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Dedicated to Full Member of the Russian Academy of Sciences B.A. Trofimov on the 65th Anniversary of His Birth

Vinyl Ethers Containing an Epoxy Group: XXI.* Synthesis and Acid-Catalyzed Cyclization of 1-[ω-(Vinyloxy)alkoxy]-3-(2-propynyloxy)-2-propanols—A Simple Route to 2-Propynyloxymethyl-Substituted Cyclic Polyethers

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Abstract—Base-catalyzed reaction of 2-[ω-(vinyloxy)alkoxy]methyloxiranes with 2-propynyl alcohol (~3 wt % of t-BuOK, 60–85°C, 3–12 h) afforded first reperesentatives of the 1-[ω-(vinyloxy)alkoxy]-3-(2-propynyloxy)-2-propanol series in up to 99% yield. Treatment of 1-[2-(vinyloxy)ethoxy]- and 1-[2-(vinyloxy)-ethoxyethoxy]-3-(2-propynyloxy)-2-propanols with trifluoroacetic acid (~0.5 wt. %) in dry diethyl ether resulted in cyclization with formation of up to 96% of (2-methyl-1,3,6-trioxocan-4-yl)methyl- and (2-methyl-1,3,6,9-tetraoxacycloundecan-4-yl)methyl 2-propynyl ethers.

Ethers derived from acetylenic alcohols, primarily from 2-propynyl alcohol (mono-, di-, and polyethers), are widely used in organic synthesis and in practice [2], e.g., as monomers for the preparation of thermosetting resins [3], components of curing compositions for manufacture of laminated plastics [4], starting materials and intermediate products in the synthesis of heterocyclic compounds (such as thiophene [5], pyrrole [6–8], carbazole [9], dihydropyridine [6], pyridine [10], dihydrofuran [11], benzopyran [12], and quinoline derivatives [7]), macrocyclic complexing agents, extragents [13], medicines, agricultural chemicals [14], etc.

Purposeful structural modification of 2-propynyl ethers via introduction of various substituents, primarily of those possessing additional reaction centers, e.g., hydroxy and vinyloxy groups, could considerably extend their synthetic potential and give rise to new practically useful properties. One of the simplest and most convenient routes to 2-(alkynyloxy)-1-alkanols, which however have found no wide application, is based on the reaction of epoxy derivatives with acetylenic alcohols in the presence of alkali metal hydroxides [15]. The use of functionalized oxiranes in reactions with alkynols provides almost unlimited access to acetylenic diol monoethers having various substituents and functional groups.

In the framework of our systematic studies in the field of functionally substituted vinyl ethers [16–19], including 2-[ω-(vinyloxy)alkoxy]methyloxiranes and their derivatives and analogs [1, 17–19] and with a view to obtain new polyfunctional 3-(2-propynyloxy)-2-propanol derivatives as promising monomers, synthons, and intermediate products, we examined the reactions of accessible 2-propynyl alcohol with 2-[2-(vinyloxy)ethoxymethyl]oxirane (**Ia**) and 2-{2-[2-(vinyloxy)ethoxy]ethoxymethyl}oxirane (**Ib**). These reactions afforded previously unknown 1-[2-

* For communication XX, see [1].

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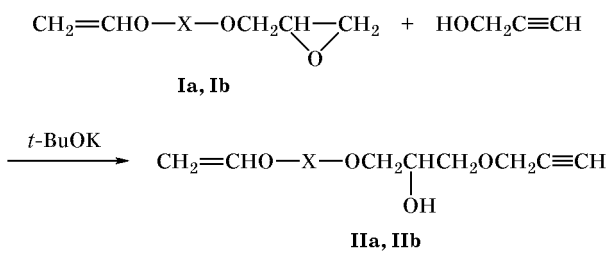
(vinyloxy)ethoxy]-3-(2-propynyloxy)-2-propanol (**IIa**) and 3,6,9,13-tetraoxa-1-hexadecen-15-yn-11-ol (**IIb**) (Scheme 1).

Scheme 1.



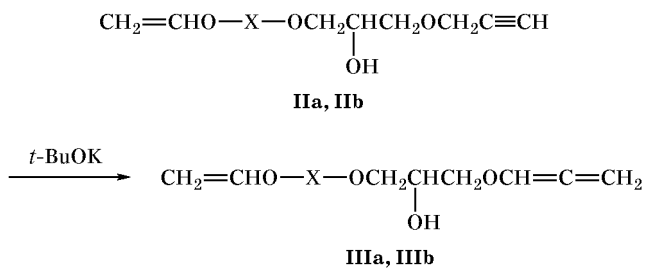
X = $(CH_2)_2$ (**a**), $(CH_2)_2O(CH_2)_2$ (**b**).

In order to achieve the maximal conversion of oxirane **I**, ~1.2–1.7 equiv of 2-propynyl alcohol was taken and potassium *tert*-butoxide was used as base catalyst. The experimental conditions are summarized in Table 1. The reactions were carried out without a solvent until the initial oxirane disappeared completely from the reaction mixture [TLC; Silufol plates, eluent benzene–ether (1 : 1), development with iodine vapor: R_f 0.45 (**Ia**), 0.25 (**IIa**), 0.42 (**Ib**), 0.20 (**IIb**)]. Finally, the end of the process was determined by IR spectroscopy. The reaction was assumed to be complete when the IR spectrum of the evacuated mixture no longer contained absorption bands typical of the oxirane ring (910–915, 1250, and 3000 cm^{-1}) but strong band belonging to hydroxy (3450 cm^{-1}) and 2-propynyloxy groups (3260–3287 cm^{-1}) appeared, the bands corresponding to vibrations of the other molecular fragments (including the vinyloxy group, ν 860, 1200, 1325, 1620–1640, 3050–3070, and 3120 cm^{-1}) being retained.

Heating of the reactants in the presence of ~3 wt % of potassium *tert*-butoxide for 3 to 12 h at 60–85°C (depending on the initial oxirane) smoothly afforded compounds **IIa** and **IIb** in up to 99% yield (Table 1). It should be noted that the yields of known 2-(2-propynyloxy)-1-alkanols which were obtained by addition of 2-propynyl alcohol to the simplest methyl-, phenyl-, and 1,2-dimethyloxiranes (NaOH or KOH, reflux, 1–3 h) as a rule did not exceed 32–37% [15]. In our case, the more efficient reaction of 2-propynyl alcohol with oxiranes **I** may be explained by not only different reaction conditions, e.g., the use of potassium *tert*-butoxide which is a stronger base, but also its activation via complex formation with both initial oxirane **I** and resulting 2-propanol **II**, by analogy with complex formation between alkali metal cations and crown ethers with linear polyether chains [20]. Presumably, the same factor is responsible for the observed difference in the reactivities of oxiranes **Ia** and **Ib** with respect to 2-propynyl alcohol. Obviously, the coordinating ability of diethylene glycol fragments should be greater than that of ethylene glycol fragments, other conditions being equal. Therefore, the ring opening in oxirane **Ib** should occur at a higher rate than in **Ia** due to more efficient solvation of potassium cations. As follows from the data presented in Table 1, in going from oxirane **Ia** to **Ib**, the reaction time shortens from 9–12 to 3 h at comparable temperatures.

The yield and purity of the target products were found to strongly depend on the isolation procedure (Table 1). Vacuum distillation of the reaction mixture without any preliminary treatment (in particular, without removal or binding of *t*-BuOK) ensured the maximal yields of compounds **IIa** and **IIb**, 80–95% (Table 1, run nos. 3, 5–7, 10) and 80% (run no. 11), respectively. However, during distillation the product partially undergoes acetylene–allene isomerization (up to 4–6% for **IIa**) by the action of base catalyst (Scheme 2). The formation of allene structures **III** was confirmed by the IR and NMR data.

Scheme 2.



In the IR spectra of the distillation products we observed an absorption band at about 1950 cm^{-1}, which is typical of an allene fragment. In the ^1H NMR spectrum, weak signals appeared at δ 5.44 (d, CH_2=) and 6.72 ppm (t, CH=).

Distillation of a mixture containing product **IIb** and potassium *tert*-butoxide, apart from acetylene–allene isomerization (~10%; compound **IIIb** was identified by ^1H NMR spectroscopy), was additionally accompanied by intramolecular cyclization of both acetylenic ether **IIb** and its allene isomer **IIIb** with participation of the hydroxy group and triple (or double) bond. These cyclizations are also catalyzed by bases, and they lead to formation of a mixture of five- and six-membered oxygen-containing heterocycles: 2-vinyl-1,3-dioxolane **IV**, 2-methylene-1,4-dioxane **V**, and 6-methyl-2,3-dihydro-1,4-dioxin **VI**

Table 1. Reactions of 2-propynyl alcohol with 2-[2-(vinyloxy)ethoxymethyl]oxirane (**Ia**) and 2-{2-[2-(vinyloxy)ethoxy]-ethoxymethyl}oxirane (**Ib**) (molar ratio **I**:2-propynyl alcohol 1:1–1.67; *t*-BuOK, ~3 wt %)

Run no.	R	Amounts of the reactants, mol		Temperature, °C	Reaction time, h	Product	Yield, %	
		oxiran **I**	$CH\equiv CCH_2OH$				crude	distilled
1[a]	$(CH_2)_2$	0.06	0.10	60–65	9	**IIa**	70	40
2[a]	$(CH_2)_2$	0.03	0.05	60–65	9	**IIa**	72.6	31.4
3[b]	$(CH_2)_2$	0.03	0.05	60–65	9	**IIa**	68.9[a, c]	45.5
						IIa	–	82.1[d, e]
4[a]	$(CH_2)_2$	0.03	0.03	60–65	9	**IIa**	–	76[f]
5[d]	$(CH_2)_2$	0.12	0.20	60–65	18	**IIa**	–	81.3[e]
6[d]	$(CH_2)_2$	0.24	0.40	70–75	12	**IIa**	–	80[e]
7[d]	$(CH_2)_2$	0.24	0.40	70–75	12	**IIa**	–	85[e]
8[a]	$(CH_2)_2$	0.24	0.40	70–75	12	**IIa**	70	47.8
9[a]	$(CH_2)_2$	0.03	0.05	80–85	5	**IIa**	99.2[g]	70.2
10[d]	$(CH_2)_2$	0.03	0.05	80–85	5	**IIa**	–	95.4[e]
11[d]	$(CH_2)_2O(CH_2)_2$	0.03	0.05	60–65	7	**IIb**	–	80[h]
12[a]	$(CH_2)_2O(CH_2)_2$	0.026	0.03	65–70	3	**IIb**	74	47
13[a]	$(CH_2)_2O(CH_2)_2$	0.06	0.10	65–70	3	**IIb**[i]	–	–
14[a]	$(CH_2)_2O(CH_2)_2$	0.026	0.03	65–70	3	**IIb**	–	70
15[a]	$(CH_2)_2O(CH_2)_2$	0.02	0.03	65–70	3	**IIb**	86	76

[a] The reaction mixture was treated first with 15% aqueous ammonium chloride and then with diethyl ether.

[b] The reaction mixture was divided into two equal parts one of which was treated as described in [a], and the other was distilled without any treatment.

[c] The product was extracted first with diethyl ether (41.5%) and then with chloroform (27.4%).

[d] The mixture was distilled without preliminary treatment (in the presence of *t*-BuOK).

[e] The IR spectrum contained a weak band at 1950 cm^{-1} from allene moiety (~4–6% of compound **III**, according to the ^1H NMR data).

[f] Calculated on the reacted oxirane **Ia** (conversion ~94%).

[g] The product was extracted first with diethyl ether (57.4%) and then with chloroform (41.8%).

[h] The product contained ~10% of allene **IIIb** and ~26% of cyclic compounds **IV**–**VI** (according to the ^1H NMR data).

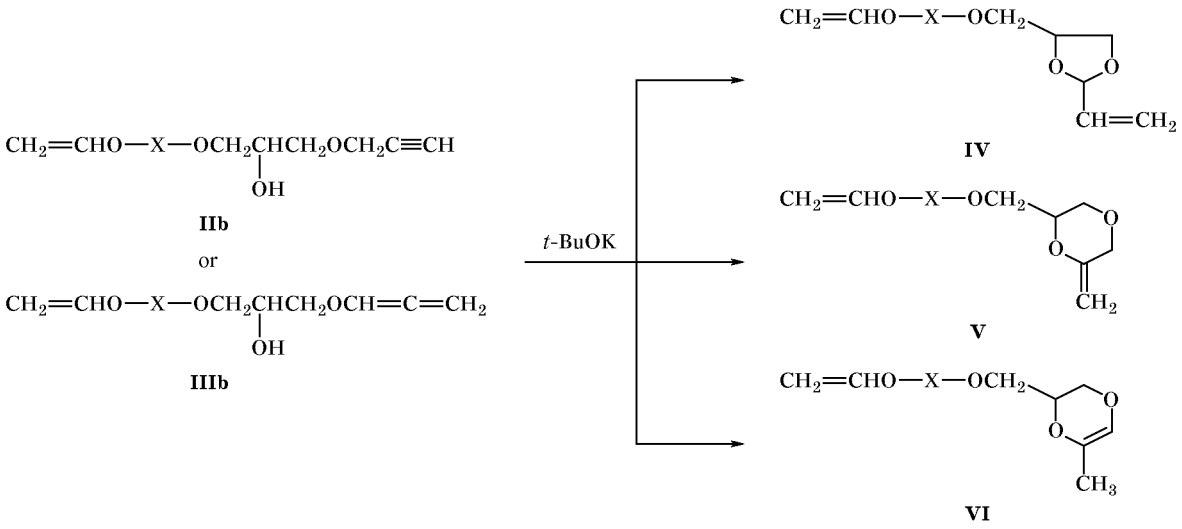
[i] Overheating during the distillation resulted in almost quantitative acetalization of the product.

(Scheme 3); the overall yield of products **IV**–**VI** was 26%; they were identified by the ^1H NMR spectra of the distillate and were not isolated as individual compounds. Apart from signals belonging to product **IIb**, the ^1H NMR spectrum of the distillate contained signals typical of structural fragments of heterocyclic compounds **IV**–**VI**, vinyl group in 1,3-dioxolane **IV**, δ 5.16–5.39 and 5.74 ppm; methylene group in 1,4-dioxane **V**, δ 5.73 ppm; and methyl group in 1,4-dioxin **VIb**, δ 1.62 ppm.

Treatment of the reaction mixtures with a ~15% aqueous solution of ammonium chloride (in order to remove the base catalyst), followed by extraction of the products into diethyl ether (**IIa**) or chloroform (**IIb**), resulted in considerable decrease in the yield of both crude (probably, due to their partial solubility in water and incomplete extraction, e.g., with diethyl ether) and distilled products. The yield of crude product **IIa** in most experiments was ~70–73% (Table 1; run nos. 1, 2, 8). Subsequent vacuum distillation of compounds **II** isolated in such a way is also accompanied by loss of an appreciable amount of the target product, primarily as a result of thermal acetalization with participation of the hydroxy and vinyloxy groups (in the above cases, the acetalization was prevented by the presence of *t*-BuOK). Eventually, the yield of compounds **II** decreases to ~31–48% (Table 1, run nos. 1–3, 8). Only in a few cases, the yield of the distilled product was appreciably greater, e.g., in run no. 4 it was 76% calculated on the reacted oxirane **Ia** or 71% of the theoretical one. This may be due to the presence of trace amounts of basic impurities (such as *t*-BuOK, K_2CO_3, or KOH) which inhibit the acetalization process.

Additional extraction of compound **IIa** with chloroform increases its yield to 69–99% (Table 1; run

Scheme 3.



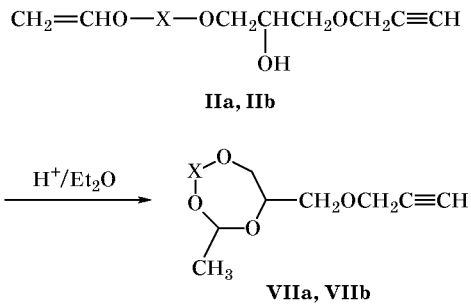
nos. 3, 9). However, in this case ~25–30% of the product is lost during distillation (owing to acetalization; the ^{1}H NMR spectra of the still residues contained a quartet signal from the acetal proton, OCHO, at δ 4.83 ppm).

The presence in molecules **IIa** and **IIb** of two highly reactive unsaturated fragments of different chemical natures (double and triple carbon–carbon bonds) makes them unique synthons and building blocks capable of undergoing various transformations, including intramolecular cyclizations according to both electrophilic and nucleophilic mechanisms (the latter type of cyclization will be the subject of the next communication).

The double bond activated by the neighboring oxygen atom is prone to electrophilic addition reactions with compounds having functional groups with a labile hydrogen atom (OH, COOH). This is the main and most typical chemical property of vinyl ethers, which gives rise to their wide application in organic synthesis and in practice [18, 19, 21]. However, known examples of intramoleular cyclizations of monovinyl ethers derived from diols, leading to cyclic acetals, are limited to those reported for 2-(vinyloxy)-ethanol [22] which is quantitatively converted into 2-methyl-1,3-dioxolane by the action of acid catalysts. On the other hand, successful intramolecular addition with participation of the hydroxy and vinyloxy groups in **II** should afford hitherto unknown cyclic polyethers with side-chain propynyloxy groups; such products are expected to combine useful properties of 2-propynyl ethers [2–14], macroheterocycles [20], and acetals [23], including cyclic ones [24]. An analogous cyclization with formation of 2-methylperhydro-1,3,6,8-trioxazecin-7-one) was observed by us previously only with 2-hydroxyethyl 2-(vinyloxy)ethylcarbamate [19].

We have found that 1-[ω-(vinyloxy)alkoxy]-3-(2-propynyloxy)-2-propanols **II** are fairly readily converted into previously unknown and difficultly accessible (by other methods) cyclic acetals of the acetylene series, (2-methyl-1,3,6-trioxocan-4-yl)methyl 2-propynyl ether (**VIIa**) and (2-methyl-1,3,6,9-tetraoxacycloundec-4-yl)methyl 2-propynyl ether (**VIIb**) (Scheme 4). The cyclization is promoted by trifluoroacetic acid (~0.5 wt %) in boiling dry diethyl ether (reaction time 15–20 h; Table 2). The formation of macrocyclic structures **VIIa** and **VIIb** was monitored by IR spectroscopy, following simultaneous disappearance of absorption bands belonging to the hydroxy (3450 cm^{-1}) and vinyloxy groups (860, 1200, 1325, 1620–1640, 3050–3070, and 3120 cm^{-1}). The yields of **VIIa** and **VIIb** were 96 and 88%, respectively (Table 2; run nos. 7, 10).

Scheme 4.



X = $(CH_2)_2$ (**a**), $(CH_2)_2O(CH_2)_2$ (**b**).

Table 2. Intramolecular cyclization of 1-alkoxy-3-(2-propynyloxy)-2-propanols **IIa** and **IIb** (Et_2O; CF_3COOH, ~0.5 wt %; 30–34°C)

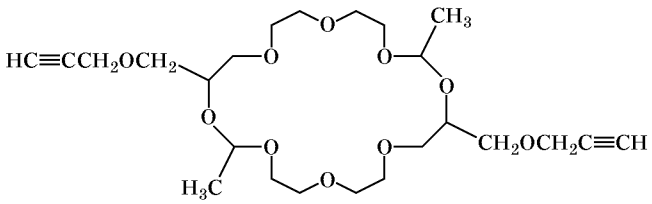
Run no.	Intital compound (mol)	Et_2O, ml	Reaction time, h	Product	Yield,[a] %
1	**IIa** (0.0025)	10	30	**VIIa**	50
2	**IIa**[b] (0.02)	50	20	**VIIa**[c]	70[d]
3	**IIa**[b] (0.04)	80	20	**VIIa**[c]	75[e]
4	**IIa**[b] (0.04)	100	20	**VIIa**[c]	70[f]
5	**IIa**[b] (0.04)	100	20	**VIIa**[c]	61[g]
6	**IIa** (0.05)	100	20	**VIIa**	90
7	**IIa** (0.05)	100	20	**VIIa**	96
8	**IIa** (0.05)	100	20	**VIIa**	94
9	**IIb**[h] (0.03)	50	15	**VIIb**[i]	80
10	**IIb** (0.03)	40	14	**VIIb**	88.4[j]
11	**IIb** (0.01)	30	14[k]	**VIIb**	87.3[l]

[a] Yield of the crude product, calculated on the initial amount of compound **II**.
[b] Initial compound **II** contained ~4–6% of allene isomer **III** (see Table 1).
[c] The product contained ~4–6% of 2-vinyl-1,3-dioxolane (**IV**).
[d] After vacuum distillation.
[e] Polymeric product, 12 wt %, was isolated (deposited on the walls of the reaction vessel).
[f] Polymeric product, 9 wt %, was isolated.
[g] Polymeric product, 14 wt %, was isolated.
[h] Initial compound **IIb** contained ~10% of allene isomer **IIIb** and ~26% of cyclic products **IV**–**VI** (see Table 1, run no. 12).
[i] The product contained ~20% of compounds **IV**–**VI**.
[j] Fractional extraction gave 37.3% of a product soluble in diethyl ether and 51.1% of a product soluble in chloroform.
[k] The reaction mixture was stored for 10 days in a refrigerator.
[l] We isolated 35.7% of a product soluble in diethyl ether and 51.6% of a product insoluble in diethyl ether.

No formation of open-chain acetal structures via intermolecular head-to-tail oligomerization was observed in the intramolecular acetalization of compound **IIa**. Among other things, this follows from the absence in the IR and NMR spectra of absorption bands and signals assignable to hydroxy and vinyloxy groups. However, in some experiments (Table 2, run nos. 3–5), after addition of a solution of compound **IIa** in ether to a solution of CF_3CO_2H in ether, a colorless polymeric material deposited on the walls of the reaction vessel. When the reaction was complete and the mixture was removed from the flask, the polymeric product was separated, washed with ether, and dried under reduced pressure (yield 9–14 wt %). Reprecipitation with hexane from benzene gave a colorless elastic (rubber-like) material which turned yellow on storage. Its IR spectrum contained absorption bands due to triple C≡CH bonds, while stretching vibration band of vinyloxy group (1620–1640 cm^{-1}) was either absent at all or very weak. The spectrum was characterized by low resolution of absorption bands, which is typical of polymeric structures; therefore, we were unable to perform a reliable assignment.

By acid-catalyzed cyclization of compound **IIb** we obtained two fractions appreciably differing in their solubilities, viscosities, and R_f values (TLC) (Table 2; run nos. 10, 11). The fraction with R_f 0.45 (Silufol plates, eluent diethyl ether, development with iodine vapor; compound **IIb** in the same system has an R_f value of 0.64) is readily soluble in diethyl ether; its amount was ~41–42 wt % of the overall amount of the isolated products. The more viscous fraction (~58–59%, R_f 0.02) can be extracted only into chloroform. However, neither elemental nor spectral (IR, ^1H and ^{13}C NMR) analyses revealed radical differences between the isolated substances. In the ^1H NMR spectra we observed only insignificant shift of some proton signals, and the spectrum was consistent with the structure of acetal **VIIb**. Presumably, the products isolated by fractional extraction are diastereoisomers (or, most likely, mixtures of *d*,*l*- and *meso*-diastereoisomers with different ratios). Their cyclic structure is also confirmed by the absence of absorption bands from hydroxy and vinyloxy groups in the IR spectra and signals from the corresponding protons in the ^1H NMR spectra of both products. On the other hand,

although cyclodimerization of compound **IIb** under the given conditions is formally possible, its probability is likely to be low, for it is difficult to explain why, e.g., the formation of 22-membered cyclic dimer **VIII** becomes not only possible but preferred.



VIII

Vacuum distillation of compounds **VII** even in the presence of hydroquinone leads to polymerization of the main part of the product. The resulting polymer is a dark red transparent glassy material, which is insoluble in diethyl ether, chloroform, benzene, and dimethyl sulfoxide. Compounds **II** and **VII** are colorless liquids with low or moderate viscosity; their structure is consistent with the data of elemental analysis and IR and NMR (^{1}H and ^{13}C) spectroscopy. Compounds **II** can be additionally purified by vacuum distillation.

A combination in molecules **II** and **VII** of various structural fragments, namely acetylenic ether, cyclic polyether, and cyclic acetal moieties, as well as their mutual influence, is anticipated to give rise to new unexpected properties. Obviously, variation of the length and structure of the X fragment (the number of methylene or oxymethylene units) in initial oxirane **I** and hence in compound **II** provides the possibility for synthesizing crown ether-like compounds with a desired number of heteroatoms and ring size, while the reactivity of the triple bond remains unchanged. Undoubtedly, this extends the synthetic potential of such structures and of the proposed approach to their preparation.

EXPERIMENTAL

The IR spectra were recorded on a Specord 75IR spectrophotometer from samples prepared as thin films. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker DPX-400 instrument (400 MHz for ^{1}H and 100 MHz for ^{13}C) from ~5–10% solutions in $CDCl_3$ containing HMDS as internal reference.

2-[2-(Vinyloxy)ethoxy]methyloxirane (**Ia**) and 2-{2-[2-(vinyloxy)ethoxy]ethoxymethyl}oxirane (**Ib**) were prepared by the procedure reported in [25]. Commercial 2-propynyl alcohol was purified by distillation prior to use.

1-[2-(Vinyloxy)ethoxy]-3-(2-propynyloxy)-2-propanol (IIa). *a*. A mixture of 5.00 g (34.7 mmol) of oxirane **Ia**, 2.80 g (50 mmol) of 2-propynyl alcohol, and 0.23 g (~3 wt %) of potassium *tert*-butoxide was stirred for 9 h at 60–65°C (Table 1, run no. 3). The mixture was cooled to 20°C and divided into two equal parts. One part was treated with 50 ml of aqueous ammonium chloride, the organic phase was separated, and the aqueous phase was extracted with diethyl ether (3 × 50 ml). The extracts were combined with the organic phase, dried over $MgSO_4$, and evaporated on a rotary evaporator. The aqueous phase was additionally treated with chloroform, the extract was dried over potassium carbonate, the solvent was removed on a rotary evaporator, and the residue was dried under reduced pressure. The overall yield of crude alcohol **IIa** was 2.39 g (68.9%); vacuum distillation gave 1.58 g (45.5%) of the product as a colorless liquid with bp 135–136°C (4 mm), n_D^{20} = 1.4688; R_f 0.25 [Silufol plates; eluent benzene–ether (1 : 1); development with iodine vapor]. IR spectrum, ν, cm^{-1}: 1620 (C=C), 2120 (C≡C), 3280 (H–C≡, split band), 3450 (OH). ^{1}H NMR spectrum, δ, ppm: 2.48 t [1H, HC≡, ^4J(CH$_2$C≡CH) = 1.2 Hz), 2.95 d [1H, OH, ^3J(HOCH) = 5.6 Hz], 3.51 d.d (1H, C**H**$_2$CHCH$_2$, part *A* of *AB* quartet, J_{AB} = 9.39, ^3J = 6.48 Hz), 3.57 d.d (1H, C**H**$_2$CHCH$_2$, part *B* of *AB* quartet, J_{AB} = 9.39, ^3J = 4.40 Hz), 3.54 d.d (1H, CH$_2$CHC**H**$_2$, part *A* of *AB* quartet, J_{AB} = 9.39, ^3J = 6.42 Hz), 3.60 d.d (1H, CH$_2$CHC**H**$_2$, part *B* of *AB* quartet, J_{AB} = 9.39, ^3J = 4.52 Hz), 3.72 t (2H, OCH$_2$CH$_2$O, *J* = 5.2 Hz), 3.82 t (2H, OCH$_2$CH$_2$O, *J* = 5.2 Hz), 3.99 m (1H, C**H**OH), 4.01 d.d (1H, CH$_2$=, ^2J = 2.0 Hz, J_{cis} = 8.0 Hz), 4.18 d (2H, CH$_2$C≡, ^4J = 1.2 Hz), 4.19 d.d (1H, CH$_2$=, ^2J = 2.0, J_{trans} = 16.0 Hz), 6.46 d.d (1H, OCH=, J_{cis} = 8.0, J_{trans} = 16.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 58.68 (**C**H$_2$C≡), 67.39 (**C**H$_2$OCH=), 69.41 (CHOH), 69.94 (**C**H$_2$CH$_2$OCH=), 71.19 (**C**H$_2$OCH$_2$C≡), 72.66 (O**C**H$_2$CH), 75.02 (HC≡), 79.70 (C≡), 86.95 (CH$_2$=), 151.77 (OCH=). Found, %: C 59.49; H 8.27. $C_{10}H_{16}O_4$. Calculated, %: C 59.98; H 8.05.

The second part of the mixture was distilled under reduced pressure without any preliminary treatment to isolate 2.85 g (82.1%) of compound **IIa** containing ~6% of allene isomer **IIIa** (according to the ^{1}H NMR data), bp 127–128°C (2 mm), n_D^{20} = 1.4698.

b. A mixture of 4.30 g (29.9 mmol) of oxirane **Ia**, 2.80 g (50 mmol) of 2-propynyl alcohol, and 0.21 g (~3 wt %) of potassium *tert*-butoxide was stirred for

5 h at 80–85°C (Table 1, run no. 9). The mixture was cooled to 20°C and treated with 50 ml of aqueous ammonium chloride. The organic phase was separated, the aqueous phase was extracted with diethyl ether (3 × 50 ml), the extracts were combined with the organic phase, washed with water, and dried over $MgSO_4$, and the solvent was removed on a rotary evaporator to isolate 3.43 g (57.4%) of compound **IIa**. The aqueous phase was additionally treated with chloroform, the extract was washed with water and dried over potassium carbonate, the solvent was removed on a rotary evaporator, and the residue was dried under reduced pressure. We thus isolated 2.50 g (41.8%) of product **IIa**. The overall yield of the crude product was 5.93 g (99.2%); vacuum distillation gave 4.2 g (70.2%) of compound **IIa** with bp 135–136°C (4 mm).

c. Vacuum distillation of the product obtained under the same conditions (Table 1, run no. 10) but without preliminary treatment of the reaction mixture gave 5.70 g (95.3%) of compound **IIa** containing ~6% of allene isomer **IIIa** (according to the ^{1}H NMR data), bp 116–117°C (1 mm), n_D^{20} = 1.4680.

3,6,9,13-Tetraoxa-1-hexadecen-15-yn-11-ol (IIb). A mixture of 3.70 g (~20 mmol) of oxirane **Ib**, 1.68 g (30 mmol) of 2-propynyl alcohol, and 0.16 g (~3 wt %) of potassium *tert*-butoxide was stirred for 3 h at 65–70°C (Table 1, run no. 15). The mixture was cooled to 20°C and treated with 50 ml of aqueous ammonium chloride, the organic phase was separated, and the aqueous phase was extracted with 50 ml of chloroform. The extract was combined with the organic phase and dried over potassium carbonate, the solvent was removed on a rotary evaporator, and the residue was kept in a high vacuum to obtain 4.13 g (86%) of compound **IIb**; after vacuum distillation, yield 3.67 g (76.4%); colorless liquid, bp 140–142°C (1 mm), n_D^{20} = 1.4708; R_f 0.20 [Silufol plates; eluent benzene–ether (1 : 1); development with iodine vapor]. IR spectrum, ν, cm^{-1}: 1620 (C=C); 2120 (C≡C); 3263, 3287 (H−C≡); 3450 (OH). ^{1}H NMR spectrum, δ, ppm: 2.51 t [1H, HC≡, ^4J(CH$_2$C≡CH) = 2.38 Hz], 2.88 d (1H, OH), 3.49 d.d (1H, C**H**$_2$CHCH$_2$, part *A* of *AB* quartet, J_{AB} = 10.04, ^3J = 6.43 Hz), 3.55 d.d (1H, C**H**$_2$CHCH$_2$, part *B* of *AB*-quartet, J_{AB} = 10.04, ^3J = 4.54 Hz), 3.53 d.d (1H, CH$_2$CHC**H**$_2$, part *A* of *AB* quartet, J_{AB} = 9.73, ^3J = 6.06 Hz), 3.58 d.d (1H, CH$_2$CHC**H**$_2$, part *B* of *AB* quartet, J_{AB} = 9.73, ^3J = 4.55 Hz), 3.66 m (4H, OCH$_2$CH$_2$O), 3.83–3.99 m (5H, OCH, OC**H**$_2$CH$_2$OCH=), 4.00 d.d (1H, CH$_2$=, ^2J = 2.06, J_{cis} = 6.81 Hz), 4.17 d [2H, CH$_2$C≡, ^4J(CH$_2$C≡CH) = 2.38 Hz], 4.20 d.d (1H, CH$_2$=, ^2J = 2.06, J_{trans} = 13.30 Hz), 6.48 d.d (1H, CH=, J_{cis} = 6.81, J_{trans} = 13.30 Hz). ^{13}C NMR spectrum, δ$_C$, ppm: 58.58 (**C**H$_2$C≡); 67.30 (**C**H$_2$OCH=); 69.31 (CHOH); 69.56 (**C**H$_2$CH$_2$OCH=); 70.59, 70.68 (OCH$_2$CH$_2$O); 71.15, 72.64 (**C**H$_2$CH**C**H$_2$); 74.98 (HC≡); 79.67 (C≡); 86.92 (CH$_2$=); 151.71 (OCH=). Found, %: C 59.54; H 8.52. $C_{12}H_{20}O_5$. Calculated, %: C 59.00; H 8.25.

2-Methyl-4-(2-propynyloxymethyl)-1,3,6-trioxocane (VIIa). A solution of 10.0 g (50 mmol) of compound **IIa** in 20 ml of dry diethyl ether was added dropwise at 20°C to a solution of 0.05 g (0.5 wt %) of trifluoroacetic acid in 80 ml of dry diethyl ether, and the mixture was stirred for 20 h on heating under reflux. The mixture was cooled to 20°C, treated with 70 ml of a 2% aqueous solution of sodium carbonate, and extracted with diethyl ether. The extract was washed with water and dried over $MgSO_4$, and the solvent was removed on a rotary evaporator. Yield of **VIIa** 9.0 g (90%), colorless, moderately viscous liquid, n_D^{20} = 1.4780. IR spectrum, ν, cm^{-1}: 2120 (C≡C), 3280 (H−C≡). ^{1}H NMR spectrum, δ, ppm: 1.27 d (3H, Me), 2.49 t (1H, HC≡), 3.42–3.53 m (4H, C**H**$_2$CHC**H**$_2$), 3.58–3.65 d.t (8H, OCH$_2$CH$_2$O), 3.90 m (1H, OCH), 4.12 d (2H, CH$_2$C≡), 4.87 q (1H, OCHO). ^{13}C NMR spectrum, δ$_C$, ppm: 19.05 (Me); 58.25 (**C**H$_2$C≡); 60.97 (O**C**H$_2$CH$_2$); 68.88 (OCH); 70.63 (OCH$_2$**C**H$_2$); 70.68, 72.18 (**C**H$_2$CHCH$_2$); 74.50 (HC≡); 79.17 (C≡); 99.62 (OCHO). Found, %: C 59.23; H 8.67. $C_{10}H_{16}O_4$. Calculated, %: C 59.98; H 8.05.

2-Methyl-4-(2-propynyloxymethyl)-1,3,6,9-tetraoxacycloundecane (VIIb). *a*. A solution of 3.70 g (15 mmol) of compound **IIb** in 5 ml of diethyl ether was added dropwise at 20°C to a solution of 0.018 g (~0.5 wt %) of trifluoroacetic acid in 35 ml of diethyl ether. The mixture was stirred for 14 h on heating under reflux and was cooled to room temperature (Table 2, run no. 10). The mixture divided into two colorless layers. It was treated with 30 ml of a ~2% aqueous solution of sodium carbonate and extracted with diethyl ether, the extract was washed with water and dried over $MgSO_4$, and the solvent was removed on a rotary evaporator. Yield of **VIIb** 1.38 g (37.3%), colorless, moderately viscous liquid, n_D^{20} = 1.4734; R_f 0.45 (Silufol plates; eluent Et_2O; development with iodine vapor). IR spectrum, ν, cm^{-1}: 2113 (C≡C); 3250, ~3270 sh (H−C≡). ^{1}H NMR spectrum, δ, ppm: 1.29 d (3H, Me, J = 5.26 Hz), 2.55 br.s (1H, HC≡), 3.48–3.75 m (12H, 6CH$_2$O), 3.92 m (1H, OCH), 4.14 m (2H, CH$_2$C≡), 4.89 q (1H, OCHO). ^{13}C NMR spectrum, δ$_C$, ppm: 19.87 (Me); 57.91, 63.18, 69.68, 70.24, 70.55, 70.62, 71.08, 71.16, 73.12, 73.45 (7OCH$_2$, OCH); 74.46 (HC≡); 79.22 (C≡); 99.42,

99.54 (OCHO). Found, %: C 58.66; H 8.37. $C_{12}H_{20}O_5$. Calculated, %: C 59.00; H 8.25.

The aqueous dispersion was additionally treated with chloroform, the extract was washed with water and dried over potassium carbonate, the solvent was removed on a rotary evaporator, and the residue was dried under reduced pressure. Yield 1.89 g (51.1%), colorless viscous liquid, n_D^{20} = 1.4756; R_f 0.02 (Silufol plates; eluent Et_2O; development with iodine vapor). IR spectrum, ν, cm^{-1}: 2114 (C≡C); 3252, 3287 sh (HC≡). ^1H NMR spectrum, δ, ppm: 1.31 d and 1.34 d (3H, Me, *J* = 5.26, 5.26 Hz); 2.45 m (1H, HC≡); 3.37–3.80 m (12H, $6OCH_2$); 3.92 m (1H, OCH); 4.14 d and 4.17 d (2H, OCH_2C≡, *J* = 2.45, 2.45 Hz); 4.77, 4.91, and 5.02 t.q (1H, OCHO, *J* = 5.26, 5.26, 5.50 Hz). ^{13}C NMR spectrum, δ_C, ppm: 20.34 (Me); 58.47, 63.82, 70.23, 70.45, 70.62, 70.78, 70.99, 71.40, 73.59, 74.05 ($7OCH_2$, OCH); 74.58 (HC≡); 79.67 (C≡); 99.98, 100.12 (OCHO). Found, %: C 58.94; H 7.91. $C_{12}H_{20}O_5$. Calculated, %: C 58.99; H 8.25. Overall yield of **VIIb** 3.27 g (88.4%).

b. A solution of 3.00 g (12 mmol) of compound **IIb** in 6 ml of diethyl ether was added dropwise at 20°C to a solution of 0.015 g (~0.5 wt %) of trifluoroacetic acid in 24 ml of diethyl ether. The mixture was stirred for 14 h on heating under reflux, cooled to room temperature, and kept for 10 days in a refrigerator (Table 2, run no. 11). During that time the mixture divided into two colorless layers. The upper (ether) layer was carefully separated by decanting, and the solvent was removed under reduced pressure to obtain 1.07 g (35.7%) of the product as a colorless, moderately viscous liquid, n_D^{20} = 1.4770. From the bottom layer we isolated 1.55 g (51.6%) of a substance insoluble in ether; colorless viscous liquid, n_D^{20} = 1.4803. Overall yield 2.62 g (87.3%). The IR and NMR spectra of the products isolated from the two layers were identical to those given above for compound **VIIb**.

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