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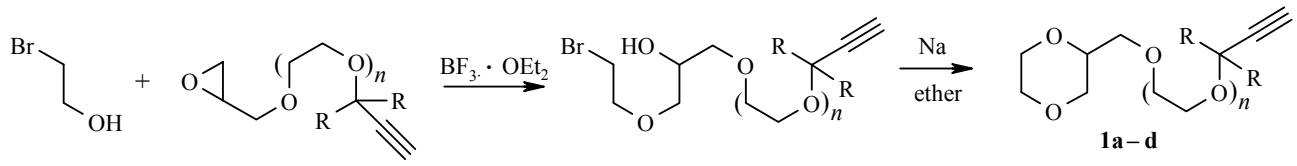
SYNTHESIS AND SOME CHEMICAL CONVERSIONS OF ACETYLENIC DERIVATIVES OF 1,4-DIOXANE

M. G. Veliev[1]*, M. I. Shatirova[1] and O. V. Askerov[1]

The possibility has been shown of synthesizing acetylenic derivatives of 1,4-dioxane in high yield by the interaction of glycidyl ethers of acetylenic alcohols with ethylene bromohydrin in the presence of boron trifluoride etherate. Dehydrobromination of the corresponding bromohydrin was then carried out in the presence of metallic sodium in absolute diethyl ether. Acetylenic derivatives of 1,4-dioxane enter into hydrosilylation, aminomethylation, and diene condensation reactions with the formation of new derivatives of 1,4-dioxane.

Keywords: acetylenic alcohols, diacetylenic derivatives, 1,4-dioxanes, ethylene bromohydrin, aminomethylation, diene condensation, hydrosilylation.

It is known that oxygen-containing heterocyclic compounds with multiple bonds are reactive and may be applied widely in organic synthesis for obtaining polyfunctional compounds with practically useful properties, particularly biologically active compounds [1-5]. The preparation of unsaturated derivatives of 1,4-dioxane from glycidyl ethers of unsaturated alcohols has been insufficiently studied [5-9]. While continuing investigations started previously [10], we have synthesized a series of acetylenic derivatives of 1,4-dioxane from glycidyl ethers of primary and tertiary acetylenic alcohols and have studied some of their chemical conversions.



1a – d

1 a, c R = H, **b, d** R = Me; **a, b** *n* = 0, **c, d** *n* = 1

* To whom correspondence should be addressed, e-mail: ipoma@science.az, mveliyev@mail.ru.

[1]Institute of Polymeric Materials, National Academy of Sciences of Azerbaijan, Sumgait Az5004, Azerbaijan.

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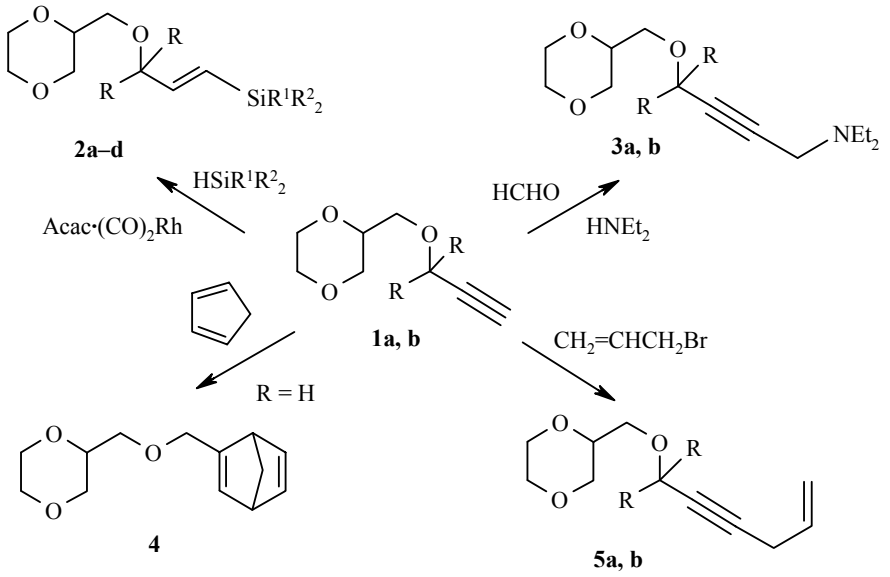
It was established that on interacting glycidyl ethers of acetylenic alcohols with ethylene bromohydrin in the presence of boron trifluoride etherate at 0-5°C bromohydrins are formed which subsequently, in the presence of metallic sodium in a medium of ethyl ether (at 25-30°C), are dehydrobrominated and as a result of intramolecular cyclization form the corresponding acetylenic 1,4-dioxane series **1a-d** in high yield (75-85%).

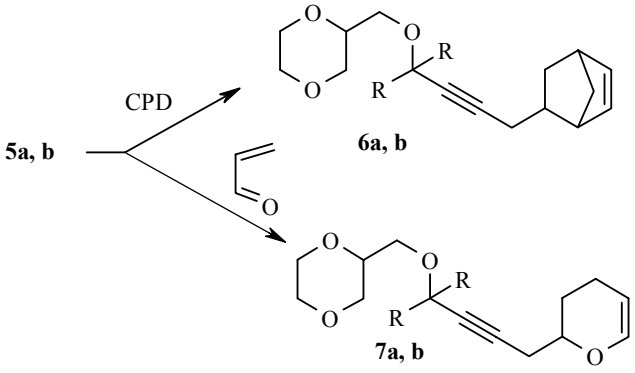
The synthesized 1,4-dioxanes of the acetylene series **1a-d** are extremely reactive compounds and enter into various reactions at the acetylenic bond, in particular, into hydrosilylation, diene condensation, and nucleophilic substitution with the formation of new derivatives of 1,4-dioxane.

It was shown that methyldiethyl- and triethoxysilanes in the presence of rhodium acetylacetonate-dicarbonyl undergo a hydrosilylation reaction (55-60°C) with acetylene derivatives of 1,4-dioxane **1a,b** at the triple bond according to Farmer's rule with the formation (80-85%) of *trans* isomers **2a-d**.



2 a R = H, R^1 = Me, R^2 = Et, **b** R = H, R^1 = R^2 = OEt, **c** R = R^1 = Me, R^2 = Et, **d** R = Me, R^1 = R^2 = OEt; **3, 5 a** R = H, **b** R = Me

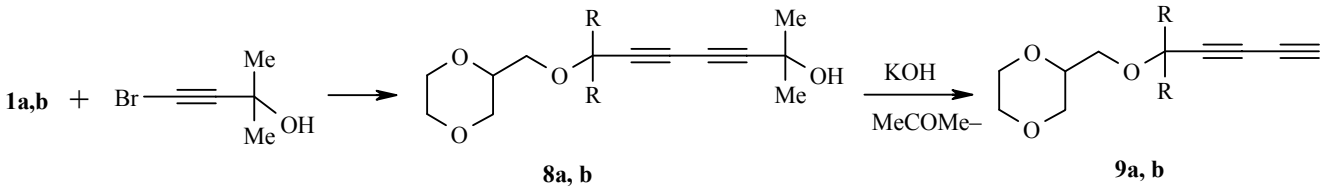
The aminomethylation reaction of acetylenic derivatives of 1,4-dioxane **1a,b** takes place under the action of formaldehyde and diethylamine with the formation of the corresponding amino derivatives **3a,b**. 2-(2-Oxapent-4-ynyl)-1,4-dioxane (**1a**) undergoes a diene condensation with cyclopentadiene (CPD) at 180-185°C with the formation of 1,4-dioxanes of the norbornadiene series **4**. Acetylenic derivatives of 1,4-dioxane **1a,b** undergo a substitution reaction with allyl bromide in the presence of CuI, triethylamine, and K_2CO_3 in DMF, in which 1,4-dioxanes of the allylacetylenic series **5a,b** are formed in 85 and 88% yield respectively.



6, 7 a R = H, **b** R = Me

It was established that the synthesized allylacetylene derivatives of 1,4-dioxane **5a,b** undergo a diene condensation with cyclopentadiene at 180-185°C and also a heterodiene condensation with acrolein at 175-180°C with the formation of derivatives of norbornene **6a,b** and dihydropyran **7a,b** in 50-65% yield.

Acetylenic derivatives of 1,4-dioxane **1a,b** under the conditions of the Khodkevich-Kadio reaction [11] (in the presence of copper monochloride, butylamine, hydroxylamine) react with 1-bromo-3-methylbut-1-yn-3-ol with the formation of the corresponding tertiary diacetylenic alcohols **8a,b**, which then under the action of powdered potassium hydroxide are subject to a reverse Favorskii reaction with the formation of conjugated diacetylenic derivatives of 1,4-dioxane **9a,b**.



8, 9 a R = H, **b** R = Me

The structure of the synthesized compounds **1-9** was confirmed by data of IR and ^{1}H NMR spectra [12-14]. Physicochemical and spectral data are given in Tables 1 and 2.

The acetylene derivatives of 1,4-dioxane synthesized in this work have considerable promise for use in directed syntheses of organic, including natural, substances and their analogs, valuable in practice.

EXPERIMENTAL

The IR spectra of the synthesized compounds were taken on a UR 20 spectrophotometer over the range 400-4000 cm^{-1} in thin films, the ^{1}H NMR spectra on a Tesla BS 487 B spectrometer (80 MHz) in CCl_4, internal standard was HMDS, δ 0.05 ppm. The homogeneity and purity of the obtained compounds was checked by TLC on Silufol UV 254 plates, eluent was benzene – diethyl ether, 5:1.

2-(2-Oxapent-4-ynyl)-1,4-dioxane (1a). Metallic sodium (1.5 g) was added in portions to a mixture consisting of dry ether (50 ml) and 10-bromo-4,8-dioxadec-1-yn-6-ol (9.6 g, 5 mmol), obtained by the interaction of 1-glycidyloxy-2-propyne with ethylene bromohydrin, and the mixture was stirred for 20 h at 25-30°C. After filtering the mixture and distilling the solvent compound **1a** was obtained.

Compounds 1b-d were synthesized analogously.

2-(5-Diethylmethylsilyl-2-oxapent-4-enyl)-1,4-dioxane (2a). A mixture of diethylmethylsilane (3.3 g, 3.2 mmol) and 2-(2-oxapent-4-ynyl)-1,4-dioxane (**1a**) (5 g, 3.2 mmol) was stirred at 55-60°C in the presence of rhodium acetylacetonate-dicarbonyl (0.01 g) for 6 h and then subjected to vacuum distillation.

Compounds 2b-d were synthesized analogously.

2-(6-Diethylamino-2-oxahex-4-ynyl)-1,4-dioxane (3a). A mixture of diethylamine (3.7 g, 5 mmol), paraformaldehyde (1.5 g), and compound **1a** (7.8 g, 5 mmol) in dioxane (25 ml) was heated for 5 h. Water (20 ml) was added, the organic layer separated, and the water layer was extracted with ether. The combined organic solution was shaken with 5 N HCl (20 ml), the ether layer was separated, and the acid solution neutralized with cooling with conc. NH_4OH (7 ml), and extracted with ether. The ether extracts were dried with potassium carbonate. After distilling off the ether, compound **3a** was obtained by distillation in vacuum.

Compound 3b was synthesized analogously from 2-(3,3-dimethyl-2-oxapent-4-ynyl)-1,4-dioxane (**1b**).

2-[3-(Bicyclo[2.2.1]hepta-2,5-dienyl)-2-oxapropyl]-1,4-dioxane (4). A mixture of CPD (3.3 g, 5 mmol) and compound **1a** (7.8 g, 5 mmol) was heated for 8-10 h in the presence of hydroquinone (0.05 g) in a sealed ampoule at 170-180°C. At the end of the reaction the mixture was subjected to vacuum distillation. Unreacted starting materials were distilled off in this way, the residue was subjected to a second distillation, and compound **4** was isolated.

2-(2-Oxaoct-7-en-4-ynyl)-1,4-dioxane (5a). DMF (100 ml), K_2CO_3 (1.5 g), CuI (9.5 g, 5 mmol), and Et_3N (0.5 ml) were placed in a three-necked flask and stirred with heating at 50°C in a current of nitrogen. After 15-20 min compound **1a** (3.7 g, 5 mmol) was added to the mixture. After stirring for 2 h allyl bromide (12.1 g, 10 mmol) was added dropwise, and stirring was continued for a further 8 h at 50-55°C. Then the cooled mixture was washed with water and extracted with ether. The ether layer was dried over $MgSO_4$. After evaporating the solvent in vacuum the desired product **5a** was isolated by distillation.

TABLE 1. Characteristics of the Synthesized 1,4-Dioxanes **1-9**

Compound	Empirical formula	Found, % / Calculated, %			bp, °C (mm Hg)	n_D^{20}	d_4^{20}	Yield, %
		C	H	Si				
1a	$C_8H_{12}O_3$	61.45 / 61.52	7.86 / 7.75	—	111-112 (2)	1.4625	1.0761	77.6
1b	$C_{10}H_{16}O_3$	65.30 / 65.19	8.61 / 876	—	108-109 (2)	1.4645	1.0310	74.9
1c	$C_{10}H_{16}O_4$	59.81 / 59.98	8.13 / 8.06	—	121-122 (2)	1.4877	1.1388	85.2
1d	$C_{12}H_{20}O_4$	63.29 / 63.13	8.94 / 8.83	—	117-118 (2)	1.4885	1.0896	80.7
2a	$C_{13}H_{26}O_3Si$	60.28 / 60.42	10.26 / 10.14	10.60 / 10.87	132-133 (1.5)	1.4790	0.9931	82.6
2b	$C_{14}H_{28}O_6Si$	52.60 / 52.47	8.68 / 8.81	8.84 / 8.76	138-139 (1.5)	1.4498	1.0628	84.8
2c	$C_{15}H_{30}O_3Si$	62.70 / 62.89	10.37 / 10.56	9.95 / 9.80	130-131 (1.5)	1.4810	0.9806	80.4
2d	$C_{16}H_{32}O_6Si$	55.30 / 55.14	9.40 / 9.26	7.89 / 8.06	135-136 (1.5)	1.4518	1.0432	83.3
3a*	$C_{13}H_{23}NO_3$	64.58 / 64.70	9.76 / 9.61	—	127-128 (1)	1.4955	1.0494	75.2
3b*²	$C_{15}H_{27}NO_3$	66.71 / 66.88	10.05 / 10.10	—	124-125 (1)	1.4980	1.0351	73.8
4	$C_{13}H_{18}O_3$	70.39 / 70.24	8.04 / 8.16	—	154-155 (1)	1.5070	1.0872	60.3
5a	$C_{11}H_{16}O_3$	67.48 / 67.32	8.36 / 8.22	—	135-136 (1)	1.4985	1.0706	85.1
5b	$C_{13}H_{20}O_3$	69.52 / 69.61	8.83 / 8.99	—	131-132 (1)	1.5025	1.0550	88.2
6a	$C_{16}H_{22}O_3$	73.38 / 73.25	8.32 / 8.45	—	148-149 (1)	1.5395	1.1360	64.3
6b	$C_{18}H_{26}O_3$	74.58 / 74.44	8.88 / 9.03	—	145-146 (1)	1.5449	1.1234	66.7
7a	$C_{14}H_{20}O_4$	66.50 / 66.64	8.22 / 7.99	—	140-141 (1)	1.5101	1.1028	50.6
7b	$C_{16}H_{24}O_4$	68.21 / 68.54	8.83 / 8.63	—	137-138 (1)	1.5135	1.0860	55.4
8a	$C_{13}H_{18}O_4$	65.66 / 65.53	7.54 / 7.61	—	143-144 (1)	1.5066	1.1007	70.5
8b	$C_{15}H_{22}O_4$	67.78 / 67.64	8.46 / 8.33	—	140-141 (1)	1.5106	1.0836	73.8
9a	$C_{10}H_{12}O_3$	66.53 / 66.65	6.88 / 6.71	—	131.5-132.5 (1)	1.5150	1.1104	88.9
9b	$C_{12}H_{16}O_3$	69.16 / 69.21	7.68 / 7.75	—	129-130 (1)	1.5195	1.0948	90.1

* Found, %: N 5.72. Calculated, %: N 5.81.

*² Found, %: N 5.35. Calculated, %: N 5.20.

TABLE 2. Spectra of Compounds **1-9**

Compound	IR spectrum, ν, cm^{-1}	^1H NMR spectrum, δ, ppm (*J*, Hz)
1	2	3
1a	850, 1080, 1126, 1190, 1260, 2110, 3300	3.45-3.75 (6H, m, OCH_2CH_2O ring and CH_2O); 2.46-2.75 (2H, m, CH_2 ring); 2.80-3.10 (1H, m, CH ring); 4.10 (2H, s, OCH_2); 2.28 (1H, t, *J* = 2.45, ≡CH)
1b	860, 1075, 1126, 1185, 1250, 2120, 3285	3.47-3.73 (6H, m, OCH_2CH_2O ring and CH_2O); 2.48-2.76 (2H, m, CH_2 ring); 2.85-3.10 (1H, m, CH ring); 1.40 (6H, s, $C(CH_3)_2$); 2.30 (1H, t, *J* = 2.52, ≡CH)
1c	865, 1075, 1126, 1190, 1255, 1300, 2115, 3305	3.55-3.84 (10H, m, OCH_2CH_2O ring, CH_2O and OCH_2CH_2O); 2.45-2.70 (2H, m, CH_2 ring); 2.80-3.05 (1H, m, CH ring); 4.12 (2H, s, OCH_2); 2.25 (1H, t, *J* = 2.50, ≡CH)
1d	855, 1070, 1126, 1195, 1270, 1310, 2130, 3295	3.56-3.85 (10H, m, OCH_2CH_2O ring, CH_2O and OCH_2CH_2O); 2.40-2.68 (2H, m, CH_2 ring); 2.82-3.15 (1H, m, CH ring); 1.38 (6H, s, $C(CH_3)_2$); 2.32 (1H, t, *J* = 2.47, ≡CH)
2a	862, 965, 1076, 1126, 1186, 1265, 1280, 1615	3.43-3.70 (6H, m, OCH_2CH_2O ring and CH_2O); 2.46-2.72 (2H, m, CH_2 ring); 2.86-3.00 (1H, m, CH ring); 4.10 (2H, s, OCH_2); 6.05 (1H, dt, *J* = 19.0, *J* = 5.5, C<u>H</u>=CHSi); 5.70 (1H, dd, *J* = 19.0, *J* = 5.5, CH=C<u>H</u>Si); 0.25-1.00 (13H, m, $(C_2H_5)_2CH_3$)Si)
2b	855, 966, 1074, 1126, 1192, 1258, 1282, 1620	3.50-3.80 (6H, m, OCH_2CH_2O ring and CH_2O); 2.38-2.65 (2H, m, CH_2 ring); 2.80-3.06 (1H, m, CH ring); 4.06 (2H, s, OCH_2); 5.10 (1H, dd, *J* = 18.5, *J* = 5.5, C<u>H</u>=CHSi); 5.42 (1H, dd, *J* = 18.5, *J* = 5.5, CH=C<u>H</u>Si); 3.45 (6H, q, *J* = 6.9, $OC\underline{H}_2CH_3$); 1.05 (9H, t, *J* = 6.9, $OCH_2C\underline{H}_3$)
2c	860, 965, 1075, 1125, 1190, 1245, 1280, 1625	3.48-3.76 (6H, m, OCH_2CH_2O ring and CH_2O); 2.45-2.70 (2H, m, CH_2 ring); 2.83-3.03 (1H, m, CH ring); 1.48 (6H, s, $C(CH_3)_2$); 5.95 (1H, d, *J* = 19.0, C<u>H</u>=CHSi); 5.64 (1H, d, *J* = 19.0, CH= C<u>H</u>Si); 0.37-1.06 (13H, m, $(C_2H_5)_2CH_3$)Si)
2d	755, 855, 960, 1080, 1126, 1195, 1256, 1285, 1605	3.53-3.87 (6H, m, OCH_2CH_2O ring and CH_2O); 2.40-2.72 (2H, m, CH_2 ring); 2.83-3.12 (1H, m, CH ring); 1.45 (6H, s, $C(CH_3)_2$); 5.16 (1H, d, *J* = 18.4, C<u>H</u>=CHSi); 5.56 (1H, d, *J* = 18.4, CH=C<u>H</u>Si); 3.38 (6H, q, *J* = 6.8, $OC\underline{H}_2CH_3$); 1.10 (9H, t, *J* =6.8, $OCH_2C\underline{H}_3$)
3a	856, 1074, 1125, 1192, 1254, 2230, 2785	3.60-3.90 (6H, m, OCH_2CH_2O ring and CH_2O); 2.42-2.70 (2H, m, CH_2 ring); 2.86-3.12 (1H, m, CH ring); 4.12 (2H, s, OCH_2); 3.23 (2H, m, ≡CCH_2); 2.30 (4H, q, *J* = 6.8, $NC\underline{H}_2CH_3$); 0.92 (6H, t, *J* = 6.8, $NCH_2C\underline{H}_3$)
3b	864, 1080, 1126, 1187, 1260, 2235, 2786	3.57-3.88 (6H, m, OCH_2CH_2O ring and CH_2O); 2.40-2.72 (2H, m, CH_2 ring); 2.84-3.08 (1H, m, CH ring); 1.43 (6H, s, $C(CH_3)_2$); 3.26 (2H, m, ≡CCH_2); 2.23 (4H, q, *J* = 7.3, $NC\underline{H}_2CH_3$); 0.88 (6H, t, *J* = 7.3, $NCH_2C\underline{H}_3$)
4	860, 1073, 1124, 1192, 1253, 1615	3.63-3.95 (8H, m, OCH_2CH_2O ring, CH_2O, CH, and CH bridgehead); 2.40-2.70 (2H, m, CH_2 ring); 2.86-3.13 (1H, m, CH ring); 4.15 (2H, s, OCH_2); 6.50-6.95 (2H, m, CH=CH); 6.35 (1H, m, CH=C); 2.05 (2H, m, CH_2 in bridge)
5a	850, 1020, 1075, 1110, 1280, 1655, 2240	3.55-3.80 (6H, m, OCH_2CH_2O ring and CH_2O); 2.43-2.72 (2H, m, CH_2 ring); 2.80-3.15 (3H, m, CH ring, CH_2); 4.10 (2H, s, OCH_2); 4.90-5.40 (2H, m, CH_2=C); 5.46-5.98 (1H, m, CH=C)
5b	840, 1005, 1050, 1125, 1260, 1660, 2235	3.48-3.73 (6H, m, OCH_2CH_2O ring and CH_2O); 2.40-2.70 (2H, m, CH_2 ring); 2.86-3.11 (3H, m, CH ring and CH_2); 1.37 (6H, s, $C(CH_3)_2$); 4.86-5.35 (2H, m, CH_2=C); 5.48-6.05 (1H, m, CH=C)
6a	845, 1015, 1074, 1120, 1275, 1645, 2245	3.50-3.78 (6H, m, OCH_2CH_2O ring and CH_2O); 2.40-2.85 (4H, m, 1,4-CH bridgehead and CH_2 ring); 2.96-3.15 (1H, m, CH ring); 4.05 (2H, m, OCH_2); 2.05 (2H, m, C≡CCH_2); 2.15 (1H, m, H-5 ring); 0.53 (1H, m, H-6); 1.68-1.95 (1H, m, H-6'); 1.10-1.50 (2H, m, CH_2 bridge); 5.90-6.15 (2H, m, CH=CH)

TABLE 2 (continued)

1	2	3
6b	865, 990, 1070, 1130, 1265, 1650, 2230	3.56-3.85 (6H, m, OCH_2CH_2O ring and CH_2O); 2.36-2.80 (2H, m, 1,4-CH brigdehead and CH_2 ring); 2.95-3.10 (1H, m, CH ring); 1.50 (6H, s, $(CH_3)_2$); 2.00 (2H, m, $C{\equiv}CCH_2$); 2.12 (1H, m, H-5 ring); 0.53 (1H, m, H-6); 1.70-1.90 (1H, m, H-6'); 1.05-1.40 (2H, m, CH_2 bridge); 5.86-6.10 (2H, m, CH=CH)
7a	882, 1020, 1075, 1095, 1160, 1245, 1300, 1615, 2245	3.56-3.85 (6H, m, OCH_2CH_2O ring and CH_2O); 2.43-2.67 (2H, m, CH_2 ring); 2.85-3.10 (4H, m, CH and CH ring, CH_2); 4.06 (2H, s, OCH_2); 2.20 (2H, m, $CH_2C{\equiv}$); 3.20-3.45 (4H, m, CH_2CH_2 ring); 5.90-6.10 (2H, m, CH=CH ring)
7b	860, 1010, 1070, 1096, 1126, 1240, 1300, 1625, 2240	3.52-3.80 (6H, m, OCH_2CH_2O ring and CH_2O); 2.40-2.72 (2H, m, CH_2 ring); 2.80-3.03 (4H, m, CH and CH ring, CH_2); 1.46 (6H, s, $C(CH_3)_2$); 2.18 (2H, m, $CH_2C{\equiv}$); 3.17-3.42 (4H, m, CH_2CH_2 ring); 5.86-6.04 (2H, m, CH=CH ring)
8a	870, 1015, 1076, 1130, 1246, 1290, 2235, 3400	3.43-3.70 (6H, m, OCH_2CH_2O ring and CH_2O); 2.37-2.69 (2H, m, CH_2 ring); 2.81-3.08 (3H, m, CH ring); 4.13 (2H, s, OCH_2); 1.49 (6H, s, $C(CH_3)_2$); 3.86 (1H, s, OH)
8b	865, 1025, 1060, 1120, 1250, 1300, 2246, 3450	3.50-3.79 (6H, m, OCH_2CH_2O ring and CH_2O); 2.41-2.70 (2H, m, CH_2 ring); 2.80-3.00 (1H, m, CH ring); 0.92 (6H, s, $C(CH_3)_2$); 1.42 (6H, s, $C(CH_3)_2$); 4.02 (1H, s, OH)
9a	845, 1020, 1075, 1125, 1230, 1305, 2120, 2238, 3300	3.56-3.87 (6H, m, OCH_2CH_2O ring and CH_2O); 2.38-2.72 (2H, m, CH_2 ring); 2.86-3.04 (1H, m, CH ring); 4.08 (2H, s, OCH_2); 1.87 (1H, t, J = 2.55, C≡CH)
9b	860, 1005, 1075, 1126, 1245, 1300, 2130, 2250, 3295	3.50-3.82 (6H, m, OCH_2CH_2O ring and CH_2O); 2.35-2.63 (2H, m, CH_2 ring); 2.78-2.96 (1H, m, CH ring); 1.42 (6H, s, $C(CH_3)_2$); 1.96 (1H, t, J = 2.50, C≡CH)

2-(3,3-Dimethyl-2-oxaoct-7-en-4-ynyl)-1,4-dioxane (5b) was obtained analogously from compound **1b** and allyl bromide.

2-[6-(Bicyclo[2.2.1]hept-2-enyl)-2-oxahex-4-ynyl]-1,4-dioxane (6a) was synthesized analogously by the method for obtaining compound **4** from cyclopentadiene (5 mmol) and 1,4-dioxane **5a** (5 mmol).

Compound 6b was synthesized analogously from 1,4-dioxane **5b** and cyclopentadiene.

2-[6-(2,3-Dihydro-4H-pyranyl)-2-oxahex-4-ynyl]-1,4-dioxane (7a). A mixture of compound **5a** (9.8 g, 5 mmol), acrolein (2.48 g, 5 mmol), and toluene (10 ml) was heated in the presence of hydroquinone (0.05 g) in a sealed ampoule at 175-180 °C for 8 h. Substance **7a** was obtained after two distillations.

Compound 7b was synthesized analogously from 1,4-dioxane **5b**.

2-(8-Hydroxy-8-methyl-2-oxanona-4,6-diynyl)-1,4-dioxane (8a). A solution of 1,4-dioxane **1a** (3.7 g, 5 mmol) in methanol (10 ml) was added with stirring to 40% aqueous ethylamine solution (12.5 ml) containing copper chloride (0.5 g) and hydroxylamine hydrochloride (0.35 g). A solution of 1-bromo-3-methylbut-1-yn-3-ol (8.2 g, 5 mmol) in MeOH (12.5 ml) was then added dropwise at such a rate that the temperature of the reaction mass did not exceed 35°C. The mixture was stirred for 1 h at 30°C, then for 2-3 h at 20°C, treated with 10% HCl, and extracted with ether. The extract was washed with dilute (1:3) HCl, and with water, and dried over $MgSO_4$. After removing the ether, compound **8a** was isolated by vacuum distillation.

Compound 8b was synthesized analogously from 1,4-dioxane **1b**.

2-(2-Oxahepta-4,6-diynyl)-1,4-dioxane (9a). 1,4-Dioxane **8a** (12 g, 5 mmol) was heated (110-115°C) in the presence of powdered potassium hydroxide (0.02 g) in a stream of nitrogen. The heating was carried out so that the products of decomposition distilled slowly into the coiled receiver. An equimolar mixture of acetone and 1,4-dioxane **9a** was obtained.

Compound 9b was synthesized analogously from 1,4-dioxane **8b**.

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