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Synthesis of Functionally Substituted Diacetylenic Alcohols and Carboxylic Acids

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Abstract—Diacetylenic alcohols were synthesized by the Glazer reaction of 1-alkynes with 1-alkyn-ω-ols. *p*-and *m*-Alkadiyne bezoic acid derivatives were prepared by the Cadiot–Hodkiewicz reaction of *p*- and *m*-ethynylbenzoic acid with 1-bromoalkynes.

Synthesis of functionally substituted diacetylenic compounds is of interest, since such derivatives can be used for production of multilayers by the Langmuir–Blodgett or other techniques [1]. Taking into account that the properties of functionally substituted diacetylenic compounds depend on the relative position of the diacetylenic and functional groups, we considered it urgent to synthesize amphiphilic compounds with various sets and positions of these groups [2–5].

In the present work we report on the synthesis of diacetylenic alcohols **IIIa**–**IIIf** by the Glaser reaction of 1-alkynes **Ie, If** with 1-alkyn-ω-ols **IIa**–**IId** [2] [scheme (1)] in 45–79% yields.

The Cadiot–Hodkiewicz reaction [4, 6] of sodium *p*-ethynylbenzoate (**VIa**) or sodium *m*-ethynylbenzoate (**VIb**) with 1-bromoalkynes **Va**–**Vd**, **Vf** {obtained by reaction of silver acetylides **IVa**–**IVd, Vf** with bromine [scheme (2)] [7]} gave *para* (**VIIa, VIIb**) and *meta* (**VIIc**–**VIIf**) alkadiyne benzoic acid derivatives in 44–65% yields [scheme (3)]. Compounds **VIIa, VIIb** were purified by recrystallization from chloroform, and compounds **VIIc**–**VIIf** were recrystallized from hexane.

Diacetylenic alcohols **IIIa, IIIc** react with benzoyl chloride in the presence of pyridine, affording benzoates **VIIIa, VIIIc**, respectively [scheme (4)] in 59–75% yields. Benzoates **VIIIa, VIIIc** were purified by column chromatography on alumina, eluent hexane.

Functionally substituted diynes **IIIa**–**IIIf**, **VIIa**–**VIIf**, and **VIIIc** are white crystalline substances quickly darkening in air and withstanding handling in sealed ampules in argon at –19°C in the dark. Benzoate **VIIIa** is a colorless liquid. The yields, constants, and elemental analyses of compounds **IIIa**–**IIIf, VIIa**–**VIIf, VIIIa**, and **VIIIc** are listed in Table 1, and their ^{1}H NMR and UV spectra, in Tables 2 and 3, respectively.

$$\underset{\textbf{Ie, If}}{\mathrm{Me(CH_2)}_n\mathrm{C{\equiv}CH}} + \underset{\textbf{IIa–IId}}{\mathrm{HC{\equiv}C(CH_2)}_m\mathrm{OH}}$$

$$\xrightarrow[(\mathrm{Me_2NCH_2})_2]{\mathrm{CuCl,\ O_2}} \underset{\textbf{IIIa–IIIf}}{\mathrm{Me(CH_2)}_n\mathrm{C{\equiv}CC{\equiv}C(CH_2)}_m\mathrm{OH},} \tag{1}$$

$$\underset{\textbf{Ia–Id, If}}{\mathrm{Me(CH_2)}_n\mathrm{C{\equiv}CH}} \xrightarrow[\mathrm{NH_4OH}]{[\mathrm{Ag(NH_3)_2}]\mathrm{NO_3}} \underset{\textbf{IVa–IVd, IVf}}{\mathrm{Me(CH_2)}_n\mathrm{C{\equiv}CAg}}$$

$$\xrightarrow[-\mathrm{AgBr}]{\mathrm{Br_2}} \underset{\textbf{Va–Vd, Vf}}{\mathrm{Me(CH_2)}_n\mathrm{C{\equiv}CBr},} \tag{2}$$

I, IV, V, n = 2 (**a**), 3 (**b**), 5 (**c**), 7 (**d**), 9 (**e**), 15 (**f**). **II**, m = 1 (**a**), 2 (**b**), 3 (**c**), 4 (**d**). **III**, n = 9, m = 1 (**a**); n = 9, m = 2 (**b**); n = 15, m = 1 (**c**); n = 15, m = 2 (**d**); n = 15, m = 3 (**e**); n = 15, m = 4 (**f**);

$$\underset{\textbf{Va–d, Vf}}{\mathrm{Me(CH_2)}_n\mathrm{C{\equiv}CBr}} + \underset{\textbf{VIa, VIb}}{\mathrm{HC{\equiv}CC_6H_4COOR}}$$

$$\xrightarrow[\mathrm{HO(CH_2)_2NH_2}]{\mathrm{CuCl}} \underset{\textbf{VIIa–VIIf}}{\mathrm{Me(CH_2)}_n\mathrm{C{\equiv}CC{\equiv}CC_6H_4COOH},} \tag{3}$$

VI, p-C_6H_4, R = Na (**a**); m-C_6H_4, R = H (**b**). **VII**, p-C_6H_4, n = 2 (**a**); p-C_6H_4, n = 3 (**b**); m-C_6H_4, n = 3 (**c**); m-C_6H_4, n = 5 (**d**); m-C_6H_4, n = 7 (**e**); m-C_6H_4, n = 15 (**f**).

$$\textbf{IIIa, IIIc} \xrightarrow[\mathrm{Py}]{\mathrm{PhCOCl}} \underset{\textbf{VIIIa, VIIIc}}{\mathrm{Me(CH_2)}_n\mathrm{C{\equiv}CC{\equiv}CCH_2O(O)CPh},} \tag{4}$$

III, VIII, n = 9 (**a**), 15 (**c**).

The IR spectra of diacetylenes **IIIa**–**IIIf** and **VIIa**–**VIIf** lack ≡C–H, C≡C, and C≡CBr absorption bands of the starting compounds **Ie, If, IIa**–**IId, Va**–**Vd, and Vf** and show $(C{\equiv}C)_2$ stretching vibration bands at 2250 ± 5 cm^{-1}. The carboxy group in alkadyine bezoic acid derivatives **VIIa**–**VIIf** contain ν(C=O) bands at 1710 ± 5 and 1690 ± 5 cm^{-1} and a series of OH absorption bands at 3650–2375 cm^{-1}. The pre-

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Table 1. Properties of compounds **IIIa–IIIf, VIIa–VIIf, VIIIa**, and **Vc**

Comp. no.	Yield, %	mp, °C	Found, %		Formula	Calculated, %		*M*	
			C	H		C	H	found	calculated
IIIa	55	41–42	81.70	10.93	$C_{15}H_{24}O$	81.76	10.93	215.7	220.4
IIIb	45	17–18	82.23	11.25	$C_{16}H_{26}O$	81.99	11.18	228.6	234.4
IIIc	79	71–72	83.11	12.07	$C_{21}H_{36}O$	82.83	11.92	288.6	304.5
IIId	53	142–143	82.93	12.41	$C_{22}H_{38}O$	82.95	12.02	307.4	318.5
IIIe	50	51–52	83.56	12.33	$C_{23}H_{40}O$	83.07	12.12	320.2	332.6
IIIf	53	50–51	83.69	12.42	$C_{24}H_{42}O$	83.17	12.20	322.0	346.6
VIIa	46	237–238	79.22	5.72	$C_{14}H_{12}O_2$	79.23	5.70	210.9	212.2
VIIb	44	206–207	79.65	6.22	$C_{15}H_{14}O_2$	79.62	6.24	223.8	226.3
VIIc	65	169–170	80.03	6.29	$C_{15}H_{14}O_2$	79.62	6.24	225.1	226.3
VIId	58	102–103	80.51	7.22	$C_{17}H_{18}O_2$	80.28	7.13	250.8	254.3
VIIe	60	103–104	80.88	7.78	$C_{19}H_{22}O_2$	80.82	7.85	281.0	282.4
VIIf	64	106–107	82.57	9.54	$C_{27}H_{38}O_2$	82.18	9.71	393.6	396.6
VIIIa[a]	75	–	81.49	9.15	$C_{22}H_{28}O_2$	81.44	8.70	318.7	324.5
VIIIc	59	52–53	82.30	10.03	$C_{28}H_{40}O_2$	82.30	9.87	394.9	408.6

[a] d_{20}^{20} 0.9996, n_D^{20} 1.5225.

Table 2. ^1H NMR spectra of compounds **IIIa–IIIf, VIIa–VIIf, VIIIa**, and **Vc**

Comp. no.	δ, ppm
IIIa	0.88 t (3H, Me), 1.10–1.75 m [16H, $(CH_2)_8$], 1.93 br.s (1H, OH), 2.29 t [2H, $C\equiv C\mathit{CH}_2(CH_2)_8$], 4.81 s (2H, CH_2O)
IIIb	0.89 t (3H, Me), 1.15–1.65 m [16H, $(CH_2)_8$], 1.95 br.s (1H, OH), 2.26 t [2H, $C\equiv C\mathit{CH}_2(CH_2)_8$], 2.54 t (2H, $C\equiv C\mathit{CH}_2CH_2OH$), 3.74 t (2H, $HO\mathit{CH}_2CH_2C\equiv C$)
IIIc	0.88 t (3H, Me), 1.10–1.65 m [28H, $(CH_2)_{14}$], 1.90 br.s (1H, OH), 2.30 t [2H, $C\equiv C\mathit{CH}_2(CH_2)_{14}$], 4.25 s (2H, CH_2O)
IIId	0.87 t (3H, Me), 1.10–1.80 m [28H, $(CH_2)_{14}$], 1.92 br. s (1H, OH), 2.26 t [2H, $C\equiv C\mathit{CH}_2(CH_2)_{14}$], 2.53 t (2H, $C\equiv C\mathit{CH}_2CH_2OH$), 3.73 t (2H, $HO\mathit{CH}_2CH_2C\equiv C$)
IIIe	0.88 t (3H, Me), 1.20–1.70 m [28H, $(CH_2)_{14}$], 1.77 t (2H, $HOCH_2\mathit{CH}_2CH_2C\equiv C$), 1.92 br.s (1H, OH), 2.15–2.48 m (4H, $2CH_2C\equiv C$), 3.49 t (2H, $HO\mathit{CH}_2CH_2CH_2C\equiv C$)
IIIf	0.87 t (3H, Me), 1.10–1.70 m [32H, $(CH_2)_2$ and $(CH_2)_{14}$], 2.12–2.37 m (4H, $2CH_2C\equiv C$), 3.67 t (2H, CH_2OH)
VIIa	1.00 t (3H, Me), 1.62 q (2H, $Me\mathit{CH}_2$), 2.42 t (2H, $CH_2C\equiv C$), 7.55–8.10 m (4H, *p*-C_6H_4), 8.90 (1H, COOH)
VIIb	0.90 t (3H, Me), 1.30–1.70 m [4H, $(\mathit{CH}_2)_2Me$], 2.45 t (2H, $CH_2C\equiv C$), 7.55–8.16 m (4H, *p*-C_6H_4), 8.80 s (1H, COOH)
VIIc	0.90 t (3H, Me), 1.20–1.65 m [4H, $(\mathit{CH}_2)_2Me$], 2.40 t (2H, $CH_2C\equiv C$), 7.30–8.30 m (4H, *m*-C_6H_4), 9.15 s (1H, COOH)
VIId	0.91 t (3H, Me), 1.15–1.75 m [8H, $(\mathit{CH}_2)_4Me$], 2.40 t (2H, $CH_2C\equiv C$), 7.30–8.30 m (4H, *m*-C_6H_4), 9.50 s (1H, COOH)
VIIe	0.90 t (3H, Me), 1.10–1.75 m [12H, $(\mathit{CH}_2)_6Me$], 2.40 t (2H, $CH_2C\equiv C$), 7.20–8.25 m (4H, *m*-C_6H_4), 8.85 s (1H, COOH)
VIIf	0.89 t (3H, Me), 1.20–1.70 m [28H, $(\mathit{CH}_2)_{14}Me$], 2.37 t (2H, $CH_2C\equiv C$), 7.32–8.30 m (4H, *m*-C_6H_4), 9.25 s (1H, COOH)
VIIIa	0.88 t (3H, Me), 1.10–1.70 m [16H, $(CH_2)_8$], 2.28 t (2H, $CH_2C\equiv C$), 4.97 s (2H, CH_2O), 7.32–8.12 m (5H, Ph)
VIIIc	0.87 t (3H, Me), 1.00–1.80 m [28H, $(CH_2)_{14}$], 2.22 t [2H, $C\equiv C\mathit{CH}_2(CH_2)_{14}$], 4.93 s (2H, CH_2O), 7.40–8.08 m (5H, Ph)

Table 3. UV spectra of compounds **IIIa–IIIf, VIIa–VIIf, VIIIa**, and **Vc**

Comp. no.	λ_{max}, nm (ε)
IIIa	202 (500), 212 (500), 221 (500), 232 (600), 245 (600), 260 (400)
IIIb	202 (400), 211 (500), 224 (400), 241 (400), 256 (250)
IIIc	204 (300), 214 (300), 224 (300), 242 (400), 256 (250)
IIId	205 (200), 215 (250), 223 (300), 241 (300), 255 (200)
IIIe	205 (200), 214 (300), 222 (300), 242 (300), 254 (250)
IIIf	205 (250), 215 (300), 223 (350), 241 (300), 255 (200)
VIIa	205 (10000), 217 (14000), 234 (15000), 272 (14000), 287 (17000), 306 (17000), 323 (10000), 338 (10000)
VIIb	204 (10000), 217 (13000), 236 (15000), 270 (14000), 289 (17000), 308 (17000), 324 (10000), 337 (9000)
VIIc	215 (24000), 221 (24000), 260 (6000), 275 (9000), 291 (8000)
VIId	215 (24000), 221 (24000), 260 (6000), 274 (9000), 291 (8000)
VIIe	212 (25000), 220 (26000), 237 (13000), 259 (13000), 270 (10000), 285 (8000)
VIIf	212 (23000), 220 (25000), 236 (3000), 255 (7000), 270 (11000), 290 (9000)
VIIIa	203 (12000), 232 (15000), 259 (1500), 268 (1500), 282 (1500)
VIIIc	203 (13000), 225 (16000), 230 (16000), 238 (15000), 245 (10000), 260 (1500), 272 (1500), 282 (1500)

sence of an aromatic nucleus is confirmed by the observation of absorption bands at 1610 ± 5, 1560 ± 10, 1500 ± 10; (CH_{Ar}) – 850 ± 5, 820 ± 5, 765 ± 5, 680 ± 5, and 660 ± 5 cm^{-1} [8]. The IR spectra of benzoates **VIIIa, VIIIc** show bands at 2265 ± 5 $(C\equiv C)_2$, 1730 ± 5 (C=O), 1600 ± 5 (Ar skeletal vibrations), and 710 ± 5 cm^{-1} ($CH_{Ar}O$).

EXPERIMENTAL

The IR spectra were recorded on a Specord IR-75 instrument in KBr pellets or in thin film (**VIIIa**). The ^1H NMR spectra were obtained on a Tesla BS-567A spectrometer in $CDCl_3$, internal reference TMS. The UV spectra were measured on a Specord UV-Vis spectrophotometer in 1×10^{-3} M solutions in hexane (**IIIa**–**IIIf, VIIIa, VIIIc**) or in 1×10^{-4} M solutions in methanol (**VIIa**–**VIIf**). The molecular weights were determined cryoscopically in benzene (**IIIa**–**IIIf, VIIIa, VIIIc**) or by alkalimetric titration with 0.1 N NaOH in the presence of phenolphthaleine as indicator (**VIIa**–**VIIf**).

1-Alkynes **Ia**–**If** were obtained according to [9, 10], sodium *p*-ethynylbenzoate (**VIa**), according to [11], and *m*-ethynylbenzoic acid (**VIb**), according to [12].

Diacetylenic alcohols IIIa–**IIIf** were obtained by the following general procedure. 1-Alkyne **Ie, If** (5 mmol) and 15 mmol of 1-alkyn-ω-ol **IIa**–**IId** were added to a solution of 2 mmol of CuCl and 2 mmol of tetramethylenediamine in 50 ml of acetone. Oxygen, 5 mmol, was barboted through the resulting mixture over the course of 5 h, after which the mixture was poured into 150 ml of 10% H_2SO_4. Compounds **IIIa, IIIc**–**IIIe** that precipitated as crystals were washed with water and dried in a vacuum in the dark. Compounds **IIIb, IIIf** were extracted with ether, the extract was dried with $MgSO_4$, the solvent was removed, and the residue was dried in a vacuum. Diacetylenic alcohols **IIIa**–**IIIf** were recrystallized from hexane.

***p*- and *m*-Alkadiyne benzoic acid derivatives VIIa**–**VIIIf.** A solution of 10 mmol of 1-bromoalkyne **Va**–**Vd, Vf** in 25 ml of dioxane was added dropwise over the course of 5–6 h at 30–35°C under argon to a vigorously stirred mixture of 6 mmol of sodium *p*-ethynylbenzoate (**VIa**) or sodium *m*-ethynylbenzoate (**VIb**), 50 ml of methanol, 5 ml of monoethanolamine, 3 ml of water, 1 g of hydroxylamine hydrochloride, and 0.05 g of CuCl. The reaction mixture was stirred at the same temperature for 3–4 h and then treated with hexane (3 × 30 ml). The water–methanol–dioxane layer was treated with 150 ml of 10% H_2SO_4. Products **VIIa**–**VIIf** were filtered off, washed with water, and dried in a vacuum. Final purification was performed by recrystallization from chloroform (**VIIa, VIIb**) or hexane (**VIIc**–**VIIf**).

1-Benzoyloxyalka-2,4-diynes VIIIa, VIIIc. To a solution of 2.5 mmol of diacetylenic alcohol **IIIa, IIIc** in diethyl ether, 3 mmol of benzoyl chloride was added at 0–5°C and then, with vigorous stirring, a solution of 4 mmol of pyridine. The reaction mixture was stirred at 20–30°C for 3–4 h and left to stand for 18 h. A precipitate formed and was filtered off. The filtrate was diluted with hexane, washed with water, 5% $NaHCO_3$, and water, and dried over $CaCl_2$. The solvent was removed. The residue was subjected to a vacuum and purified on a column of Al_2O_3 (Brockmann activity grade II), eluent hexane. Compound **VIIIc** was recrystallized from hexane.

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