Organic Chemistry

Synthesis of long-chain terminal diacetylenic compounds

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Cleavage of long-chain 2-methyl-3,5-alkadiyne-2-ols in anhydrous benzene in the presence of KOH (Favorsky retroreaction) is accompanied by migration of the triple bonds and it affords 2,4-alkadiynes. Proton-donor additives (alcohol or water) completely suppress the isomerization process and enable preparation of terminal acetylenes in high yields.

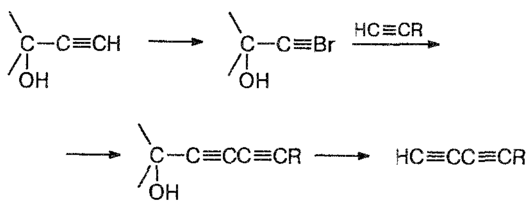
Key words: diacetylenic alcohols, diacetylenic hydroxy acids, alkaline cleavage, long-chain terminal diacetylenes.

Interest in investigation of long-chain polyacetylenic compounds was stimulated by their ability for stereoregular photopolymerization in ordered structures of single crystals and Langmuir—Blodgett films.[1] The unique physical and chemical properties of these polymers encouraged the search for methods of synthesis of the original monomers. We developed a method of obtaining long-chain terminal diacetylenic compounds as intermediates for synthesis of such monomers.

One approach to the synthesis of terminal diacetylenes is based upon the alkaline cleavage of tertiary diacetylene alcohols (Favorsky retroreaction[2]), which are readily obtained from the simplest dialkylethynylcarbinols and monosubstituted acetylenes[3] (Scheme 1).

Cleavage of tertiary alcohols is normally carried out by heating under reduced pressure, while the reaction products are distilled off. Such technique was successfully applied for the synthesis of butadiynylarenes and functionally substituted 1,3-diynes.[4—7] However, it is not very suitable for the synthesis of high-boiling labile diacetylenic compounds since they are resinified completely at higher temperatures.[8] Meanwhile, this procedure of cleavage is not unique. Assumimg that there are no principal obstacles to obtain long-chain 1,3-diynes using this technique, which is favorable in many respects, we attempted to find the acceptable conditions for cleavage of corresponding alcohols, either with or without the additional functional groups.

Scheme 1



The starting alcohols **1a—e** were synthesized from ethynyl(dimethyl)carbinol (**2**) and iodoacetylenes (**3**) or bromoacetylenes (**4**) and acetylenes (**5**) *via* the Cadiot—Chodkiewicz reaction[3,5] (Scheme 2) in 65 to 85 % yields (Table 1).

Cleavage of **1a—c,e** was carried out in anhydrous benzene at 60 to 65 °C in argon flow using the excess of

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Table 1. Characteristics and spectra of the compounds synthesized

Compound	Yield (%)	M.p./°C or n_D (T/°C)[a]	IR, ν/cm^{-1}	^{1}H NMR,[b] δ, J/Hz	Found / Calculated (%)		Molecular formula
					C	H	
1a	81	Viscous liquid	2265($C\equiv C$); 3610(OH)	0.87 (t, J = 7, 3 H, $\underline{CH}_3CH_2$); 1.26 (s, 20 H, $-CH_2-$); 1.51 (s, 6 H, $\underline{CH}_3COH$); 2.27 (t, J = 7, 2 H, $CH_2C\equiv C$)	$\underline{82.29}$ 82.54	$\underline{11.68}$ 11.66	$C_{19}H_{32}O$
1b	70	42—43	2265($C\equiv C$); 3610(OH)	0.87 (t, J = 7, 3 H, $\underline{CH}_3CH_2$); 1.25 (s, 30 H, $-CH_2-$); 1.51 (s, 6 H, MeCOH); 2.27 (t, J = 7, 2 H, $CH_2C\equiv C$)	$\underline{82.93}$ 83.17	$\underline{12.06}$ 12.22	$C_{24}H_{42}O$
1c	72	1.5069 (20)	1730(C=O); 2265($C\equiv C$); 3610(OH)	1.42 (s, 6 H, MeCOH); 2.57 (s, 4 H, $-CH_2CH_2-$, A_2B_2 system); 3.63 (s, 3 H, MeO); 4.5 (s, 1 H, OH)	$\underline{67.97}$ 68.02	$\underline{7.33}$ 7.27	$C_{11}H_{14}O_3$
1d	67	1.4944 (21)	1735(C=O); 2260($C\equiv C$); 3615(OH)	1.24 (t, J = 7.2, 3 H, $\underline{CH}_3CH_2O$); 1.27 (s, 6 H, $-CH_2-$); 1.45 (s, 6 H, $\underline{CH}_3COH$); 2.19—2.28 (m, 4 H, $CH_2C\equiv$ and CH_2CO); 3.63 (s, 3 H, MeO); 4.07 (q, J = 7.2, 2 H, $MeCH_2O$)	$\underline{72.17}$ 71.97	$\underline{8.76}$ 8.86	$C_{15}H_{22}O_3$
1e	84	1.4920 (20)	1734(C=O); 2262($C\equiv C$); 3614(OH)	1.26 (s, 12 H, $-CH_2-$); 1.45 (s, 6 H, MeCOH); 2.19—2.28 (m, 4 H, $CH_2C\equiv$ and CH_2CO); 3.62 (s, 3 H, MeO)	$\underline{73.03}$ 73.34	$\underline{9.49}$ 9.41	$C_{17}H_{26}O_3$
6a	90	1.4758 (22)[18]	2235($C\equiv C$); 3223($\equiv$CH)	0.88 (t, J = 6.9, 3 H, Me); 1.25 (s, 20 H, $-CH_2-$); 1.96 (t, J = 1.1, 1 H, $HC\equiv C$); 2.20—2.30 (m, 2 H, $CH_2C\equiv C$)	—	—	$C_{16}H_{26}$
6b	90—96	28—29	2235($C\equiv C$); 3223($\equiv$CH)	0.88 (t, J = 6.9, 3 H, Me); 1.25 (s, 30 H, $-CH_2-$); 1.96 (t, J = 1.1, 1 H, $HC\equiv C$); 2.20—2.30 (m, 2 H, $CH_2C\equiv C$)	$\underline{87.33}$ 87.42	$\underline{12.41}$ 12.58	$C_{21}H_{36}$
6c	70	88—89[19]	1715(C=O); 2236($C\equiv C$); 3320($\equiv$CH)	1.95 (s, 1 H, $HC\equiv C$); 2.56 (s, 4 H,$-CH_2CH_2-$, A_2B_2 system); 9.1 (s, 1 H, OH)	—	—	$C_7H_6O_2$
6d	74	38—39 (from pentane)	1715(C=O); 2235($C\equiv C$); 3320($\equiv$CH)	1.26 (s, 6 H, $-CH_2-$); 1.94 (t, J = 1.1, 1 H, $HC\equiv C$); 2.20—2.30 (m, 4 H, $CH_2C\equiv$ and CH_2CO); 10.2 (s, 1 H, OH)	$\underline{73.09}$ 73.14	$\underline{7.42}$ 7.37	$C_10H_{12}O_2$
6e	69	43—43.5	1715(C=O); 2240($C\equiv C$); 3325($\equiv$CH)	1.26 (s, 12 H, $-CH_2-$); 1.95 (t, J = 1.1, 1 H, $HC\equiv C$); 2.20—2.30 (m, 4 H, $CH_2C\equiv$ and CH_2CO); 10.8 (s, 1 H, OH)	$\underline{75.71}$ 75.69	$\underline{9.00}$ 8.80	$C_{13}H_{18}O_2$
7a	90	31—32	2275($C\equiv C$) vw	0.86 (t, J = 6.7, 3 H, $\underline{CH}_3CH_2$); 1.25 (s, 18 H, $-CH_2-$); 1.87 (t, J = 1, 3 H, $MeC\equiv C$); 2.20—2.30 (m, 2 H, $CH_2C\equiv C$)	$\underline{87.94}$ 88.00	$\underline{11.86}$ 12.00	$C_{16}H_{26}$
7b	73	37—38	2275($C\equiv C$) vw	0.86 (t, J = 6.7, 3 H, $\underline{CH}_3CH_2$); 1.25 (s, 28 H, $-CH_2-$); 1.87 (t, J = 1, 3 H, $MeC\equiv C$); 2.20— 2.30 (m, 2 H, $CH_2C\equiv C$)	$\underline{87.12}$ 87.42	$\underline{12.85}$ 12.58	$C_{21}H_{36}$
7c	83	121—122[20]	1718(C=O); 2273($C\equiv C$)	1.91 (t, J = 1, 3 H, Me); 3.41 (q, J = 1, 2 H, CH_2); 8.7 (s, 1 H, OH)	—	—	$C_7H_6O_2$
7e	80	67—68 (from pentane)	1720(C=O); 2270($C\equiv C$)	1.25 (s, 10 H, $-CH_2-$); 1.91 (s, 3 H, Me); 2.20—2.30 (m, 4 H, $CH_2C\equiv$ and CH_2CO); 9.6 (s, 1 H, OH)	$\underline{75.68}$ 75.69	$\underline{8.73}$ 8.80	$C_{13}H_{18}O_2$
9	51	107—108	1715(C=O); 2230($C\equiv C$)	0.88 (t, J = 6.7, 3 H, Me); 1.26 (s, 12 H, $-CH_2-$); 2.2 (t, J = 7.2, 2 H, $(CH_2)_6\underline{CH_2}C\equiv C$)); 2.65 (s, 4 H, $(CH_2)_2CO$, A_2B_2 system); 10.8 (s, 1 H, OH)	$\underline{78.81}$ 79.03	$\underline{8.53}$ 8.58	$C_{17}H_{22}O_2$

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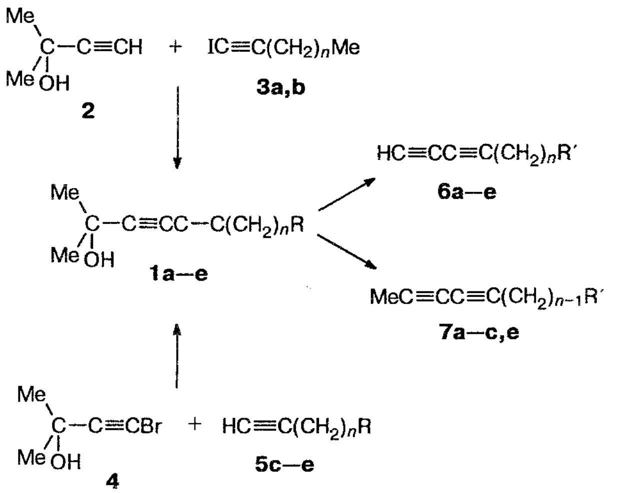
[a] Solid specimens were purified by recrystallization from hexane; liquids were purified by preparative thin-layer chromatography (SiO_2, $CHCl_3$). [b] In the ^{1}H NMR spectra, the signal of protons of the polymethylene chain ranges from 1.25 to 1.27 ppm and has a shoulder at ~1.4 ppm; the hydroxyl group does not appear in the spectra of compounds **1a,b,d,e**.

calcined KOH powder. Under these conditions, which were used earlier for the synthesis of some ethynylarenes and -heteroarenes,[9] the major reaction products were not the expected terminal diacetylenes **6a—c,e**, but the isomeric 2,4-diynes **7a—c,e**. Cleavage of hydroxy esters **1c,e** resulted in salts of diacetylenic acids **7c,e**.

Scheme 2

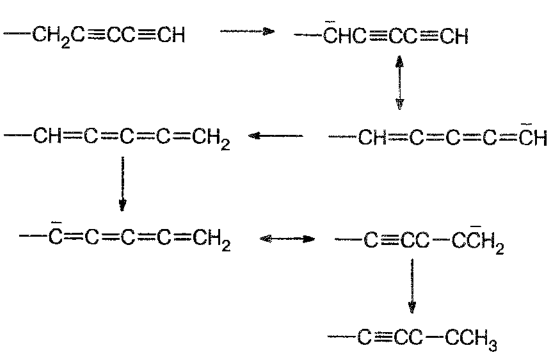


a: $R = R' = Me$, $n = 11$
b: $R = R' = Me$, $n = 16$
c: $R = COOMe$, $R' = COOH$, $n = 2$
d: $R = COOEt$, $R' = COOH$, $n = 5$
e: $R = COOMe$, $R' = COOH$, $n = 8$

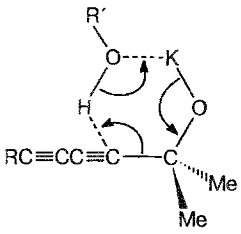
Chromatographic monitoring of **1b** cleavage showed that terminal diacetylene **6b** is formed at the initial stage, then its isomer **7b** is formed and accumulated, and the final product contains only an admixture of **6b**. Since the prototropic isomerization of compounds **6** is the process catalyzed by bases, one could suppose that the transformation of **6** into **7** is caused by KOH. However, the direct experiments showed that **6b** is not subjected to isomerization when heated up to 65 °C in the presence of KOH.

We supposed that the isomerization of **6** is initiated by the substituted diacetylenide anions generated upon cleavage of tertiary alcohols **1**. Indeed, the Favorsky retroreaction proceeds with intermediate formation[2] of alkoxide of the starting alcohol and its further cleavage by the C(sp^3)—C(sp) bond, yielding the acetylenide anion and ketone; then the acetylenide anion without leaving the cage takes-off an acid proton from ketone. Then the predominant escape of one or another anion to the bulk is determined by the acidity ratio of a terminal acetylene and a ketone. There are no precise data on the acidity of the corresponding compounds under comparable conditions. Upon transition from a terminal monoacetylene to a diacetylene, the acidity increases by approximately 5 to 6 orders of magnitude.[10] pK$_a$ of phenylacetylene is 1 to 2 orders of magnitude higher than that of acetone (in water),[11] and alkylacetylenes are still weaker acids than phenylacetylene by ~2 orders of magnitude.[12,13] These relationships show that the probability of escape of a diacetylenide anion to the bulk, which is a weaker base, is significantly higher than that of a monoacetylenide anion and, likely, of an enolate anion. Taking a proton from the α-methylene group of the terminal diacetylene, which is formed simultaneously, this anion initiates the isomerization (Scheme 3).

Scheme 3



If the above reasons are correct, it follows that the introduction of a sufficiently strong proton donor into the reaction mixture should suppress the undesirable isomerization process. We found experimentally that the addition of ethanol in the concentration, which is somewhat higher than that of **1**, excludes almost completely the formation of the isomeric product **7**. Moreover, the cleavage rate of **1** increases significantly. Therefore, we suppose that the proton donor is involved in the elementary reaction act proceeding as concerted electron transfer.



Compensation of the energy loss for cleavage of the C—C bond by the energy gain from formation of the C—H bond in the concerted process decreases the activation energy and increases the reaction rate. Note that the alkaline cleavage of α-acetylene ketones, which is relative to Favorsky retroreaction, proceeds in general only in the presence of proton donors as it was found earlier.[14]

It should be noted that water as a proton donor also suppresses the isomerization of **6** into **7**, but its effect on the reaction rate is ambiguous. Though it should accelerate the alcoholate cleavage, water shifts the alcohol—alkoxide equilibrium to the left, and overdose of water causes agglutination of the powdered KOH particles and thus reduces the overall reaction rate.

Thus, introduction of proton donors upon the alkaline cleavage of long-chain diacetylene alcohols enables prevention of the resulting terminal diynes from isomerization, which proceeds almost quantitatively in the absence of these donors.

Under the conditions found, alcohols **1a—e** were transformed into **6a—e** in 69 to 95 % yields (see Table 1). The terminal diacetylenic acids obtained were used for the synthesis of alkatriynic acids as shown for **6c**.

$$\mathbf{6c} + \underset{\mathbf{8}}{\mathrm{IC{\equiv}C(CH_2)_7Me}} \longrightarrow$$

$$\longrightarrow \underset{\mathbf{9}}{\mathrm{Me(CH_2)_7C{\equiv}CC{\equiv}CC{\equiv}C(CH_2)_2COOH}}$$

Synthesis and photopolymerization in the Langmuir—Blodgett films for a series of other long-chain triacetylenic acids were described earlier.[16]

Experimental

IR spectra were recorded in $CHCl_3$ using an UR-20 spectrophotometer; ^1H NMR spectra were registered in $CDCl_3$ with TMS standard using a 90 MHz Jeol FX90Q spectrometer. The esters of terminal acetylenic acids **5c—e** were synthesized by boiling alcohol solutions of the corresponding acids in the presence of 2 % H_2SO_4 for 4 h followed by vacuum distillation of the ester. Iodoalkines **3a,b** and **8** were obtained as earlier.[16] Table 1 represents physicochemical and spectral characteristics of the compounds synthesized.

Synthesis of tertiary diacetylenic alcohols

2-Methyl-3,5-octadecadiyne-2-ol (1a). Iodoalkyne **3a** (17 g, 52 mmol) in 100 mL of MeOH was added at ~20 °C over 2 h in an Ar atmosphere to a mixture of 18 g (214 mmol) of **2**, 0.37 g (2.6 mmol) of CuBr, and 110 mL of 25 % aqueous $MeNH_2$ in 300 mL of DMF. When a blue color appeared, several crystals of $NH_2OH \cdot HCl$ were added up to decolorization. After stirring for two hours, the reaction mixture was extracted with pentane, and the extract was washed with water and dried over $MgSO_4$. Chromatography on SiO_2 (ASKG grade) with benzene as eluent afforded 11.7 g of compound **1a** in the form of a colorless viscous liquid.

2-Methyl-3,5-tricosadiyne-2-ol (1b) was obtained similarly to **1a** (**3b** was added in THF—MeOH, 1 : 1).

Methyl 14-hydroxy-14-methyl-10,12-pentadecadiynoate (1e). Ester **5e** (3 g, 15.3 mmol) in 20 mL of THF—MeOH was added gradually in an Ar atmosphere to a solution of 0.15 g (1.5 mmol) of CuCl in 5 mL of 25 % aqueous $MeNH_2$ decolorized with several crystals of $NH_2OH \cdot HCl$, then 3.2 g (20 mmol) of **4** [17] in 10 mL of MeOH was added over 30 min, and the mixture was stirred further for 2 h. During the addition of **4**, the temperature of the reaction mixture has increased up to *ca.* 30 °C, and the suspension formed initially was transformed into transparent solution. When the green color appeared, the mixture was decolorized by several crystals of $NH_2OH \cdot HCl$; a small amount of aqueous $MeNH_2$ was added upon the reduction of pH in the solution. After exposure, the mixture was diluted with 50 mL of water and extracted with ether. The extract was washed with water and dried over $MgSO_4$, the solvent was removed *in vacuo*. The residue was dissolved in hot hexane, cooled, and filtered; after removal of hexane *in vacuo*, the mixture was heated at 55 to 60 °C *in vacuo* (0.5 Torr) to remove the admixture of **4**. Chromatography on SiO_2 (hexane and hexane—ether, 3 : 2 as eluents) afforded 3.57 g of compound **1e**.

Using the same technique, **methyl 8-hydroxy-8-methyl-4,6-nonadiynoate 1c** and **ethyl 11-hydroxy-11-methyl-7,9-dodecadiynoate 1d** were obtained.

Favorsky retroreaction in anhydrous medium

2,4-Hexadecadiyne (7a). A solution of 10 g (36 mmol) of diacetylenic alcohol **1a** in 150 mL of anhydrous benzene was stirred for 1.5 h in the presence of 4 g (72 mmol) of calcined KOH powder at 65 to 70 °C in an Ar atmosphere. The reaction mixture was diluted with pentane and filtered through a layer (~2 cm) of Al_2O_3. After removal of the solvent, 6.3 g of compound **7a** was obtained.

2,4-Heneicosadiyne (7b) was obtained similarly.

9,11-Tridecadiynic acid (7e). A mixture of 1 g (3.6 mmol) of **1e** and 0.4 g (7.1 mmol) of KOH powder was stirred for 0.5 h in 30 mL of anhydrous benzene at 60 °C in an Ar atmosphere. The precipitate was filtered off, dissolved in a small amount of water, acidified with concentrated HCl, and extracted with ether. The ethereal solution was dried over $MgSO_4$ and filtered through a thin layer of SiO_2, and the solvent was distilled off. The residue was recrystallized from hexane with activated carbon; 0.59 g of product was obtained in the form of white crystals that turned rose-colored in the light. **3,5-Heptadiynic acid (7c)** was obtained in the same manner.

Favorsky retroreaction in the presence of proton donors

1,3-Heneicosadiyne (6b). *A.* A mixture of 0.174 g (0.5 mmol) of **1b**, 0.056 g (1 mmol) of KOH powder, and 0.1 mL of EtOH in 6 mL of anhydrous benzene was stirred in an Ar atmosphere for 0.5 h at 60 °C. The reaction mixture was diluted with pentane and filtered through a thin layer of Al_2O_3. The yield of **6b** was 0.135 g.

B. The same amounts of reagents were used, but 0.1 mL of water was added instead of alcohol; the reaction duration was 1.25 h; the yield of **6b** was 0.127 g.

1,3-Hexadecadiyne (6a). A mixture of 1 g (3.63 mmol) of **1a**, 0.6 g (10.7 mmol) of KOH powder, and 0.1 mL of water in 15 mL of benzene was stirred for 2 h in an Ar atmosphere at 60 to 65 °C. 0.74 g of compound **6a** was isolated.

7,9-Decadiynic acid (6d). A mixture of 0.25 g (1 mmol) of ester **1d**, 0.11 g (2 mmol) of KOH powder, and 0.1 mL of EtOH in 6 mL of benzene was stirred for 1 h in an Ar atmosphere at 60 to 65 °C. The isolation procedure was the same as that for **7e**. After recrystallization from hexane, 0.14 g of compound **6d** was obtained.

4,6-Heptadiynic acid 6c and **10,12-tridecadiynic acid 6e** were obtained using the same procedure, but water was used as the proton donor.

Synthesis of triacetylenic acid

4,6,8-Heptadecatriynic acid (9). Several crystals of $NH_2OH \cdot HCl$ were added to decolorize a solution of 0.06 g (0.6 mmol) of CuCl in 4 mL of 25 % aqueous $MeNH_2$ in an Ar atmosphere, and 0.68 g (5.7 mmol) of **6c** in 10 mL of MeOH was added 0 °C. 1.4 g (5.3 mmol) of **8** in 10 mL of MeOH was added with stirring to the resulting dark yellow solution over the course of 45 min; the temperature was maintained between 3 and 5 °C; stirring was continued further for 2.5 h at 20 °C. The mixture was diluted with 50 mL of water, acidified with HCl upon cooling, decolorized with a small amount of Na_2SO_3, and extracted with ether. After removal of the solvent *in vacuo*, the residue was recrystallized from hexane with activated carbon. Compound **9** (0.74 g) was obtained in the form of white crystals that rapidly turned blue- and then violet-colored in the light.

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