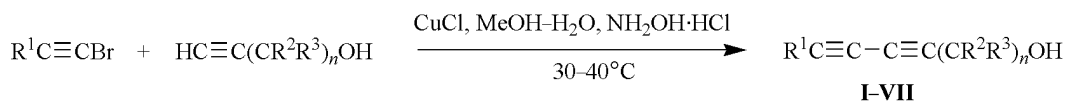
Evidently the bulky *tert*-butyl groups provide a stabilizing effect preventing the close contact of polyyne chains. Trimethylsilyl groups as substituents at the terminal *sp*-atoms also increase the stability of terminal polyynes. These polyynes are more stable at storage [3].

The azide groups also energy-rich (ΔH°_f 167 kJ mol^{-1}). Therefore the combination in the same molecule of this group and the diacetylene fragment should result in the formation of an energy-rich compound.
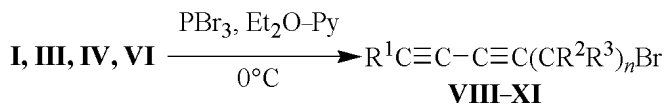
The route of the synthesis of target compounds included the synthesis of primary and tertiary acetylene alcohols, their oxidative coupling by Cadiot–Chodkiewicz reaction into diacetylene alcohols, conversion of the latter into the corresponding bromides that were used in the preparation of diacetylene azides.

The first stage consisted in the coupling of bromo-alkynes with the corresponding terminal acetylene alcohols (see the scheme). Due to the features of the Cadiot–Chodkiewicz reaction the alkynes with a hydro-

Scheme.

$$R^1C{\equiv}CBr \; + \; HC{\equiv}C(CR^2R^3)_nOH \; \xrightarrow[\text{30–40°C}]{\text{CuCl, MeOH–H}_2\text{O, NH}_2\text{OH·HCl}} \; R^1C{\equiv}C{-}C{\equiv}C(CR^2R^3)_nOH$$

$$\textbf{I–VII}$$

$R^1 = Bu$, $R^2 = R^3 = H$, $n = 1$ (**I**), 2 (**II**), 4 (**III**); $R^1 = C_6H_{13}$, $R^2 = R^3 = H$, $n = 4$ (**IV**); $R^1 = Pr$, $R^2 = R^3 = Me$, $n = 1$ (**V**); $R^1 = Bu$, $R^2 = R^3 = Me$, $n = 1$ (**VI**); $R^1 = C_6H_{13}$, $R^2 = R^3 = Me$, $n = 1$ (**VII**).

$$\textbf{I, III, IV, VI} \xrightarrow[\text{0°C}]{\text{PBr}_3,\ \text{Et}_2\text{O–Py}} \text{R}^1\text{C}\equiv\text{C}-\text{C}\equiv\text{C(CR}^2\text{R}^3)_n\text{Br}$$

VIII–XI

$R^1 = \text{Bu},\ R^2 = R^3 = \text{H},\ n = 1\ (\textbf{XII}),\ 4\ (\textbf{XIII});\ R^1 = C_6H_{13},$

$R^2 = R^3 = \text{H},\ n = 4\ (\textbf{XIV});\ R^1 = \text{Bu},\ R^2 = R^3 = \text{Me},\ n = 1\ (\textbf{XV}).$

philic function were used as an acetylene component The bromoalkynes were synthesized from terminal acetylene hydrocarbons [4].

Diacetylene bromides **VIII–XI** were obtained from the corresponding diacetylene alcohols **I, III, IV**, and **VI** by treating with PBr$_3$ in ether with the addition of several drops of pyridine at 0°C [5].

The bromination of diacetylene alcohols of propargyl type **I** and **VI** occurred easier and with higher yields (62 and 66%) compared to alcohols with a nonactivated hydroxy group **III** and **IV** (21 and 13%). Inasmuch as the tosyl group is a good leaving group in the nucleophilic substitution reactions we attempted to obtain tosylates of diacetylene alcohols **V** and **VII** and triacetylene alcohols **XVIII** and **XX**. However we failed to isolate the tosylation products for the process proceeded with a strong tarring.
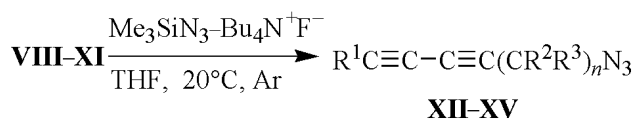
An only example was published of diacetylene dibromide azidation [6]. 1,6-Dibromohexa-2,4-diyne treated with sodium azide in a water−alcohol mixture and left standing for a day formed the corresponding bisazide in 56% yield; the product was stable only at –25°C. It was shown [7] that the presence of a propargyl group in the propargyl bromide and propargyl chloride activated the halogen atom in the azidation under the microwave irradiation. Under these conditions the yield of propargyl azide attained 88 and 60% respectively. For comparison: The yield of propyl azide from 1-bromopropane under the similar conditions was only 20%.

It was presumable that diacetylenes where the systems of the triple bonds and the azide function would be separated by two or more methylene groups would be potentially less explosive. In this event the azidation should proceed like the azidation of alkyl bromides that is performed by several published methods under conditions of phase-transfer catalysis at 80–100°C [8, 9]. To carry out the azidation of diacetylene compounds at elevated temperature is unsuitable for in these conditions azide group may enter into 1,3-dipolar cycloaddition with the triple bond giving mono- or bis-1,2,3-triazoles [10, 11]. We observed the possibility of these transformation

analyzing the behavior of azide **XV** during recording the mass spectrum: At elevated temperature in the vaporizing chamber of the mass spectrometer we observed the appearance of a peak with a double mass at *m/z* 378 corresponding to the intermolecular cycloaddition of the azide group to one of the triple bonds of compound **XV**.

Therefore we tried to perform the azidation at room temperature. One of such procedures is the modified Mitsunobu reaction [12]. In the presence of diisopropyl azodicarboxylate and triphenylphosphine primary and secondary alcohols react at room temperature with zinc azide complex with dipyridyl (ZnN$_6$·2Py) giving the corresponding azides in 76–87% yields. The disadvantage of this method is a fairly complex set of reagents and a low stability of the zinc azide complex with dipyridyl.
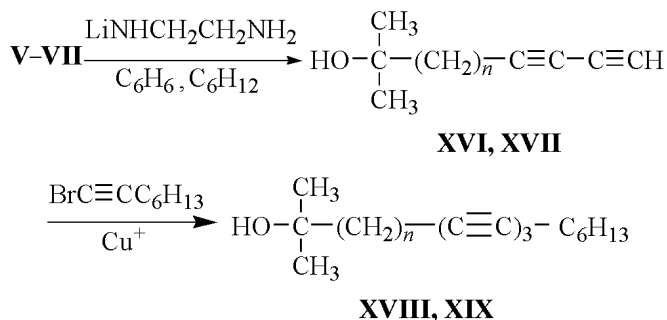
More than a decade ago the azidation of alkyl bromides at room temperature was performed by a complex of trimethylsilyl azide–tetrabutylammonium fluoride [13]. It turned out that this method was suitable for the synthesis of diacetylene azides both of the primary and tertiary structure.

$$\textbf{VIII–XI} \xrightarrow[\text{THF, 20°C, Ar}]{\text{Me}_3\text{SiN}_3\text{–Bu}_4\text{N}^+\text{F}^-} \text{R}^1\text{C}\equiv\text{C}-\text{C}\equiv\text{C(CR}^2\text{R}^3)_n\text{N}_3$$

XII–XV

$R^1 = \text{Bu},\ R^2 = R^3 = \text{H},\ n = 1\ (\textbf{VIII});\ 4\ (\textbf{IX});\ R^1 = C_6H_{13},$
$R^2 = R^3 = \text{H},\ n = 4\ (\textbf{X});\ R^1 = \text{Bu},\ R^2 = R^3 = \text{Me},\ n = 4\ (\textbf{XI}).$

The azidation of tertiary alcohols with a complex Me$_3$SiN$_3$–SnCl$_4$ [14] cannot be applied to the synthesis of tertiary diacetylene azides because of the high sensitivity of the latter to Lewis acids. A promising method of azide synthesis among others might be the use of the sodium azide molecules on a polymer matrix [15].
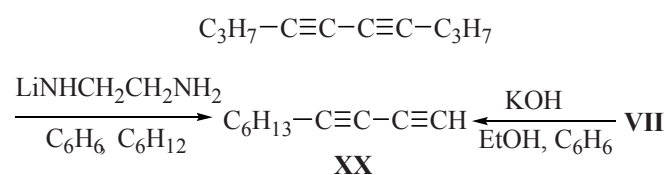
We also attempted to synthesize triacetylene alcohols along the following synthesis procedure.
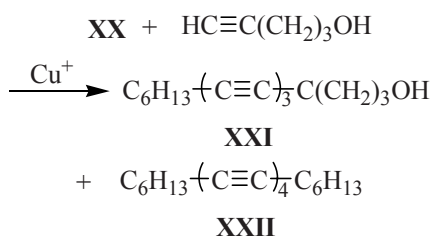
$$\textbf{V–VII} \xrightarrow[\text{C}_6\text{H}_6,\ \text{C}_6\text{H}_{12}]{\text{LiNHCH}_2\text{CH}_2\text{NH}_2} \text{HO}-\underset{\underset{\text{CH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}-(\text{CH}_2)_{\overline{n}}\text{C}\equiv\text{C}-\text{C}\equiv\text{CH}$$

XVI, XVII

$$\xrightarrow[\text{Cu}^+]{\text{BrC}\equiv\text{CC}_6\text{H}_{13}} \text{HO}-\underset{\underset{\text{CH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}-(\text{CH}_2)_{\overline{n}}-(\text{C}\equiv\text{C})_3-\text{C}_6\text{H}_{13}$$

XVIII, XIX

$n = 3\ (\textbf{XVI, XVIII}),\ 6\ (\textbf{XVII, XIX}).$

The reaction of prototropic isomerization ("acetylene zipper") [16] provided terminal diacetylene alcohols **XVI** and **XVII** in 43 and 21% yields respectively. They were completely characterized by spectral methods and elemental analysis. In reactions of these diynes with 1-bromooct-1-yne we obtained triacetylene alcohols **XVIII** and **XIX** in 78 and 69% yields respectively. These compounds were of low stability and quickly get dark on standing.

Therefore we decided to synthesize primary triacetylene alcohols hoping to get more stable compounds. To this end we prepared pentadeca-4,6,8-triyn-1-ol (**XXI**). The initial deca-1,3-diyne (**XX**) was obtained by two methods: 1) By prototropic isomerization of deca-4,6-diyne prepared by oxidative dimerization of pent-1-yne; 2) By the reverse Faworsky reaction from diyne alcohol **VII**.

$$C_3H_7-C{\equiv}C-C{\equiv}C-C_3H_7$$

$$\xrightarrow[\text{C}_6\text{H}_6,\ \text{C}_6\text{H}_{12}]{\text{LiNHCH}_2\text{CH}_2\text{NH}_2} C_6H_{13}-C{\equiv}C-C{\equiv}CH \xleftarrow[\text{EtOH, C}_6\text{H}_6]{\text{KOH}} VII$$

$$\mathbf{XX}$$

In reaction of deca-1,3-diyne (**XX**) with excess pent-4-yn-1-ol under Glaser reaction conditions we obtained pentadeca-4,6,8-triyn-1-ol (**XXI**), and by column chromatography on silica gel eicosa-7,9,11,13-tetrayne (**XXII**) was isolated as the side product of the oxidative dimerization of diyne **XX**.

$$\mathbf{XX}\ +\ HC{\equiv}C(CH_2)_3OH$$

$$\xrightarrow{Cu^+}\ C_6H_{13}{\left(C{\equiv}C\right)}_3C(CH_2)_3OH$$

$$\mathbf{XXI}$$

$$+\ C_6H_{13}{\left(C{\equiv}C\right)}_4C_6H_{13}$$

$$\mathbf{XXII}$$

The spectral data and elemental analysis of tetrayne **XXII** were in full agreement with the published data [17].

Triacetylene alcohols **XVIII, XIX**, and **XXI** are viscous nondistillable fluids. Their low stability is apparently caused by absorption of air oxygen followed by decomposition. In contrast, the triacetylene acids are as a rule crystalline compounds. For instance, the heptadeca-4,6,8-triynecarbozylic acid has an mp 107–108°C and in the daylight quickly gets first light-blue and then violet due to proceeding of a solid-phase topochemical polymerization [17].

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer Specord 75IR from 3% solutions of compounds in CCl_4 or $CHCl_3$. ^1H and ^{13}C NMR spectra were registered on a spectrometer Bruker DPX-300 (300 MHz), from solutions in $CDCl_3$. Mass spectra were measured on a GC-MS instrument MKh-1330 at the energy of ionizing electrons 70 eV. Elemental analysis was carried out on a CHN-analyzer Hewlett-Packard 185 B. Analytical TLC was performed on Polygram Sil G/UV_{254} plates, preparative TLC, on silica gel Silpearl, development under UV irradiation.

Diacetylene alcohols **I–VII** were prepared by oxidative coupling (Cadiot–Chodkiewicz reaction). Into a flask were charged 10 g (0.14 mol) of $NH_2OH{\cdot}HCl$ in 35 ml of water, 80 ml of 70% water solution of butylamine, 1.5 g (15 mmol) of CuCl, and 100 ml of methanol. The air was flashed from the flask with argon, and at stirring was added 0.2 mol of acetylene component. To the formed yellow dispersion 0.2 mol of bromoalkyne was added within 1 h at 30–35°C. After 15 min of stirring at 40°C 5 g (77 mmol) of KCN and 20 g (0.31 mol) of NH_4Cl in 300 ml of water was added at vigorous stirring. The reaction product was extracted into ether. The extract was washed with water, with concentrated solution of NH_4Cl, and dried with $MgSO_4$.

Initial nona-2,4-diyn-1-ol (**I**) was obtained by procedure [18]. Deca-3,5-diyn-1-ol (**II**), dodeca-5,7-diyn-1-ol (**III**) were prepared by method [19], tetradeca-5,7-diyn-1-ol (**IV**), 2-methylnona-3,5-diyn-2-ol (**V**), and 2-methyldodeca-3,5-diyn-2-ol (**VII**) were synthesized as described in [20]. 2-Methyldeca-3,5-diyn-2-ol (**VI**) was obtained as described in [21].

Nona-2,4-diyn-1-ol (I). Yield 69%, bp 79–81°C (1 mm Hg), n_D^{17} 1.5492.

Deca-3,5-diyn-1-ol (II). Yield 64%, n_D^{16} 1.5122. Found, %: C 79.78; H 9.59. $C_{10}H_{14}O$. Calculated, %: C 79.95; H 9.69.

Dodeca-5,7-diyn-1-ol (III). Yield 54%, n_D^{16} 1.5054. Found, %: C 80.57; H 10.21. $C_{12}H_{18}O$. Calculated, %: C 80.84; H 10.17.

Tetradeca-5,7-diyn-1-ol (IV). Yield 41%, n_D^{17} 1.4997.

2-Methylnona-3,5-diyn-2-ol (V). Yield 66%, bp 74°C (1 mm Hg), n_D^{18} 1.5030.

2-Methyldeca-3,5-diyn-2-ol (VI), Yield 64%, n_D^{18} 1.4989.

2-Methyldodeca-3,5-diyn-2-ol (**VII**), Yield 36%, bp 100–101°C (1 mm Hg), n_D^{18} 1.4934. Found, %: C 81.40; H 10.49. $C_{13}H_{20}O$. Calculated, %: C 81.20; H 10.48.

Diacetylene bromides VIII–XI. To a solution of 2.5 mmol of diacetylene alcohol in 5 ml of anhydrous ether containing several drops of pyridine was added dropwise 1.1 mmol of PBr_3 while stirring and cooling to –10°C for tertiary alcohols and to 0°C for primary alcohols. The bromination was monitored by TLC on silica gel, eluent hexane, R_f 0.8. The stirring was continued for 2.5 h at room temperature. Then the reaction mixture was poured on ice-water mixture and extracted with ether. The extracts were washed with water, with the saturated NaCl solution, and dried with $MgSO_4$. The diacetylene bromides were purified by column chromatography on silica gel, eluent hexane.

1-Bromonona-2,4-diyne (VIII). Yield 62%. Found, %: C 54.15; H 5.53; Br 40.32. $C_9H_{11}Br$. Calculated, %: C 54.33; H 5.57; Br 40.13.

1-Bromododeca-5,7-diyne (IX). Yield 21%. Found, %: C 59.96; H 7.10; Br 32.91. $C_{12}H_{17}Br$. Calculated, %: C 60.38; H 6.92; Br 33.13.

1-Bromotetradeca-5,7-diyne (X). Yield 13%. Found, %: C 62.60; H 7.87; Br 29.49. $C_{14}H_{21}Br$. Calculated, %: C 62.45; H 7.86; Br 29.67.

1-Bromo-2-methyldeca-3,5-diyne (XI). Yield 66%. IR spectrum (CCl_4), ν, cm^{-1}: 2930 s, 2870 s (C–H), 2250 m (C≡C), 680 s (C–Br). Found, %: C 58.23; H 6.56; Br 35.05. $C_{11}H_{15}Br$. Calculated, %: C 58.16; H 6.67; Br 35.18

Diacetylene azides XII–XV. In an atmosphere of dry argon to a mixture of 1 mmol of diacetylene bromide amd 1 mmol of trimethylsilyl azide was added 1.5 ml of 1 M solution of tetrabutylammonium fluoride in anhydrous THF. The azidation was monitored by TLC on silica gel, eluent hexane, R_f 0.5–0.6. After the appropriate time of stirring at room temperature (see below) the solvent was removed in a vacuum, and the residual oily fluid was subjected to column chromatography on silica gel, eluent hexane. After removing the solvent the diacetylene azides were obtained and characterized.

1-Azidonona-2,4-diyne (XII). Reaction time 48 h. Yield 60%, d_4^{15} 0.9274. IR spectrum, ν, cm^{-1}: 2910 s, 2840 s (C–H), 2240 m (C≡C), 2100 v.s (N_3 asymm.), 1240 m (N_3 symm.). ^{1}H NMR spectrum, δ, ppm: 0.88 t (3H, CH$_3$, J 6 Hz), 1.30–1.55 m (8H, CH$_2$CH$_2$CH$_3$, CH$_2$CH$_2$CH$_2$N$_3$), 2.33 t (2H, C≡CCH$_2$CH$_2$, J 7 Hz), 3.97

C (2H, CH$_2$N$_3$). Mass spectrum, m/z, (I_{rel}, %): 161 (79) [M]$^+$, 119 (14) [M–N$_3$]$^+$, 104 (11), 91 (100), 77 (57), 64 (30), 63 (39), 51 (29), 50 (21), 43 (29), 41 (64), 39 (29).

1-Azidododeca-5,7-diyne (XIII). Reaction time 96 h. Yield 87%. IR spectrum (CCl_4), ν, cm^{-1}: 2930 s, 2860 s (C–H), 2.100 v.s (N_3 asymm.). ^{1}H NMR spectrum, δ, ppm: 0.85 t (3H, CH$_3$, J 6 Hz), 1.30–1.75 m (8H, CH$_2$CH$_2$CH$_3$, CH$_2$CH$_2$CH$_2$N$_3$), 2.18 t [2H, C≡CCH$_2$(CH$_2$)$_2$CH$_3$], 2.23 t [2H, C≡CCH$_2$(CH$_2$)$_3$N$_3$], 3.26 t (2H, CH$_2$N$_3$). Mass spectrum, m/z (I_{rel}, %): 174 (3), 160 (13), 146 (23), 134 (32), 132 (32), 118 (52), 104 (45), 91 (97), 77 (68), 65 (39), 51 (45), 43 (71), 41 (100), 39 (38).

1-Azidotetradeca-5,7-diyne (XIV). Reaction time 32 h. Yield 95%, d_4^{15} 0.9172. IR spectrum, ν, cm^{-1}: 2900 s, 2850 s (C–H), 2090 v.s (N_3 asymm.). ^{1}H NMR spectrum, δ, ppm: 0.85 t (3H, CH$_3$, J 6 Hz), 1.20–1.80 m (12H, 6CH$_2$), 2.23 t [2H, C≡CCH$_2$(CH$_2$)$_4$CH$_3$, J 7 Hz], 2.28 t [2H, C≡CCH$_2$(CH$_2$)$_3$N$_3$, J 7 Hz], 3.28 t (2H, CH$_2$N$_3$, J 6 Hz). Mass spectrum: [M]$^+$ 231.338.

2-Azido-2-methyldeca-3,5-diyne (XV). Reaction time 48 h. Yield 46%, d_4^{20} 0.8929. IR spectrum ($CHCl_3$), ν, cm^{-1}: 2910 s, 2850 s (CH), 2230 m (C≡C), 2100 s (N_3 asymm.), 1240 m (N_3 symm.). ^{1}H NMR spectrum, δ, ppm: 0.88 t (3H, CH$_3$CH$_2$, J 6 Hz), 1.37–1.55 m [10H, (CH$_3$)$_2$CN$_3$, CH$_2$CH$_2$CH$_3$], 2.29 t (2H, C≡CCH$_2$, J 7 Hz). Mass spectrum, m/z (I_{rel}, %): 189 (5) [M]$^+$, 147 (100) [M–N$_3$]$^+$, 119 (10), 117 (12), 105 (24), 91 (26), 77 (24), 65 (14), 63 (15), 55 (13), 51 (15), 41 (27).

2-Methylnona-6,8-diyn-2-ol (XVI). Yield 43%, bp 80–81°C (0.1 mm Hg), n_D^{20} 1.5003. IR spectrum ($CHCl_3$), ν, cm^{-1}: 3600, 3450 br (OH), 3300 v.s(HC≡C). ^{1}H NMR spectrum, δ, ppm: 1.16 s (6H, 2CH$_3$), 1.51–1.55 m (4H, 2CH$_2$), 1.96 t (1H, HC≡C), 2.07 s (1H, OH), 2.26 t.d (2H, α-CH$_2$). Found, %: C 79.72; H 9.76. $C_{10}H_{14}O$. Calculated, %: C 79.95; H 9.52.

2-Methyldodeca-9,11-diyn-2-ol (XVII). Yield 21%, viscous oily substance. IR spectrum ($CHCl_3$), ν, cm^{-1}: 3600 s (OH), 3300 s (C≡CH), 2285 w, 2210 s 2060 w [(C≡C)$_2$]. ^{1}H NMR spectrum, δ, ppm: 1.08 s (6H, 2CH$_3$), 1.18–1.54 m (10H, 5CH$_2$), 1.81 t (1H, Ca''CH), 2.16 t.d (2H, α-CH$_2$), 2.30 s (1H, OH). Found, %: C 81.24; H 10.76. $C_{13}H_{20}O$. Calculated, %: C 81.20; H 10.49.

2-Methylheptadeca-6,8,10-triyn-2-ol (XVIII). Yield 78%, viscous oily substance. n_D^{20} 1.4950. IR spectrum ($CHCl_3$), ν, cm^{-1}: 3600 s, 3450 br (OH), 2230 s [(C≡C)$_3$]. Found, %: 83.41; H 9.98. $C_{18}H_{26}O$. Calculated, %: C 83.62; H 10.14.

2-Methyleicosa-9,11,13-triyn-2-ol (XIX). Yield 68%, dark oily substance. IR spectrum (CHCl$_3$), ν, cm^{-1}: 3600 s, 3445 br (OH), 2235 s [(C≡C)$_3$]. Found, %: C 83.82; H 10.67. C$_{21}$H$_{32}$O. Calculated, % C 83.94; H 10.74.

Pentadeca-4,6,8-triyn-1-ol (XXI). A mixture of 0.3 g (3 mmol) of CuCl and 0.33 g (3 mmol) of tetramethyl-ethylenediamine in 20 ml of acetone was stirred by a magnetic stirrer at passing an oxygen flow till dissolution of CuCl. Then a mixture was added of 1.1 g (8 mmol) of deca-1,3-diyne (**XX**) and 2.7 g (32 mmol) of 4-pentyn-1-ol in 20 ml of acetone. The reaction mixture was stirred for 1 h at room temperature and 3 h at 30–40°C. On the next day into the flask was added 20 ml of 10% H$_2$SO$_4$, the reaction mixture was extracted with ether, the extract was washed with water, and dried with MgSO$_4$. On removing the ether the reaction products were separated by column chromatography on silical gel. First eicosa-7,9,11,13-tetrayne (**XXII**) was isolated (eluent hexane–ether, 2:1), then triacetylene alcohol **XXI** (eluent hexane–ether, 1:1). Yield 0.32 g (19%). Viscous quickly darkening oily substance. IR spectrum (CHCl$_3$), ν, cm^{-1}: 3635 s, 3400 br (OH), 2225 s [(C≡C)$_3$]. Found, %: C 83.41; H 9.20. C$_{15}$H$_{20}$O. Calculated, %: C 83.35; H 9.32.

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