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Vinyl Ethers Containing an Epoxy Group: XXII.* Synthesis and Base-Catalyzed Transformations of 1-(Allyloxy)- and 1-[2-(Vinyloxy)ethoxy]-3-(2-propynyloxy)propan-2-ols

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Abstract—Reactions of 2-(allyloxymethyl)- and 2-[2-(vinyloxy)ethoxy]methyloxiranes with 2-propynol (~3 wt % of *t*-BuOK, 75–85°C, 5–10 h) lead to formation of new 1-organyloxy-3-(2-propynyloxy)propan-2-ols (yield 65–95%). On heating to 45–100°C in the presence of bases (KOH, *t*-BuOK), 1-allyloxy- and 1-[2-(vinyloxy)ethoxy]-3-(2-propynyloxy)propan-2-ols are transformed into the corresponding 2-vinyl-1,3-dioxolane, 6-methyl-2,3-dihydro-1,4-dioxine, 6-methylene-1,4-dioxane, and 2,3-dihydro-5*H*-1,4-dioxepine derivatives, whose yield and ratio strongly depend on the solvent nature, catalyst, and substituent at the hydroxy group. 2-Vinyl-1,3-dioxolane and 6-methyl-2,3-dihydro-1,4-dioxine derivatives are formed as the major products (yield 70–99%) in the presence of *t*-BuOK in aprotic media (toluene, THF, DMSO) or in the absence of a solvent as a result of prototropic isomerization followed by intramolecular heterocyclization. Intramolecular nucleophilic cyclization of 3-(2-propynyloxy)propan-2-ols to 6-methylene-1,4-dioxane is the predominant process in water in the presence of KOH. In all cases, the fraction of 2,3-dihydro-5*H*-1,4-dioxepine derivatives among the cyclization products ranges from 0 to 5% (KOH) or to 14% (*t*-BuOK).

Base-catalyzed intramolecular cyclizations of ω-(2-propynyloxy)- [2–8], ω-(2-propynylsulfanyl)- [9], and ω-(2-propynylamino)alkan-1-ols [10, 11], as well as of their 2-haloallyl analogs [4, 5, 9], have been studied in sufficient detail. Such cyclizations (which involve intramolecular nucleophilic addition of functional group at the acetylenic triple bond) are among the most widespread reactions leading to five-, six-, or seven-membered heterocycles containing one or two heteroatoms (N, O, S) [8, 12, 13]. However, in the series of ω-(2-propynyloxy)alkan-1-ols, only 2-(2-propynyloxy)ethanol and its simplest derivatives $R^1C{\equiv}CC(R^2)(R^3)OCH(R^4)CH(R^5)OH$ ($R^1 = R^2 = R^3 = R^4 = R^5 = H$ [3, 4, 7]; $R^1 = R^2 = R^3 = R^4 = H$, $R^5 = Me$, Ph; $R^1 = R^2 = R^3 = R^5 = H$, $R^4 = Ph$; $R^1 = R^2 = R^3 = H$, $R^4 = R^5 = Me$ [3, 6]; $R^1 = R^2 = R^4 = R^5 = H$, $R^3 = Me$ [7]; $R^1 = R^4 = R^5 = H$, $R^2 = Me$, $R^3 = Ph$ [8]; $R^1 = R^2 = R^4 = H$, $R^3 = R^5 = Me$ [3, 6, 7]; $R^1 = Me$, $R^2 = R^3 = R^4 = R^5 = H$ [7]), 3-(2-propynyloxy)propan-1-ol [5], 2-(2-propynyloxy)cyclopentanol [7], and 2-(2-propynyloxy)cyclohexanol [3, 6, 7] were studied.

Obviously, introduction of additional reaction centers, e.g., olefinic fragments with qualitatively different chemical natures of the double carbon–carbon bonds (specifically vinyloxy and allyloxy groups), into (2-propynyloxy)alkanol molecules should strongly extend the synthetic potential of both initial alkanols [1–8, 12] and their cyclization products [1, 8, 14], as well as the range of their useful properties and the scope of practical application. Known representatives of this class of compounds are used in various fields (see, e.g., references in [1]), including the synthesis of dendrimers, dienes, α-hydroxy and α-oxo acids, α-hydroxymethyl ketones, α,α'-dihydroxy ketones, polycyclic compounds (via functionalization or transformations of 1,4-dioxines) [15], and enediyne antibiotics (through key intermediates containing 2-vinyl-1,3-dioxolane fragments) [16]. In turn, the synthetic and practical significance of vinyl and allyl ethers and materials based thereon is so high that even the most

* For communication XXI, see [1].

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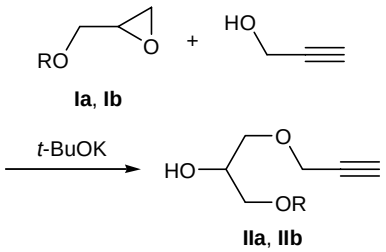
important fields of their application could not be listed in the framework of the present article. Among these, preparation of unique polymers and copolymers for medicine and technics, pharmaceuticals, technically important products, etc. [17–19].

Hydroxy-containing alkynyl ethers (1,2-diol mono-2-propynyl ethers) can be synthesized via opening of oxirane ring by the action of acetylenic alcohols, including accessible 2-propynol, in the presence of alkali metal hydroxide (methyl-, phenyl-, or 1,2-dimethyloxirane; NaOH or KOH; reflux, 1–3 h; yield 32–37%) [3, 6], tertiary amines (oxirane or methyloxirane; *N*,*N*-dimethylaniline; high-pressure reactor, 60–150°C, 7–8 h; yield 69–74%) [20] or acid catalysts [oxirane, methyloxirane, 2-(chloromethyl)oxirane, 1-(3,3-dimethyloxiran-2-yl)ethanone, 1,2-epoxycyclopentane, 1,2-epoxy-1-ethylcyclopentane, or 1,2-epoxycyclohexane; boron trifluoride–ether complex; –5 to 20°C, 3–15 h; yield up to 85%] [21]. Usually, 2–5 equiv of acetylenic alcohol (with respect to oxirane) is taken.

By reacting 2-propynol with functionally substituted oxiranes [18], e.g., 2-(allyloxymethyl)- and 2-[2-(vinyloxy)ethoxy]methyloxiranes **Ia** and **Ib**, we succeeded in synthesizing in a simple way new representatives of polyfunctional 3-(2-propynyloxy)-propan-2-ols, 1-allyloxy-3-(2-propynyloxy)propan-2-ol (**IIa**) and 1-[2-(vinyloxy)ethoxy]-3-(2-propynyloxy)-propan-2-ol (**IIb**) [1], which are promising as monomers, synthons, and starting compounds for fine organic (including heterocyclic [1]) synthesis, as well as convenient models for studying prototropic rearrangements and intramolecular cyclizations.



R = CH_2=$CHCH_2$ (**a**), CH_2=$CHOCH_2CH_2$ (**b**).

Taking into account that molecules **Ib** and **IIb** possess an additional reaction center (vinyloxy group) which is sensitive to acid compounds [1, 18] (extremely high reactivity of the electron-rich double bond toward electrophiles is the most general and well known property of vinyl ethers [1, 18, 19]), the condensation of 2-propynol with oxiranes **I** was performed in the presence of potassium *tert*-butoxide as base catalyst. The reaction was carried out in the absence of a solvent by heating a mixture of the reactants and catalyst (~3 wt %). To attain high conversion and suppress side processes (in particular, stepwise oligomerization via polyaddition), 2-propynol was taken in a ~1.1–1.7 molar excess with respect to oxirane **I**. It is known [22] that base-catalyzed reactions of oxiranes with alcohols and phenols, apart from the corresponding monoadducts, give considerable amounts of polyglycol ethers as a result of addition of initially formed 1,2-diol monoether to oxirane. Moreover, the process may be accompanied by homopolymerization of oxiranes **I** in the presence of alkaline initiators [22]. Obviously, the reaction outcome is determined by the ratio of the rates of the main and side processes.

The reaction course was monitored by IR spectroscopy, following the intensity of the IR absorption band at 3000 cm^{-1}, which corresponds to stretching vibrations of the C–H bond in the oxirane ring. The disappearance of that band was accompanied by appearance of absorption bands due to vibrations of hydroxy (3430–3450 cm^{-1}) and 2-propynyloxy groups (~2120 and ~3280 cm^{-1}); the other absorption bands, specifically those belonging to the allyloxy (840–850, 1270, 1340–1360, 1640, 3010, and 3080 cm^{-1}) or vinyloxy group (860, 1200, 1330, 1620–1640, 3050–3070, and 3120 cm^{-1}) remained essentially unchanged. The conversion of initial oxiranes **Ia** and **Ib** was estimated on the basis of the intensities of signals from protons in the oxirane ring in the ^{1}H NMR spectra, δ, ppm: 3.08–3.10 m (1H, OCH), 2.73–2.74 d.d and 2.55–2.56 q (2H, OCH_2). The conditions for reactions of 2-(allyloxymethyl)oxirane (**Ia**) with 2-propynol and the yields of 1-allyloxy-3-(2-propynyloxy)propan-2-ol (**IIa**) are given in Table 1.

As might be expected, the reaction time and the yield of 2-propanols **II** depended on the structure of oxirane **I** and temperature. The maximal yield of 3-(2-propynyloxy)propan-2-ol (**IIa**, isolated product) was 65–68% (yield of the crude product >80%) in the reaction of oxirane **Ia** with 2-propynol (1.18–1.25 equiv) at 75–85°C (reaction time 9.5–10 h; Table 1, run nos. 5, 7, 8). 3-(2-Propynyloxy)propan-2-ol (**IIb**) was synthesized in a similar way by heating a mixture of oxirane **Ib** and 2-propynol at a ratio of 1:1.67 in the presence of ~3 wt % of *t*-BuOK (80–85°C, 5 h; yield up to 95%); this reaction was considered in detail in the preceding communication [1].

When the reaction was performed with equimolar amounts of oxirane **Ia** and 2-propynol, up to 45% of

Table 1. Reaction of oxirane **Ia** with 2-propynol in the presence of ~3 wt % of *t*-BuOK

Run no.	Amounts of reactants, mol		Temperature, °C	Reaction time, h	Yields of products,[a] %				
	oxirane **Ia**	2-propynol			imitial oxirane **Ia**	crude **IIa**	distilled **IIa**	high-boiling fraction	undistillable residue
1[b]	0.04	0.05	60	1.5	100				
			60	9	–	29[c]	–	–	–
			70	5.5	5	54	33	5	5
2[b]	0.09	0.10	70	6	70	30[c]	–	–	–
3[b]	0.09	0.10	75–80	8	19	70	47.4	11	–
4[b]	0.31	0.36	75–80	8					
			80–85	10	9.5	62	35.9	5	5
5[d]	0.11	0.13	75–80	10	7.9	–	68.2	3	
6[d]	0.35	0.35	80–85	15	45	–	36.7	1	1
7[d]	0.11	0.13	75–80	9.5	13	84[e]			
8[d]	0.04	0.05	80–85	9.5	16.7	67[e]			

[a] Calculated on the reacted oxirane **Ia**.
[b] The reaction mixture was treated first with a ~15% aqueous solution of ammonium chloride and then with diethyl ether.
[c] The yield was determined from the ^{1}H NMR spectra by the intensity of signals from protons in residual epoxy groups.
[d] The mixture was dissolved in diethyl ether, and the solution was passed through a layer of neutral aluminum oxide.
[e] The products obtained in run nos. 7 and 8 were combined and distilled under reduced pressure to isolate 65.4% of compound **IIa** and 5% of a high-boiling substance.

the initial reactants was recovered from the reaction mixture, and the yield of **IIa** did not exceed 37% even when the reaction time was 15 h (80–85°C; Table 1, run no. 6). Lowering the temperature to 60–70°C also considerably slows down the process (Table 1, run nos. 1, 2). After heating for 9 h at 60°C or for 6 h at 70°C, the concentration of 2-propanol **IIa** in the reaction mixture did not exceed 30%. Under analogous conditions, the yields of the target product in the reaction of 2-propynol with oxirane **Ib** were 69–73% [1]. It follows from the above data that oxirane **Ib** is much more reactive than **Ia** in the base-catalyzed reaction with 2-propynol. Probable factors responsible for the higher reactivity of oxirane **Ib** were discussed previously [1].

Under the examined conditions, the fraction of high-boiling and undistillable products (probably polyethers) is insignificant (2–11%, Table 1). These data may be treated as an evidence for reduced reactivity of initial oxirane **Ia** and resulting 1,2-diol monoether **IIa** with respect to each other.

It should be noted that we observed no further transformations of 3-(2-propynyloxy)propan-2-ols **IIa** and **IIb**, such as prototropic rearrangements in the 2-propynyl or allyl (in **IIa**) fragments (e.g., acetylene–allene [12, 23] and/or allyl–propenyl isomerization [24–26]) or intramolecular cyclizations involving hydroxy group and triple bond [2–8, 12], which are usually promoted by bases. A probable reason is the low concentration of the catalyst (~0.05 mol per mole of oxirane). In some cases, some of the above side processes occurred (as a rule, to an insignificant extent) during isolation of 3-(2-propynyloxy)propan-2-ol (**IIb**) from crude reaction mixtures, i.e., during distillation in the presence of base catalyst. These instances were analyzed in detail in [1].

We did not examine the regioselectivity of oxirane ring opening by the action of 2-propyn-1-ol in the presence of potassium *tert*-butoxide specially. However, numerous published data [18, 22], including the results of special studies [27], suggest that opening of the oxirane ring in compounds **I**, as well as in other monosubstituted oxiranes (e.g., in methyloxirane), by nucleophilic attack in neutral and basic media is regioselective; it leads to formation of secondary hydroxyl group, i.e., primary ethers. As a rule, the fraction of secondary ether is negligible. As shown in [27], the ratio of the rates of addition of methoxide ion (MeO^-) to CH_2 and CH(Me) groups of methyloxirane is ~97:3, i.e., the corresponding secondary alcohol is in fact the only reaction product.

3-(2-Propynyloxy)propan-2-ols **IIa** and **IIb** are colorless mobile liquids which can readily be purified by vacuum distillation. Their structure was confirmed

by the data of elemental analysis and IR and ^{1}H and ^{13}C NMR spectroscopy. To minimize undesirable processes during vacuum distillation, the catalyst must be removed from the reaction mixture, e.g., by treatment with a ~15% aqueous solution of ammonium chloride or by dissolution of the products in a minimal amount of diethyl ether and subsequent passing of the solution through a layer of neutral aluminum oxide. The latter procedure is more advantageous, for it ensures considerably lesser loss of the target product than in the aqueous treatment.

In the preceding communication [1] we showed for the first time that 1-[ω-(vinyloxy)alkoxy]-3-(2-propynyloxy)propan-2-ols, in particular compound **IIb** and its analog synthesized from 2-propynol and 2-{2-[2-(vinyloxy)ethoxy]ethoxymethyl}oxirane according to the above scheme, are smoothly converted into 2-methyl-4-(2-propynyloxymethyl)-1,3,6-trioxocane and 2-methyl-4-(2-propynyloxymethyl)-1,3,6,9-tetraoxacycloundecane, respectively, in the presence of a catalytic amount (~0.5 wt %) of trifluoroacetic acid in anhydrous diethyl ether (via intramolecular electrophilic addition of hydroxy group at the vinyloxy group). This reaction opens a simple route to previously unknown but undoubtedly promising cyclic polyether acetals possessing highly reactive 2-propynyloxy groups in the side chain. Karaev *et al*. [28] previously desribed an example of acid-catalyzed cyclization of 2-(1,1-dimethyl-2-propynyloxy)cyclohexanol with participation of the hydroxy group and the triple bond under hydration conditions (H_2O, $HgO–H_2SO_4$, 50–60°C, 2 h); the product of this reaction was 2,3,3-trimethyloctahydro-1,4-benzodioxin-2-ol (yield 50%).

On the other hand, no data on reactions of (2-propynyloxy)alkanols **II** in the presence of bases have been reported so far, primarily because these compounds have been unknown prior to our studies (see above). In order to elucidate the effect of the substituent on the carbon atom attached to hydroxy group on the cyclization direction and synthesize new families of oxygen-containing heterocycles having highly reactive centers (allyloxy and vinyloxy groups), we examined base-catalyzed intramolecular cyclization of 1-allyloxy- and 1-[2-(vinyloxy)ethoxy]-3-(2-propynyloxy)propan-2-ols **IIa** and **IIb**. The reaction conditions and product yields are collected in Tables 2 and 3.

It was found previously [4, 7, 9, 11] that the direction of cyclization of alkynols containing a heteroatom (N, O, S) between the hydroxy group and triple bond and the yield of the resulting heterocycles depend most strongly on the solvent nature (in addition to the nature of the heteroatom). In particular, the cyclization of 2-(2-propynyloxy)ethanol catalyzed by alkali metal hydroxides was shown [4, 7] to produce four products: 2-vinyl-1,3-dioxolane, 2-methylene-1,4-dioxane, 2-methyl-2,3-dihydro-1,4-dioxine, and 2,3-dihydro-5*H*-1,4-dioxepine whose ratio depended on the conditions. In the reaction in water in the presence of NaOH or KOH (70–100°C, 12 h), the major products were 2-methylene-1,4-dioxane (36–45%) and 2,3-dihydro-5*H*-1,4-dioxepine (36–48%), while the fraction of 2-vinyl-1,3-dioxolane was smaller (7–24%) and only traces of 2-methyl-2,3-dihydro-1,4-dioxine (less than 1–2%) were detected. 2-Vinyl-1,3-dioxolane was formed as the major product in the reaction carried out in *tert*-butyl alcohol in the presence of KOH (reflux, 12 h); its fraction in the mixture of cyclic products was 65% (overall yield 61%) [7]. Finally, the same reaction in aprotic solvents such as decahydronaphthalene (100–180°C), dimethyl sulfoxide (70–150°C, 0.7 h), and triethylene glycol dimethyl ether (100–190°C) afforded 2-methyl-2,3-dihydro-1,4-dioxine (41–86%) and 2-vinyl-1,3-dioxolane (18–48%) as the major products, while the two other heterocyclic compounds were formed in small amounts (1–10%) [4, 7]. The highest yield (58%) and regioselectivity of the process (86% of 2-methyl-2,3-dihydro-1,4-dioxine) were observed in the system KOH–triethylene glycol dimethyl ether (180–190°C, 0.5 h) [7]. In the other cases, the overall yield of heterocyclic products ranged from 21 to 33% [4, 7].

On the other hand, the nature of the catalyst (as follows from the data of [4, 7]) affects the overall yield of the cyclization products but almost does not affect their ratio. In going from NaOH to KOH, other conditions being equal (water, 100°C, 12 h), the yield increases from 54 to 72%, while the ratio 2-methylene-1,4-dioxane–2,3-dihydro-5*H*-1,4-dioxepine (36:44) changes only slightly in favor of the former (39:36) [7]. When the cyclization in the presence of sodium hydroxide was performed at lower temperature (70°C), both the overall yield and the fraction of 2-vinyl-1,3-dioxolane decreased (from 54 to 37% and from 20 to 7%, respectively) [4].

However, introduction of even the simplest substituents (Me, Ph) into the ethanol or propynyl moiety of the 2-(2-propynyloxy)ethanol molecule [3, 4, 6–8] often gives rise to an appreciably different (from that considered above) pattern of the effect of the solvent and other factors on the ratio and overall yield of

Table 2. Isomerization and intramolecular cyclization of 3-(2-propynyloxy)propan-2-ols **IIa** and **IIb** in the presence of potassium hydroxide (molar ratio **II**–KOH 0.01:0.004)

Run no.	Initial compound no.	Solvent (10 ml)	Temperature, °C	Reaction time, h	Overall yield, %	Product composition,[a] %						
						II	**III**	**IV**	**V**	**VI**	**VII**	**VIII**
1	**IIa**	H_2O	~100	4	70	50	–	–	40	10	–	–
2	**IIb**	H_2O	~100	7	80	63	–	~1	23	2	9	2
3[b]	**IIa**	H_2O	~75	16.5	70	60	–	30	9	~1	–	–
4[b]	**IIb**	H_2O	~100	7	80	7	~1	5	55	14	17	2
5	**IIa**	DMSO	~75	~1 min	90	–	<1	–	20	<1	40	40
6	**IIb**	DMSO	~65	~1 min	90	–	–	–	24	4	37	35
7	**IIa**	DMSO	~75	0.5	80	–	–	–	20	~1	40	40
8	**IIb**	DMSO	~65	2	90	–	–	–	19	6	41	34
9	**IIa**	THF	~65	7.5	70	45	40	–	<1	<1	5	10
10	**IIb**	THF	~65	2	80	39	26	–	14	5	7	9
11	**IIa**	Toluene	~100	2	80	–	10	–	5	5	37	43
12	**IIb**	Toluene	~100	1	90	–	–	–	14	4	23	59
13[b]	**IIa**	–	~65	12	80	50	20	–	10	10	10	–
14[c]	**IIb**	–	~65	2	80	80	8	–	9	–	2	<1

[a] Here, as well as in Table 3, the yields were estimated on the basis of the ^{1}H NMR spectra.
[b] 0.012 mol of KOH.
[c] No solvent.

the cyclization products, mainly for stereoelectronic reasons.

We studied the cyclizations of 1-allyloxy- and 1-[2-(vinyloxy)ethoxy]-3-(2-propynyloxy)propan-2-ols **IIa** and **IIb** in water, DMSO, THF, and toluene and without a solvent. As catalyst we used KOH and *t*-BuOK. The progress of reactions was monitored by IR and ^{1}H and ^{13}C NMR spectroscopy; both reaction mixtures and products isolated by distillation were examined. In the IR spectra, we observed decrease in the intensity of absorption bands due to vibrations of the hydroxy group (3430–3450 cm^{-1}) and terminal triple bond [2120 (C≡C), 3280 (≡C–H) cm^{-1}] up to their complete disappearance. Simultaneously, the regions corresponding to stretching vibrations of allene fragment (~1950 cm^{-1}, C=C=C), internal triple bond (2170 cm^{-1}, –C≡C–), and double C=C bonds (1650–1660 and 1680–1700 cm^{-1}; in the spectrum of **IIb**, the first band usually appears as a shoulder on the strong absorption band at 1610–1640 cm^{-1} due to vinyloxy group) were monitored. The yields were calculated from the ^{1}H NMR spectra by comparing the intensities of characteristic signals from protons in the acetylene–allene isomerization [δ, ppm: **III**: 5.44 d (CH_2=), 6.74 t (CH=); **IV**: 1.40 s (Me–C≡C)] and intramolecular cyclization products [δ, ppm: **V**: 4.24–4.43 s (CH_2=); **VI**: 4.62–4.77 d.d.t (*exo*-CH=), 6.24–6.35 d.d.d (*exo*-OCH=); **VII**: 5.12–5.29 d (OCHO), 5.22–5.38 d (CH_2=), 5.41–5.43 d.d.d (CH=); **VIII**: 1.66 d (Me), 5.68–5.77 q (*exo*-OCH=)] with those of protons in the vinyloxy [**IIb**, δ, ppm: 4.01 d.d, 4.19 d.d (CH_2=), 6.46 d.d (OCH=)] or allyloxy group [δ, ppm: 5.17 d.d.t, 5.26 d.d.t (CH_2=), 5.89 d.d.t (CH=)] or with the overall intensity of signals from the allyloxy and 1-propenyloxy groups [**IIa**, δ, ppm: 1.55 d (Me), 4.41 d.q (CH=), 5.93 d.q (OCH=)]. The conversion of 2-propanols **II** and the overall yield of products were estimated from the residual intensity of the OH (δ 2.95–3.01 ppm, d) and ≡CH protons (δ 2.48 ppm, t). The complete absence of signals from acetylenic protons and carbon atoms [δ_C 74.94–75.02 (≡CH), 79.61–79.70 ppm (≡C)] in the ^{1}H and ^{13}C NMR spectra indicated 100% conversion of 3-(2-propynyloxy)propan-2-ols **IIa** and **IIb**.

Scheme 1 shows possible reaction pahways (according to our and published data [4, 6, 7]) and products. The reaction mechanisms (the main mechanism including pathways *1–5* was proposed in [4], and alternative mechanism including pathways *6–10* was proposed in [6, 7]) imply base-catalyzed prototropic rearrangement of 3-(2-propynyloxy)propan-2-ols **II** into

Table 3. Isomerization and intramolecular cyclization of 3-(2-propynyloxy)propan-2-ols **IIa** and **IIb** in the presence of potassium *tert*-butoxide (molar ratio **II**–*t*-BuOK 0.01:0.004)

Run no.	Initial compound no.	Solvent (10 ml)	Temperature, °C	Reaction time, h	Overall yield, %	Product composition, %				
						III	**V**	**VI**	**VII**	**VIII**
1	**IIa**	DMSO	~75	~5 min	90[a]	–	–	<5	35	60
2	**IIb**	DMSO	~45	~1 min	90	–	5	<1	40	55
3	**IIa**	DMSO[b]	~75	2	90[c]	5	10	5	45	25
4	**IIb**	DMSO	~65	1	90	–	–	~1	53	46
5	**IIa**	THF	~45	1	90[d]	–	10	–	18	72
6	**IIb**	THF	~65	2	90	–	22	3	18	57
7	**IIa**	Toluene	~100	0.75	80[e]	–	7	~1	42	50
8	**IIb**	Toluene	~100	10	90	–	18	4	22	56
9[f]	**IIa**	–	~65	2.5	70	7	10	3	50	30
10[f]	**IIb**	–	~65	7	90	3	–	–	39	58

[a] 100% of 1-propenyloxy derivatives **VIc**–**VIIIc**.
[b] 5 ml.
[c] The mixture contained 10% of initial alcohol **IIa**.
[d] The mixture contained ~5% of 1-propenyloxy derivatives.
[e] ~25% of 1-propenyloxy derivatives.
[f] Without a solvent.

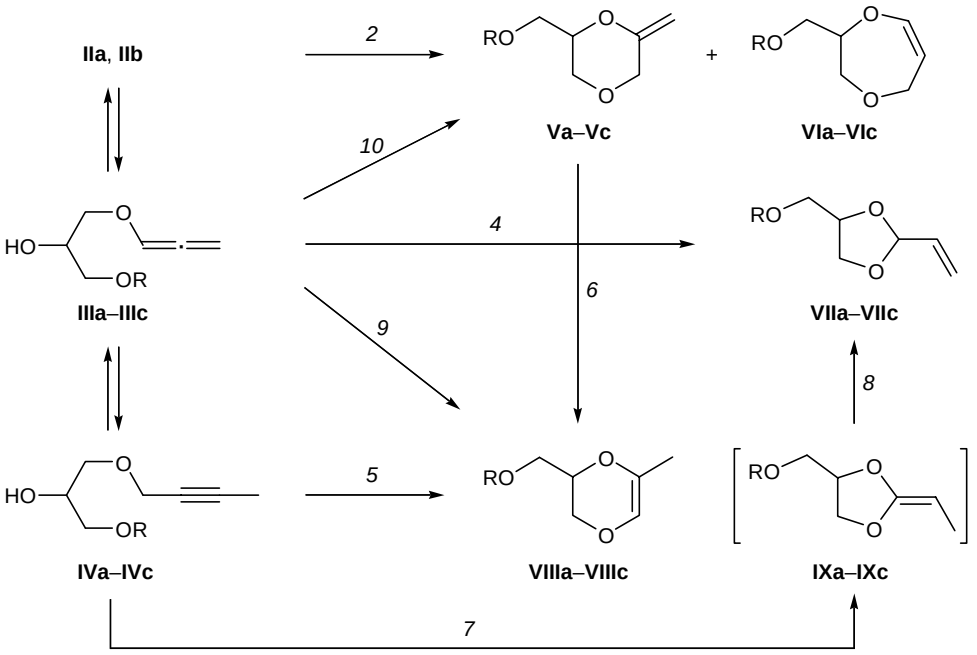
the corresponding 3-(1,2-propadienyloxy)propan-2-ols **III** and 3-(1-propynyloxy)propan-2-ols **IV** and their cyclization to compounds **V**–**IX**, as well as prototropic rearrangements of 6-methylene-1,4-dioxane **V** into 6-methyl-2,3-dihydro-1,4-dioxine **VIII** and of 2-ethylidene-1,3-dioxolane **IX** into 2-vinyl-1,3-dioxolane **VII**.

In fact, the reaction outcome is determined primarily by the ratio of rates of two concurrent processes, base-catalyzed acetylene–allene isomerization of 3-(2-propynyloxy)propan-2-ol **II** (pathway *1*) and its cyclization via intramolecular nucleophilic addition of the hydroxy group at the internal or terminal triple-bonded carbon atom, leading to 6-methylene-1,4-dioxane **V** and/or 2,3-dihydro-5*H*-1,4-dioxepine **VI** (pathway *2*). In turn, the formation of 2-vinyl-1,3-dioxolane **VII** and 6-methyl-2,3-dihydro-1,4-dioxine **VIII** is determined by the ratio of rates of two other concurrent processes, prototropic rearrangement of 3-(1,2-propadienyloxy)propan-2-ol **III** (pathway *3*) and its cyclization via intramolecular nucleophilic addition of the hydroxy group at the allene C^1 atom (pathway *4*).

In keeping with published data [6, 7], apart from intramolecular cyclization of 3-(1-propynyloxy)propan-2-ol (**IV**) (pathway *5*) [4], 6-methyl-2,3-dihydro-1,4-dioxine (**VIII**) may be formed by base-catalyzed rearrangement of 6-methylene-1,4-dioxane (**V**), which is accompanied by migration of the exocyclic double bond into the ring (pathway *6*). Moreover, Faure and Descotes [6] believed that this is the only pathway leading to 1,4-dioxines. According to [4, 7], the contribution of pathway *6* strongly depends on the structure of 2-(2-propynyloxy)ethanol and reaction conditions. Such isomerization was shown in [7] to proceed at a low rate and only in DMSO: when a mixture of cyclic products in the presence of KOH was heated at 120°C, the concentration of 2-methylene-1,4-dioxane decreased from 38 to 21% in 0.7 h and to 3% in 4.8 h; simultaneously, the concentration of 2-methyl-2,3-dihydro-1,4-dioxine increased from 4 to 25 and 41%, respectively. The isomerization can be accelerated by raising the temperature: after heating for 0.7 h at 190°C in the KOH–DMSO system, the concentration of 2-methyl-2,3-dihydro-1,4-dioxine increased from 3 to 38% [7]. As noted in [4], both thermal and hydroxide ion-induced isomerization of 2-methylene-1,4-dioxane contribute very little to the formation of 2-methyl-2,3-dihydro-1,4-dioxine in the reaction of 2-(2-propynyloxy)ethanol with NaOH in DMSO at 120°C.

It was also presumed [6] that 2-vinyl-1,3-dioxolane can be formed in aprotic solvents via cyclization of 3-(1-propynyloxy)propan-2-ol **IV** (in our case) to 2-ethylidene-1,3-dioxolane **IX** (pathway *7*), followed by rearrangement involving migration of the double

Scheme 1.



R = CH_2=$CHCH_2$ (**a**), CH_2=$CHOCH_2CH_2$ (**b**), MeCH=CH (**c**).

bond from the oxygen atom to the terminal carbon atom (pathway *8*), though ketene acetals like **IX** usually cannot be detected due to their instability under the reaction conditions [29]. Also, there exists the possibility for formation (in addition to 1,3-dioxolane **VII**, pathway *4*) of some amounts of compounds **V**, **VI**, and **VIII** by intramolecular cyclization of 3-(1,2-propadienyloxy)-propan-2-ols **III** as a result of addition of the hydroxy group at the central or terminal carbon atom of the 1,2-propadienyloxy group (pathways *9*, *10*). Proofs in support of the transformation of allenyloxyethanols into 1,4-dioxines were given in [7].

However, analysis of our results showed that, even though some of the above alternative reaction pathways are actually operative, their contribution to the overall yield of compounds **V**–**VIII** is quite insignificant. Although transformation of oxygen-containing heterocycles with an exocyclic double bond into their isomers with endocyclic double bond is possible, it obviously requires more severe conditions. For example, the base-catalyzed cyclizations reported in [4, 7] were effected in a 2 M solution of 2-(2-propynyloxy)ethanol and base at 100–190°C, while the isomerizations of 2-methylene-1,4-dioxanes into 6-methyl-2,3-dihydro-1,4-dioxines occurred at a base–cyclic product molar ratio of (0.5–1) : 1 in DMSO at 100–190°C (0.7–12 h). By contrast, the isomerization of 5-methylene-1,3-dioxanes into the corresponding 4*H*-1,3-dioxines was performed using a very large excess of the base, though at room temperature in the system *t*-BuOK–*t*-BuOH (6 equiv of *t*-BuOK, 5 equiv of *t*-BuOH, THF, 12 h, yield 82–91%) [30]. Our studies were performed with considerably more dilute solutions of the reagent and catalyst [1 M solutions of 3-(2-propynyloxy)propan-2-ols **II** and ~0.4 M solutions of base in appropriate solvent], the relative concentration of the base was appreciably lower (0.4 mol of base per mole of **II** against equimolar ratio of the reagent and base in [4, 7]), and the temperature was also considerably lower (45–100°C). Therefore, we succeeded in detecting formation of 1,2-propadienyloxy (**III**) and 1-propynyloxy (**IV**) isomers of **II** as intermediates in the synthesis of cyclic ethers and hence obtained experimental proofs for the reaction under study to follow pathways *1–5*. Previously [4, 7], this mechanism of cyclization of propynyloxyalkanols was assumed on the basis of only indirect evidences.

Thus we have shown that reactions of 1-allyloxy- and 1-[2-(vinyloxy)ethoxy]-3-(2-propynyloxy)propan-2-ols **IIa** and **IIb** with potassium hydroxide (Table 2) or *tert*-butoxide (Table 3), depending on the conditions, follow preferentially or exclusively pathways *1–5*. By contrast, no reliable experimental proofs have been obtained for pathways *6–10*. These results will be considered in more detail below.

Insofar as the rate of prototropic rearrangements in water is known [12, 23] to be considerably lower than in aprotic solvents [4, 6, 7, 11], the major products in the reactions with aqueous solutions of alkali metal hydroxides (as noted above) are 2-methylene-1,4-dioxanes and 2,3-dihydro-5*H*-1,4-dioxepines; they are formed in approximately equal amounts, but the latter always predominate [in the reactions with unsubstituted 2-(2-propynyloxy)alkanols]. This means that under the above conditions the rate of intramolecular cyclization of 2-(2-propynyloxy)alkanol is considerably higher than the rate of its isomerization. On the whole, our results are consistent with such views on the reaction mechanism, though in our case the yield of 1,4-dioxanes **V** strongly exceeds (by a factor of ~4 to 12) the yield of 1,4-dioxepines **VI** (Table 2, run nos. *1–4*). The corresponding difference for the reported examples is usually smaller [7].

As is seen from the data in Table 2, the only products of cyclization of 1-allyloxy-3-(2-propynyloxy)-propan-2-ol (**IIa**) in water in the presence of KOH (100°C, 4 h) were 2-(allyloxymethyl)-6-methylene-1,4-dioxane (**Va**, 40%) and 2-(allyloxymethyl)-2,3-dihydro-5*H*-1,4-dioxepine (**VI**, 10%). Here, up to 50% of initial alcohol **IIa** was recovered from the reaction mixture (Table 2, run no. 1). Replacement of the allyl group by 2-(vinyloxy)ethyl appreciably affects the reactivity. The conversion of 1-[2-(vinyloxy)ethoxy]-3-(2-propynyloxy)propan-2-ol (**IIb**) in the reaction with KOH in water (100°C) did not exceed 37% even when the reaction time was prolonged to 7 h (Table 2, run no. 2). Moreover, unlike the reaction with **IIa**, the process was less selective, and 9% of 2-vinyl-4-[2-(vinyloxy)ethoxymethyl]-1,3-dioxolane (**VIIb**) was formed together with 6-methylene-2-[2-(vinyloxy)-ethoxymethyl]-1,4-dioxane (**Vb**, 23%, the major product). The concentrations of 2-[2-(vinyloxy)ethoxymethyl]-2,3-dihydro-5*H*-1,4-dioxepine (**VIb**) and 6-methyl-2-[2-(vinyloxy)ethoxymethyl]-2,3-dihydro-1,4-dioxine (**VIIIb**) each did not exceed 2%. Presumably, in contrast to compound **IIa**, 3-(2-propynyloxy)-propan-2-ol **IIb** partially undergoes acetylene–allene isomerization despite inhibitory effect of aqueous medium.

Lowering the temperature from 100 to 75°C with simultaneous increase of the reaction time from 4 to 16.5 h and of the amount of KOH from 0.4 to 1.2 mol per mole of **IIa** resulted in formation of a mixture of linear and cyclic products containing 60% of initial compound **IIa**, 30% of its isomerization product, 1-allyloxy-3-(1-propynyloxy)propan-2-ol (**IVa**), 9% of 6-methylene-1,4-dioxane **Va**, and ~1% of 2,3-dihydro-5*H*-1,4-dioxepine **VIa** (Table 2, run no. 3). In the IR spectrum of the reaction mixture we observed an absorption band at 2170 cm^{-1} due to stretching vibrations of the internal triple C≡C bond, and the ^1H NMR spectrum displayed a singlet at δ 1.40 ppm from protons in the MeC≡C group. Obviously, under these conditions prototropic isomerization of **IIa** appreciably predominates over cyclization processes. This follows from both large concentration of isomeric 2-propanol **IVa** in the product mixture and reduction in the yields of compounds **Va** and **VIa** (from 40 to 9% and from 10 to ~1%, respectively), as well as from the absence of cyclization products **VIIIa** and **VIIa** which could be formed from 3-(1-propynyloxy)propan-2-ol **IVa** or its allene precursor **IIIa**, respectively.

Analogous increase in the amount of KOH in the reaction with compound **IIb**, other conditions being equal (Table 2; run nos. 2, 4), sharply raised the conversion (from 37 to 93%) and appreciably increased the concentration of 6-methylene-1,4-dioxane **Vb** (from 23 to 54%). In addition to 2,3-dihydro-5*H*-1,4-dioxepine **VIb** and 1,3-dioxolane **VIIb** (which were also formed in run no. 2; only their concentration increased from 2 to 14% and from 9 to 17%, respectively), we identified products of prototropic isomerization of compound **IIb**, 1-[2-(vinyloxy)ethoxy]-3-(1,2-propadienyloxy)propan-2-ol (**IIIb**, ~1%) and 1-[2-(vinyloxy)ethoxy]-3-(1-propynyloxy)propan-2-ol (**IVb**, ~5%).

In nonaqueous media (DMSO, toluene) in the presence of both KOH and *t*-BuOK, compounds **II** mainly undergo intramolecular ring closure to 2-vinyl-1,3-dioxolanes **VII** and 6-methyl-2,3-dihydro-1,4-dioxines **VIII** whose overall concentration in the product mixture reaches 70–99% in DMSO and 78–92% in toluene (Tables 2, 3). 6-Methylene-1,4-dioxanes **V** and 2,3-dihydro-5*H*-1,4-dioxepines **VI** are also formed, but the concentration of **VI** does not exceed 6% (1–6%), and it remains unchanged on prolonged reaction. Compound **V** is formed in an amount of 5 to 24%; its concentration in the product mixture was the maximal (19–24%) when the reaction was carried in DMSO in the presence of KOH (Table 2, run nos. 5–8). Presumably, increased basicity of the medium favors not only acetylene–allene isomerization of compound **II** but also its cyclization. The ratio of the main products, compounds **V**, **VII**, and **VIII**, obtained in DMSO in the presence of KOH is ~1:2:2. The reaction occurs at

moderate temperature and at a fairly high rate (~1 min at 65–75°C,) and is sometimes accompanied by strong heat evolution. Increase of the reaction time to 0.5–2 h almost does not affect the overall yield (80–90%) and the product ratio (Table 2; run nos. 7, 8). This may be regarded as an evidence for the absence of isomerization of 6-methylene-1,4-dioxanes **V** into 1,4-dioxines **VIII** (pathway *6* in Scheme 1) under the given conditions. It is interesting that the reaction outcome in the system KOH–DMSO does not depend on the substrate structure. Unlike the reaction in water, the conversion of compounds **II** both in DMSO and in toluene was quantitative.

The effect of the structure of compounds **II** on the ratio of cyclization products was observed most clearly when the reaction was carried out in boiling toluene. From alcohol **IIa** in the presence of potassium hydroxide (toluene, 100°C, 2 h) we obtained compounds **IIIa**, **Va**, **VIIa**, and **VIIIa** in 10, 5, 37, and 43% yield, respectively (Table 2, run no. 11), while the major cyclization product obtained from compound **IIb** under analogous conditions (100°C, 1 h) was 2,3-dihydro-1,4-dioxine **VIIIb**; its concentration exceeded that of **VIIb** by a factor of ~2.5 (59 and 23%, respectively; Table 2, run no. 12). On the other hand, the yield of **Vb** was almost 3 times greater than the yield of **Va** (14 and 5%, respectively). Analogous results were obtained in toluene in the presence of potassium *tert*-butoxide (Table 3; run nos. 7, 8).

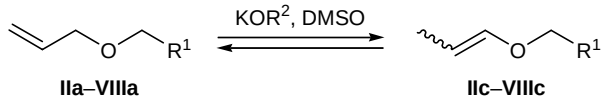
The rate of cyclization in other aprotic solvents, e.g., tetrahydrofuran, was considerably lower than in DMSO. In boiling THF in the presence of KOH, even after 7.5 h the reaction mixture contained up to 45% of initial compound **IIa**, and the major product was 1-allyloxy-3-(1,2-propadienyloxy)propan-2-ol (**IIIa**, 40%) (Table 2, run no. 9). The fraction of cyclic products was insignificant (15%), the main of these being 2,3-dihydro-1,4-dioxine **VIIIa** (10%) in a mixture with 5% of 1,3-dioxolane **VIIa**. Only traces of **Va** and **VIa** were detected. Compound **IIIa** showed in the ^{1}H NMR spectrum a doublet signal at δ 5.44 ppm (CH_2=) and a triplet at δ 6.74 ppm (CH=) from protons in the allene fragment. Obviously, under these conditions the rates of isomerization of **IIIa** into **IVa** and its cyclization to 1,4-dioxine **VIIIa** clearly exceed the rate of cyclization of **IIIa** to 1,3-dioxolane **VIIa**. On the other hand, the reaction catalyzed by potassium *tert*-butoxide was fast and effective: the conversion of **IIa** reached 90% on heating for 1 h at 45°C (Table 3, no. 5). Moreover, the process is fairly selective: product **VIIIa** is formed in 72% yield.

It should be emphasized that, under comparable conditions, both in THF and in toluene in the presence of both potassium hydroxide and potassium *tert*-butoxide the yield of **Vb** is greater by a factor of ~2–3 than the yield of **Va**. Presumably, these data indicate both relatively higher rate of acetylene–allene isomerization of compound **IIa** as compared to **IIb** and lower rate of intramolecular cyclization with participation of the terminal triple bond. The latter follows, e.g., from the results of run no. 9 (Table 2) considered above: After heating for 7.5 h at 65°C in the system KOH–THF, the reaction mixture contained 45% of initial propanol **IIa** and only traces (less than 1%) of its direct cyclization products, compounds **Va** and **VIa**, while the overall fraction of the isomerization products was 55%. A different pattern was observed with compound **IIb**: the reaction mixture contained 19% of the direct cyclization products (**Vb** and **VIb**) and 40% of the isomerization products (Table 2, run no. 10). These data refer to 2 h elapsed from the reaction start, i.e., the overall reactivity of compound **IIb** in THF and toluene in the presence of KOH is appreciably higher than the reactivity of **IIa** (Table 2, run nos. 9–12).

The main transformation products obtained from compound **IIa** by the action of potassium *tert*-butoxide in the absence of a solvent were 1,3-dioxolane **VIIa** (50%) and 2,3-dihydro-1,4-dioxine **VIIIa** (30%) (Table 3, run no. 9). The reaction mixture also contained compounds **IIIa**, **Va**, and **VIa** (7, 10, and 3%, respectively). Interestingly, analogous results were obtained in the system *t*-BuOK–DMSO (Table 3, run no. 3). The selectivity of cyclization of **IIb** under solvent-free conditions was even higher: the overall fraction of 1,3-dioxolane **VIIb** and 2,3-dihydro-1,4-dioxine **VIIIb** was 97%, although their ratio was the reverse (39 and 58%, respectively; Table 3, run no. 10). The reaction catalyzed by KOH in the absence of a solvent was very slow and nonselective (Table 2, run nos. 13, 14). Here, the conversion of **IIa** was 50% after heating for 12 h at 65°C, and of **IIb**, only 20% (2 h). In addition to (1,2-propadienyloxy)propanol **IIIa** (20%), compounds **Va**, **VIa**, and **VIIa** were formed (10% each). No 2,3-dihydro-1,4-dioxine **VIIIa** was detected. Among the transformation products of compound **IIb**, we identified allenyl alcohol **IIIb** (8%), small amounts of cyclic ethers **Vb** and **VIIb** (9 and 2%, respectively), and traces (<1%) of 2,3-dihydro-1,4-dioxine **VIIIb**.

As we already noted, apart from the heterocyclizations and acetylene–allene rearrangement considered above, 1-allyloxy-3-(2-propynyloxy)propan-2-ol (**IIa**)

and its derivatives **IIIa**–**VIIIa** can be involved in another base-catalyzed prototropic isomerization, namely allyl–propenyl rearrangement [24–26] which implies migration of the double C=C. Insofar as preparative version of that rearrangement was not the aim of the present study, we did not optimize its conditions but only analyzed the NMR spectra of the products obtained under the conditions summarized in Tables 2 and 3, as well as in other experiments.



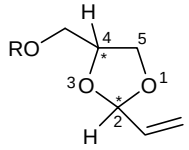
IIa–**VIIIa** **IIc**–**VIIIc**

R^2 = H, *t*-Bu.

As in the acetylene–allene rearrangement, the ease of allyl–propenyl isomerization is determined by the solvent nature, temperature, and reaction time (Table 4). In most cases, e.g., in toluene (100°C, 2 h) and THF (65°C, 7.5 h) in the presence of potassium hydroxide, no allyl–propenyl isomerization occurred (Table 4; run nos. 1, 4). Replacement of KOH by *t*-BuOK displaced the equilibrium toward the 1-propenyl isomer to an insignificant extent (25% in toluene and 5% in THF; Table 4, run nos. 3 and 5). This is consistent with the data of [25], according to which the reaction rate attains its maximal value in polar aprotic solvents like DMSO: at 25°C, the half-conversion period of allyl phenyl ether in a 0.68 M solution in DMSO by the action of 0.05 M *t*-BuOK was 1.5 min. In 1,2-dimethoxyethane, the half-conversion period was 160 min, though the concentration of *t*-BuOK was 0.66 M. In fact, in the superbasic system *t*-BuOK–DMSO, the rate of allyl–propenyl rearrangement of compound **IIa** was the highest (Table 4, run no. 8), and the substrate conversion was quantitative within a few minutes. However, twofold reduction of the volume of DMSO completely inhibited the allyl–propenyl isomerization (Table 4, run no. 9). The isomerization showed an unexpectedly strong dependence on the substrate structure. By heating compound **IIa** in the system KOH–DMSO for 7 h at 70°C (Table 4, run no. 7) we obtained a mixture of 4-allyloxymethyl-2-vinyl-1,3-dioxolane (**VIIa**), 2-allyloxymethyl-6-methyl-2,3-dihydro-1,4-dioxine (**VIIIa**), and 2-(1-propenyloxymethyl)-6-methyl-2,3-dihydro-1,4-dioxine (**VIIIc**) which were isolated by column chromatography and identified by the ^{1}H and ^{13}C NMR spectra. The conversion of allyloxymethyl-1,4-dioxine **VIIIa** into the corresponding 1-propenyloxymethyl derivative **VIIIc** was only 40%, while allyloxymethyl-1,3-dioxolane **VIIa** failed to undergo rearrangement into 1-propenyl isomer **VIIc** under the same conditions.

No allyl–propenyl isomerization occurred in the absence of a solvent (Table 4; run nos. 10, 11) even under catalysis by *t*-BuOK. The most probable reason is relatively low temperature (60°C) and insufficient reaction time (3 h). As shown in [26], prototropic rearrangement of allyl ethers under solvent-free conditions requires heating to 150–175°C over a period of 3–163 h in the presence of 2–15 wt % of base catalyst (*t*-BuOK, MeONa) in a nitrogen atmosphere (yield 35–99%).

The structure of the cyclization and isomerization products was confirmed by the ^{1}H and ^{13}C NMR and IR spectra. In the ^{1}H NMR spectra of the 1-propenyl isomers, the doublet signal from the methyl protons is located at δ 1.55 ppm, and multiplets at δ 4.42 and 5.95 ppm belong to protons at the double bond in the MeCH=CH–O fragment. The isomeric composition of the cyclic products was not examined specially; however, it should be noted that cyclization of compounds **II** gives mixtures of diastereoisomeric 2-vinyl-1,3-dioxolanes **VIIa**–**VIIc** due to the presence in their molecules of two asymmetric carbon atoms (C^2 and C^4) in the OCHO and O**C**HCH$_2$OR fragments.



VIIa–**VIIc**

R = CH_2=$CHCH_2$ (**a**), CH_2=$CHOCH_2CH_2$ (**b**), MeCH=CH (**c**).

The existence of two diastereoisomers follows from doubling of all signals in the ^{1}H and ^{13}C NMR spectra of compounds **VII**. Differences in the position of resonance signals from diastereotopic carbon atoms in the ^{13}C NMR spectra are insignificant: the $\Delta\delta_C$ range is 0.06 to 0.55 ppm. The largest difference is observed in the ^{13}C signals from the acetal (OCHO) and vinyl groups (CH_2=): $\Delta\delta_C$ = is 0.51–0.55 and 0.59–0.68 ppm, respectively. The =CH signals are the least sensitive: $\Delta\delta_C$ = 0.06–0.12 ppm. The maximal difference in the chemical shifts of protons (Δδ) does not exceed 0.13 ppm (OCHO), and the minimal Δδ value (0.01–0.02 ppm) is observed for the CH_2= protons.

Cyclization products derived from 3-(2-propynyloxy)propan-2-ols **II** are colorless mobile liquids which are distilled under reduced pressure as azeotropic mix-

Table 4. Allyl–propenyl isomerization of 1-allyloxy-3-(2-propynyloxy)propan-2-ol (**IIa**) and its derivatives **IIIa**–**VIIIa**

Run no.	Base catalyst	Solvent (10 ml)	Temperature, °C	Reaction time, h	Product composition,[a] %	
					allyloxy derivatives	1-propenyloxy derivatives
1	KOH	Toluene	~100	2	100	–
2	*t*-BuOK	Toluene	~65	5	100	–
3	*t*-BuOK	Toluene	~100	0.75	75	25
4	KOH	THF	~65	7.5	100	–
5	*t*-BuOK	THF	~45	1	95	5
6	KOH	DMSO	~75	0.16	100	–
7	KOH	DMSO	~75	7	80	20
8	*t*-BuOK	DMSO	~75	0.1	–	100
9	*t*-BuOK	DMSO[b]	~75	2	100	–
10	KOH	No solvent	~65	12	100	–
11	*t*-BuOK	No solvent	~65	3	100	–

[a] The degree of isomerization was determined from the intensity ratio of signals at δ 1.55 (Me), 4.40 (MeC**H**=), and 5.25/5.15 ppm (CH_2=) in the ^{1}H NMR spectra of mixtures **IIa**–**VIIIa**.

[b] 5 ml.

tures boiling in a narrow temperature range (~3°C). Pure compounds **VIIa** and **VIIIa** were isolated by column chromatography.

EXPERIMENTAL

The IR spectra were recorded on a Specord 75IR spectrometer from samples prepared as thin films. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker DPX-400 instrument at 400 and 100 MHz, respectively, from ~5–10% solutions in $CDCl_3$ or CCl_4–$CDCl_3$ using HMDS as internal reference and on a Bruker DPX-250 spectrometer at 250 and 62.9 MHz, respectively, from ~5–10% solutions in $CDCl_3$ using TMS as internal reference. Toluene was purified by the known procedure [31]. Dimethyl sulfoxide was heated with KOH for a short time to 120°C, left to stand for 10–12 h at room temperature, and distilled under reduced pressure over *t*-BuOK. Tetrahydrofuran was kept over KOH and was then distilled over calcium hydride in the presence of benzophenone. 2-[2-(Vinyloxy)ethoxy]methyloxirane (**Ib**) was synthesized by the procedure reported in [32]. Commercial 2-(allyloxymethyl)oxirane (**Ia**) and 2-propynol were purified by distillation. The purity of the initial compounds was checked by NMR spectroscopy.

2-(Allyloxymethyl)oxirane (Ia). IR spectrum, ν, cm^{-1}: 770, 800, 840 sh, 850, 920, 990, 1100, 1140 sh, 1160 sh, 1270, 1340, 1410, 1450, 1640, 2850, 2900, 2930, 3000, 3050, 3070. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 5.88 m (1H, CH=), 5.25 d.m and 5.15 d.m (1H each, CH_2=), 4.00 m (2H, OCH_2), 3.66 d.d and 3.36 q (1H each, OCH_2), 3.08 m (1H, CH), 2.73 d.d and 2.55 q (1H each, CH_2). ^{13}C NMR spectrum (CCl_4–$CDCl_3$), δ_C, ppm: 134.30 (CH=), 116.68 (CH_2=), 71.81 (OCH_2), 70.47 (OCH_2), 50.32 (CH), 43.69 (CH_2).

2-[2-(Vinyloxy)ethoxy]methyloxirane (Ib). IR spectrum, ν, cm^{-1}: 760, 830 sh, 840, 860 sh, 880 sh, 920, 970, 1040, 1130, 1160 sh, 1200, 1250, 1330, 1370, 1460, 1620, 1640 sh, 2870, 2930, 3000, 3050, 3120. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.44 q (1H, OCH=), 4.15 d.d and 3.97 d.d (1H each, CH_2=), 3.82–3.66 m [4H, $(CH_2)_2$], 3.41 q (2H, OCH_2), 3.10 m (1H, CH), 2.74 d.d and 2.56 q (1H each, CH_2). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 155.56 (OCH=), 86.55 (CH_2=), 71.86 (OCH_2), 69.54 (OCH_2), 67.08 (OCH_2), 50.48 (CH), 43.74 (CH_2).

1-Allyloxy-3-(2-propynyloxy)propan-2-ol (IIa). *a*. A mixture of 5.6 g (100 mmol) of 2-propynol, 10 g (87.7 mmol) of oxirane **Ia**, and 0.47 g (~3 wt %) of *t*-BuOK was stirred for 8 h at 75–80°C (Table 1, run no. 3). It was then cooled to 20°C and poured into 60 ml of aqueous ammonium chloride, the organic layer was separated, and the aqueous layer was treated with diethyl ether (3×50 ml). The extracts were combined with the organic phase, washed with water, dried over $MgSO_4$, and evaporated on a rotary evaporator. The residue was 10.44 g (70%) of **IIa**; vacuum distillation gave 7.03 g (47.2%) of the product.

b. The reaction mixture obtained under the conditions of run no. 5 (Table 1) was cooled to room tem-

perature and immediately dissolved in ~20–30 ml of diethyl ether. The solution was passed through a small (2.5–3.0 cm) layer of Al_2O_3, the solvent was removed on a rotary evaporator, and the residue was distilled under reduced pressure. Yield 11.9 g (68.2%), colorless liquid, bp 81–82°C (1 mm), n_D^{20} = 1.4630. IR spectrum, ν, cm^{-1}: 560, 630, 680, 840, 920, 950, 1000, 1100, 1205, 1270, 1330, 1360, 1400 sh, 1405, 1440, 1640 (C=C), 2120 (C≡C), 2850, 2900, 3010, 3080, 3280 (H–C≡), 3430 (OH). ^{1}H NMR spectrum, δ, ppm: 2.48 t (1H, HC≡, ^4J = 2.35 Hz), 3.01 d (1H, OH, ^3J = 4.0 Hz), 3.46 and 3.50 (2H, C**H**$_2$CCH$_2$, *AB* quartet, each component of which was split into a doublet due to coupling with CHOH, J_{AB} = 9.88, ^3J = 6.36, ^3J = 4.06 Hz), 3.54 and 3.60 (2H, CH$_2$CHC**H**$_2$, *AB* quartet split into doublets due to coupling with CHOH, J_{AB} = 9.78, ^3J = 6.26, ^3J = 4.50 Hz), 3.96 m (1H, C**H**OH), 4.00 d.t (2H, =CHC**H**$_2$O, ^3J = 5.67, ^4J = 1.47 Hz), 4.17 d (2H, CH$_2$C≡, ^3J = 2.35 Hz), 5.17 d.d.t (1H, CH$_2$=, J_{cis} = 10.37, ^2J = ^4J = 1.57 Hz), 5.26 d.d.t (1H, CH$_2$=, J_{trans} = 17.31, ^2J = ^4J = 1.66 Hz), 5.89 d.d.t [1H, CH=, J_{trans} = 17.3, J_{cis} = 10.37, ^3J(CH$_2$CH) = 5.67 Hz]. ^{13}C NMR spectrum, δ_C, ppm: 58.62 (O**C**H$_2$C≡), 69.38 (**C**HOH), 71.35 and 71.38 (O**C**H$_2$CH**C**H$_2$O), 72.35 (=CH**C**H$_2$), 74.94 (H**C**≡), 79.61 (**C**≡), 117.24 (CH$_2$=), 134.64 (CH=). Found, %: C 63.83; H 8.36. $C_9H_{14}O_3$. Calculated, %: C 63.51; H 8.29.

3-(2-Propynyloxy)-1-[2-(vinyloxy)ethoxy]-propan-2-ol (IIb) was synthesized in a similar way from 2-propynol and oxirane **Ib** [1]. Yield 95.3%, bp 122–123°C (1 mm), n_D^{20} = 1.4680. IR spectrum, ν, cm^{-1}: 860, 1200, 1330, 1620, 1640 sh (C=C), 2120 (C≡C), 2860, 2930, 3050, 3120, 3280 split (H–C≡), 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 and 3.57 d.d (1H each, C**H**$_2$CHCH$_2$, *AB* quartet split into doublets due to coupling with CHOH, J_{AB} = 9.39, ^3J = 6.48, ^3J = 4.40 Hz), 3.54 d.d and 3.60 d.d (1H each, CH$_2$CHC**H**$_2$, *AB* quartet split into doublets due to coupling with CHOH, J_{AB} = 9.39, ^3J = 6.42, ^3J = 4.52 Hz), 3.72 t (2H, OC**H**$_2$CH$_2$O, *J* = 5.2 Hz), 3.82 t (2H, OCH$_2$C**H**$_2$O, *J* = 5.2 Hz), 3.99 m (1H, C**H**OH), 4.01 d.d (1H, CH$_2$=, J_{cis} = 8.0, ^2J = 2.0 Hz), 4.18 d (2H, CH$_2$C≡, ^4J = 1.2 Hz), 4.19 d.d (1H, CH$_2$=, J_{trans} = 16.0, ^2J = 2.0 Hz), 6.46 d.d (1H, OCH=, J_{trans} = 16.0, J_{cis} = 8.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 58.68 (**C**H$_2$C≡), 67.39 and 69.94 (OCH$_2$CH$_2$O), 69.41 (CHOH), 71.19 and 72.66 (O**C**H$_2$CH**C**H$_2$O), 75.02 (HC≡), 79.70 (C≡), 86.95 (CH$_2$=), 151.77 (OCH=). Found, %: C 59.49; H 8.27. $C_{10}N_{16}O_4$. Calculated, %: C 59.98; H 8.05.

Transformations of compounds IIa and IIb in the presence of bases (*general procedure*). A mixture of 10 mmol of 3-(2-propynyloxy)propan-2-ol **IIa** or **IIb** and 4 mmol of *t*-BuOK or KOH in 10 ml of appropriate solvent was stirred under the conditions specified in Tables 2 and 3. The mixture was cooled to 20°C and poured into 50–60 ml of an aqueous solution of ammonium chloride (with *t*-BuOK as base) or 50–60 ml of water acidified with 1–2 ml of hydrochloric acid (with KOH). The organic phase was separated, the aqueous phase was extracted with diethyl ether (2 × 50 ml), the extracts were combined with the organic phase, washed with water, dried over $MgSO_4$, and evaporated under reduced pressure, and the residue was subjected to vacuum distillation to isolate fractions boiling in the temperature range from 48 to 51°C (1 mm) (mixture of compounds **Va**–**VIIIa**) or from 85 to 88°C (1 mm) (**Vb**–**VIIIb**).

2-Allyloxymethyl-6-methylene-1,4-dioxane (Va). ^{1}H NMR spectrum of the cyclic fragment, δ, ppm: 3.60–4.00 m (4H, CH$_2$OCH$_2$), 4.24 s (2H, *exo*-C=CH$_2$). ^{13}C NMR spectrum, δ_C, ppm: 66.14 (CH**C**H$_2$O), 66.68 (O**C**H$_2$C=), 73.80 (OCH), 91.73 (C=**C**H$_2$), 154.26 (**C**=CH$_2$). The other ^{1}H and ^{13}C resonance signals were obscured by signals of isomeric cyclic compounds.

6-Methylene-2-[2-(vinyloxy)ethoxymethyl]-1,4-dioxane (Vb). ^{1}H NMR spectrum of the cyclic fragment, δ, ppm: 3.60–4.00 m (4H, CH$_2$OCH$_2$), 4.43 s (2H, *exo*-C=CH$_2$). ^{13}C NMR spectrum, δ_C, ppm: 65.64 and 66.16 (CH$_2$OCH$_2$), 75.19 (OCH), 91.32 (C=**C**H$_2$), 154.45 (**C**=CH$_2$). Signals from the other fragments in the spectra of mixtures of isomeric products were difficult to assign.

2-Allyloxymethyl-2,3-dihydro-5*H*-1,4-dioxepine (VIa). ^{1}H NMR spectrum of the cyclic fragment, δ, ppm: 3.60–4.00 m (4H, CH$_2$OCH$_2$), 4.62 d.d.d (1H, 6-H, $J_{6,7}$ = 7.58, ^3J = 4.89, ^3J = 3.67 Hz), 6.24 d.d.d (1H, 7-H, $J_{6,7}$ = 7.58, ^4J = 2.08, ^4J = 0.98 Hz). ^{13}C NMR spectrum, δ_C, ppm: 66.13 and 67.50 (CH$_2$OCH$_2$), 72.80 (OCH), 105.55 (C^6), 145.09 (C^7). The other ^{1}H and ^{13}C resonance signals were obscured by signals of isomeric cyclic compounds.

2-[2-(Vinyloxy)ethoxymethyl]-2,3-dihydro-5*H*-1,4-dioxepine (VIb). ^{1}H NMR spectrum, δ, ppm: 3.60–4.00 m (4H, CH$_2$OCH$_2$), 4.77 d.d.d (1H, 6-H, $J_{6,7}$ = 7.60, ^3J = 4.91, ^3J = 3.63 Hz), 6.35 d.d.d (1H, 7-H, $J_{6,7}$ = 7.60, ^4J = 2.09, ^4J = 1.00 Hz). ^{13}C NMR spectrum, δ_C, ppm: 67.65 and 69.08 (CH$_2$OCH$_2$), 74.46 (OCH), 105.89 (C^6), 145.33 (C^7). The other ^{1}H and ^{13}C

resonance signals were obscured by signals of isomeric cyclic compounds.

2-Vinyl-1,3-dioxolane **VIIa** and 2,3-dihydro-1,4-dioxine **VIIIa** were isolated as individual substances by column chromatography on Silica gel 60 (0.063–0.200 mm) using benzene as eluent.

(*d,l*/*meso*)-4-Allyloxymethyl-2-vinyl-1,3-dioxolane (VIIa). ^{1}H NMR spectrum, δ, ppm: 3.38 d.d and 3.48 d.d (1H each, *d*/*l*-C^{5}H$_2$, *AB* part of *ABX* spin system, $^2J_{AB}$ = 10.00, $^3J_{AX}$ = $^3J_{BX}$ = 5.00 Hz), 3.44 d.d and 3.50 d.d (1H each, *meso*-C^{5}H$_2$, *AB* part of *ABX* spin system, $^2J_{AB}$ = 10.00, $^3J_{AX}$ = $^3J_{BX}$ = 5.50 Hz), 3.66 d.d and 4.06 d.d (1H each, *d,l*-4-CH$_2$, *AB* part of *ABX* spin system, $^2J_{AB}$ = 9.00, ^3J = 6.50, ^3J = 7.50 Hz), 3.76 d.d and 3.90 d.d (1H each, *meso*-4-CH$_2$, *AB* part of *ABX* spin system, $^2J_{AB}$ = 9.50, ^3J = 5.50, ^3J = 5.00 Hz), 3.96 m (2H, OC**H**$_2$CH=), 4.20 m (1H, *d*/*l*-4-H), 4.24 m (1H, *meso*-4-H), 5.12 d (2H, C**H**$_2$=CHCH$_2$), 5.21 d (2H, C**H**$_2$=CHCH$_2$, J_{trans} = 17.00 Hz), 5.16 d (1H, *d*/*l*-2-H, ^3J = 6.00 Hz), 5.29 d (1H, *meso*-2-H, ^3J = 5.38 Hz), 5.26 d (2H, *d*/*l*-C**H**$_2$=CHC^2, J_{cis} = 10.50 Hz), 5.29 d (2H, *meso*-C**H**$_2$=CHC^2, J_{cis} = 10.50 Hz), 5.41 d.d.d (2H, *d*/*l*-C**H**$_2$=CHC^2, J_{trans} = 17.36, ^2J = 1.10, ^4J = 0.98 Hz), 5.43 d.d.d (2H, *meso*-C**H**$_2$=CHC^2, J_{trans} = 17.36, ^2J = 1.10, ^4J = 0.86 Hz), 5.70–5.90 d.d.t (1H, CH$_2$=C**H**CH$_2$), 5.70–5.90 d.d.d (1H, CH$_2$=C**H**C^2). ^{13}C NMR spectrum, δ$_C$, ppm: 67.14 and 67.38 (C^5), 70.23 and 70.64 (=CH**C**H$_2$O), 72.25 (4-CH$_2$), 74.54 and 74.98 (C^4), 103.67 and 104.21 (C^2), 117.04 and 117.06 (**C**H$_2$=CHCH$_2$), 119.53 and 120.21 (**C**H$_2$=CHC^2), 134.35 (CH$_2$=**C**HCH$_2$), 134.42 and 134.52 (2-CH=).

(*d,l*/*meso*)-2-Vinyl-4-[2-(vinyloxy)ethoxymethyl]-1,3-dioxolane (VIIb). ^{1}H NMR spectrum, δ, ppm: 5.12 d (1H, OCHO, ^3J = 7.00 Hz), 5.25 d (1H, OCHO, ^3J = 7.00 Hz), 5.22 d (1H, C**H**$_2$=CHC^2, J_{cis} = 8.00, ^2J = 1.22, ^4J = 0.61 Hz), 5.24 d (1H, C**H**$_2$=CHC^2, J_{cis} = 8.00 Hz), 5.36 d (1H, C**H**$_2$=CHC^2, J_{trans} = 16.00 Hz), 5.38 d (1H, C**H**$_2$=CHC^2, J_{trans} = 16.00 Hz). The other ^{1}H resonance signals of compound **VIIb** were obscured by signals of the other isomeric cyclic ethers. ^{13}C NMR spectrum, δ, ppm: 67.06 and 67.39 (C^5), 74.60 and 74.88 (C^4), 104.08 and 104.59 (C^2), 120.06 and 120.65 (CH$_2$=), 134.40 and 134.52 (**C**H=C).

(*d,l*/*meso*)-4-(1-Propenyloxymethyl)-2-vinyl-1,3-dioxolane (VIIc). ^{1}H NMR spectrum, δ, ppm: 1.55 d.d (3H, Me, ^3J = 6.85, ^4J = 1.59 Hz), 1.56 d.d (3H, Me, ^3J = 6.85, ^4J = 2.08 Hz), 3.88 d.d (1H, CHC**H**$_2$O, *A* part of *AB* quartet, J_{AB} = 8.19, ^3J = 5.14 Hz), 3.96 d.d (1H, CHC**H**$_2$O, *B* part of *AB* quartet, J_{AB} = 8.19, ^3J = 6.72 Hz), 4.13 m (1H, OC**H**CH$_2$), 4.39 d.q (1H, MeC**H**=, ^3J = 6.85, J_{cis} = 6.60 Hz), 5.22 d (1H, OCHO, ^3J = 6.11 Hz), 5.33 d (1H, OCHO, ^3J = 5.33 Hz), 5.32 d.d.d (1H, C**H**$_2$=CH, J_{cis} = 10.27 Hz), 5.34 d.d.d (1H, C**H**$_2$=CH, J_{cis} = 10.30, ^2J = 1.22, ^4J = 0.61 Hz), 5.46 d.d.d (1H, C**H**$_2$=CH, J_{trans} = 17.24, ^2J = 1.22, ^4J = 0.73 Hz), 5.47 d.d.d (1H, C**H**$_2$=CH, J_{trans} = 17.24, ^2J = 1.22, ^4J = 0.73 Hz), 5.95 m (1H, OCH=). Signals from the =CHOCH$_2$ fragment were overlapped by signals from the OCH$_2$ groups of dioxine derivative **VIII**. ^{13}C NMR spectrum, δ, ppm: 9.22 (Me), 67.11 and 67.22 (C^5), 71.88 and 72.18 (4-CH$_2$), 74.48 and 74.91 (C^4), 103.58 and 104.13 (C^2), 119.43 and 120.11 (CH$_2$=), 134.37 and 134.46 (**C**H=C), 134.40 and 134.51 (Me**C**H=), 145.57 and 145.58 (OCH=).

2-Allyloxymethyl-6-methyl-2,3-dihydro-1,4-dioxine (VIIIa). ^{1}H NMR spectrum, δ, ppm: 1.66 d (3H, Me, ^4J = 1.22 Hz), 3.53 d.d (1H, OC**H**$_2$CH, *A* part of *AB* quartet, $^2J_{AB}$ = 10.27, ^3J = 5.75 Hz), 3.60 d.d (1H, OC**H**$_2$CH, *B* part of *AB* quartet, J_{AB} = 10.27, ^3J = 5.14 Hz), 3.75 d.d (1H, 3-H, *A* part of *AB* quartet, J_{AB} = 11.00, ^3J = 6.97 Hz), 4.06 d.d (1H, 3-H, *B* part of *AB* quartet, J_{AB} = 11.00, ^3J = 2.32 Hz), 4.06 d.t (2H, =CHC**H**$_2$O, ^3J = 5.75, ^4J = 1.34 Hz), 4.12 m (1H, CHO), 5.18 d.d.t (1H, C**H**$_2$=CH, J_{cis} = 10.39, ^2J = ^4J = 1.34 Hz), 5.26 d.d.t (1H, C**H**$_2$=CH, J_{trans} = 17.24, ^2J = ^4J = 1.47 Hz), 5.77 q (1H, 5-H, ^4J = 1.22 Hz), 5.88 d.d.t (1H, C**H**=CH$_2$, J_{trans} = 17.24, J_{cis} = 10.39, ^3J = 5.75 Hz). ^{13}C NMR spectrum, δ$_C$, ppm: 15.65 (Me), 64.86 (C^3), 68.64 (O**C**H$_2$CH=), 72.03 and 72.33 (2-CH$_2$), 74.58 and 75.02 (C^2), 117.16 (CH$_2$=), 121.10 (C^5), 133.21 (C^6), 134.36 (**C**H=CH$_2$).

6-Methyl-2-[2-(vinyloxy)ethoxymethyl]-2,3-dihydro-1,4-dioxine (VIIIb). ^{1}H NMR spectrum, δ, ppm: 1.66 d (3H, Me, ^4J = 1.2 Hz), 3.90 d.d (1H, CH$_2$=, J_{cis} = 8.00, ^2J = 2.40 Hz), 4.00 m (1H, CHO), 4.08 d.d (1H, CH$_2$=, J_{trans} = 16.00, ^2J = 2.40 Hz), 5.68 q (1H, 5-H, ^4J = 1.2 Hz), 6.37 d.d (1H, OCH=, J_{trans} = 16.00, J_{cis} = 8.00 Hz). ^{13}C NMR spectrum of the cyclic fragment, δ$_C$, ppm: 15.53 (Me), 64.63 (C^3), 74.91 (C^2), 121.04 (C^5), 133.02 (C^6). The other ^{1}H and ^{13}C resonance signals were obscured by signals of isomeric compounds.

6-Methyl-2-(1-propenyloxymethyl)-2,3-dihydro-1,4-dioxine (VIIIc). ^{1}H NMR spectrum, δ, ppm: 1.55 d.d (3H, **Me**CH=, ^3J = 6.83, ^4J = 1.71 Hz), 1.65 d (3H, 6-Me, ^4J = 1.22 Hz), 3.87 d.d (1H, 2-CH$_2$, *A* part of *AB* quartet, J_{AB} = 10.88, ^3J = 5.14 Hz), 4.03 d.d (1H, 3-H, *A* part of *AB* quartet, J_{AB} = 11.00, ^3J = 2.32 Hz), 3.67–3.82 (2H, 2-CH, 3-H, *B* parts of overlapping *AB* quartets from OCH$_2$ groups), 4.28 m (1H, OCH),

4.41 d.q (1H, MeC**H**=, J_{cis} = 6.7, ^3J = 6.6 Hz), 5.77 q (1H, 5-H, ^4J = 1.22 Hz), 5.93 d.q (1H, OC**H**=CH, J_{cis} = 6.7, ^4J = 1.71 Hz). ^{13}C NMR spectrum, δ, ppm: 9.20 (**Me**CH=), 15.80 (6-Me), 64.67 (C^3), 70.81 (2-CH_2), 72.95 (C^2), 121.32 (C^5), 133.40 (C^6), 134.50 (Me**C**H=), 145.60 (OCH=).

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