Vinyl Ethers Containing an Epoxy Group: XXIII.*
Reactions of Alkynylmagnesium Bromides
with Glycidol Ethers: Synthesis and Thermal Transformations
of 1-[2-(Vinyloxy)ethoxy]- and 1-(Allyloxy)-5-hexyn-2-ols,
-5-phenyl-4-pentyn-2-ols, and -3-bromo-2-propanols

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Abstract—Reaction of 2-[2-(vinyloxy)ethoxy]methyl- and 2-(allyloxymethyl)oxiranes with 2-propynyl- and phenylethynylmagnesium bromides (10–55°C, 0.5–4 h) resulted in new representatives of the series of 1-organyloxy-5-hexyn-2-ols, -5-phenyl-4-pentyn-2-ols, and -3-bromo-2-propanols in 50–99% yields. During distillation the 1-[2-(vinyloxy)ethoxy]-5-phenyl-4-pentyn-2-ol and -3-bromo-2-propanol transform respectively into 2-methyl-4-(3-phenyl-2-propynyl)- and 2-methyl-4-(bromomethyl)-1,3,6-trioxocanes via intramolecular cyclization involving the hydroxy and vinyloxy groups.

The reaction of organomagnesium compounds (Grignard [2, 3] and Iotsich reagents [3, 4]) with oxiranes is a classical building up method of alcohol synthesis (with formation of a C–C bond) [3, 5–11], also used for acetylene and allene alcohols [6–11]. The best studied reaction is that of the Grignard reagents with the simplest epoxides: unsubstituted oxirane, methyl-, phenyl-, 2,2-dimethyl-, and 2,3-dimethyloxiranes, although other examples of this process are also described (with naturally occurring epoxides, epoxyalcohols, epoxyketones, epoxyesters, diepoxides etc.) [5–11]. The reaction finds an industrial application in production of various technically important alcohols, in particular, those used in fragrance industry: 2-phenyl-1-ethanol (rose oil) [12], 3-phenyl-1-propanol (with the hyacinth fragrance) [13], 3,7-dimethyl-6-octen-1-ol (rhodinol) with a rose scent [14], alcohols with the properties of sex attractants and plant growth regulators. [15].

The preparation was reported of chiral homoallyl alcohols in reaction of vinylmagnesium halides with glycidol derivatives containing as protection functions benzyl, methoxtphenylmethyl, *tert*-butyldimethylsilyl, and *tert*-butyldiphenylsilyl groups [16]. (*R*)-1-(Benzyloxy)-5-hexen-2-ol, the key intermediate in the stereoselective synthesis of *trans*-2,5-dioxymethylpyrrolidone derivatives posses-

sing C_2-symmetry, was obtained by treating with allylmagnesium chloride the optically active (*S*)-2-[(benzyloxy)methyl]oxirane [17]; reactions were performed of 2-(methoxymethyl)- and 2-(phenoxymethyl)-oxiranes with ethyl- and phenylmagnesium bromides [18].

Alkynols and allenols originate from both reactions of alkynylmagnesium halides with oxiranes [6–10] and of 2-ethynyloxiranes with Grignard reagents 11]. The alkynols combining the properties of the three most important classes of organic compounds (alcohols [19], acetylenes [20], and CH-acids when the compounds contained fragments C≡CH and/or $CH_2C≡C$ [21, 22]) are valuable intermediates in preparation of a lot of synthetically and commercially significant products (chemicals for agriculture, drugs, and fragrant substances [9, 23]). They are widely used in the synthesis of functionalized acetylene alcohols and diols [1, 24], heterocycles, including derivatives of furan [25], pyran [26], pyrrole [27], indole [28], pyrazole [29], 2,3-dihydropyridine, pyridine [30], benzazepine-1,5-dione [31], thiophene [32], various allene systems [20, 23, 24, 33], in particular, allenols that are invaluable monomers and key building blocks [23, 24, 34], naturally occurring compounds: indolizine [35] and quinolizine [36] alkaloids, etc.

In extension of our systematic investigations in the area of the chemistry of unsaturated glycidol ethers [1,

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* For communication XXII, see [1].

37, 38] we studied for the first time reactions of 2-[2-(vinyloxy)ethoxy]methyl- (**Ia**) and 2-(allyloxymethyl)- (**Ib**) oxiranes with organomagnesium reagents, in particular, with alkynylmagnesium halides: 2-propynylmagnesium bromide (**IIa**) and phenylethylylmagnesium bromide (**IIb**), aiming also on developing a preparation procedure for new representatives of polyfunctional acetylene alcohols: 1-[2-(vinyloxy)ethoxy]- (**IIIa** and **IVa**) and 1-(allyloxy)- (**IIIb** and **IVb**) -5-hexyn-2-ols and -5-phenyl-4-pentyn-2-ols, promising monomers and intermediate products for organic synthesis, also for the synthesis of heterocyclic structures [1, 38].

First representatives of this type compounds, namely, 1-[ω-(vinyloxy)alkoxy]-4-pentyn-2-ols, were obtained formerly by reaction of 2-[ω-(vinyloxy)alkoxy]methyl-oxiranes, including oxirane **Ia**, with lithium acetylide [39] or sodium acetylide [40] in liquid ammonia. The epoxy ring opened at the side of the most hydrogenized carbon affording compounds with a secondary hydroxy group [41]. These results are in agreement with our [1, 37, 38] and other published data [10, 42] showing that the base-catalyzed opening of the oxirane ring occurs as a rule with the attack of the nucleophile on the least substituted carbon atom (β-opening); in the terminal oxiranes this is the methylene carbon atom (cleavage of the $O-CH_2$ bond).

The reaction of organomagnesium compounds with substituted oxiranes commonly affords mixtures of alcohols (primary and/or secondary) originating from both the normal Grignard reagent addition and from the ring opening under the action of diorganylmagnesium and/or magnesium halide ($2\,RMgX \rightleftarrows MgX_2 + MgR_2$) [3, 5, 6]. In the latter case a formation of the corresponding halohydrins is observed. Sometimes the competing reaction providing halohydrins becomes the main pathway. The process can be additionally complicated by

isomerization of the oxirane into a ketone catalyzed by magnesium halides followed by reaction of the ketone with RMgX to give a secondary alcohol. The output of the reaction (yields, the structure and the ratio of products) as expected depends essentially both on the character of the reagents (of oxirane as well as the Grignard reagent), on the factors governing their reactivity (stereoelectronic effects of substituents), and on the reaction conditions (solvent, catalyst, molar ratio and concentration of the initial reagents, method of their introduction, temperature and duration of the synthesis). The terminal oxiranes gave rise predominantly to secondary alcohols (with selectivity 80–100%) [5, 6], and in going from RMgCl to RMgI the proportion of the secondary alcohol often (but not always) grew [6]. The crucial factor in these processes is the temperature. When the initially formed complex of the Grignard reagent with oxirane is treated with water without preliminary heating the resulting product is a halo-hydrin. The yield of the latter decreases with growing temperature of the treatment before decomposition of the complex (boiling in the ethyl ether [43] or replacement of the ether by a higher boiling solvent [44, 45]). However a better method preventing nearly completely the halohydrin formation consists in distilling off the ether before the treatment of the reaction mixture [46], or in precipitation of MgX_2 by adding dioxane [45].

We used as solvents ethyl ether and tetrahydrofuran. The synthesis of 2-propynylmagnesium bromide (**IIa**) (from 3-bromo-1-propyne and magnesium in the presence of $HgCl_2$) and its reaction with oxirane **I** was carried out in ethyl ether.

The reaction progress was monitored by the decrease in intensity till complete disappearance of the absorption band at 3000 cm^{-1} belonging to the stretching vibrations of the C–H bond in the epoxy ring and by simultaneous appearance of the absorption bands of the hydroxy (3400–
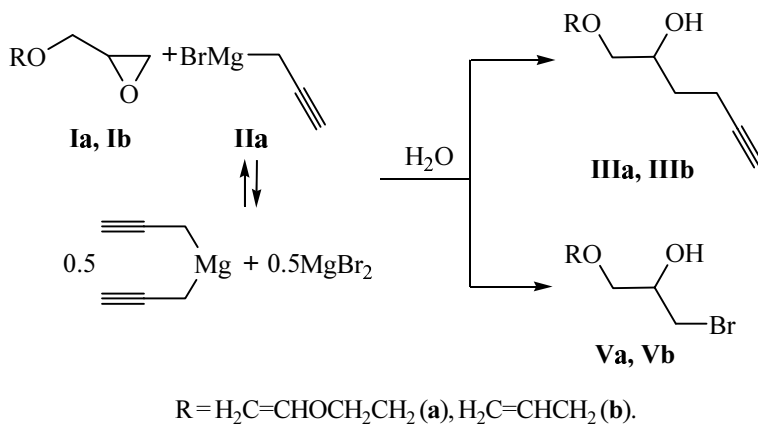

R = H$_2$C=CHOCH$_2$CH$_2$ (**a**), H$_2$C=CHCH$_2$ (**b**).

Table 1. Reaction conditions [molar ratio oxirane **I**–2-propynylmagnesium bromide (**IIa**) 1:1.1-1.8][a], yields, and characteristics of 1-[2-(vinyloxy)ethoxy]- (**IIIa**) and 1-(allyloxy)- (**IIIb**) -5-hexyn-2-ols and 1-[2-(vinyloxy)ethoxy]- (**Va**) and 1-(allyloxy)- (**Vb**) -3-bromo-2-propanols

| Run no. | Oxirane **I**, mol | RMgBr **IIa**, mol | Et$_2$O, ml | Time, min | Reaction product prior to distillation | | Main fraction | | | | | |
					n_D^{20}	yield, %[b]	bp, °C (≤ 1 mm Hg)	n_D^{20}	yield, %	5-hexyn-2-ol **III**, %[d]	3-bromo-2-propanol **V**, %[d]	bromine, %[e]
1	0.06 (**Ia**)	0.11	60	60	1.4680	~85	92–93	1.4700	61	85.6	14.4	5.12
2	0.06 (**Ia**)	0.11	60	40	1.4650	~100	86–87	1.4720	64	57.6	42.4	15.05
3	0.08 (**Ia**)	0.11	60	f	–	~63	86–92	1.4700	3219	70.1	29.9	10.61
							96–104	1.4890		40.1	59.9	20.94
4[g]	0.06 (**Ia**)	0.10	60	60	1.4658	~57[h]	90–91	1.4680	26	95.8	4.2	1.50
5[g]	0.06 (**Ia**)	0.11	50	30	1.4709	~100[h,i,j]	–	–	–	68.2[k]	31.8[k]	11.28[k]
6	0.04 (**Ib**)	0.05	40	a	–	~100	67–68	1.4700	72	66.4	33.6	13.76
7	0.10 (**Ib**)	0.11	50	a	1.4700	~96[i]	–	–	–	44.0[k]	55.0[k]	22.57[k]
8	0.08 (**Ib**)	0.11	40	a	1.4770	~85	60–64	1.4770	57	50.0[l]	50.0[l]	–
9[g]	0.08 (**Ib**)	0.11	50	a	1.4740	~100[h,m]	60–61	1.4778	41	34.2	65.8	27.00

[a] After adding oxirane **I** to a solution of RMgBr **IIa** in Et$_2$O (at −1...4°C within 20−40 min) the temperature of the reaction mixture was raised to 20°C (in reaction with oxirane **Ia**) during the time indicated in Table 1. In the case of oxirane **Ib** the reaction mixture was worked up as soon as it warmed to 10°C.

[b] Calculated on oxirane **I**.

[c] After a vacuum distillation of the crude product.

[d] Calculated from the bromine content in the reaction products.

[e] According to elemental analysis.

[f] The reaction mixture was worked up immediately after oxirane addition.

[g] In the presence of 0.5 g of CuBr.

[h] Contains ~5% of allenol **VI**.

[i] The compound was not distilled.

[j] Without additional purification with the help of Al$_2$O$_3$.

[k] Before distillation.

[l] Compounds content was calculated from the ^{1}H NMR spectra (from the integral intensity of signals of OH groups: δ 2.89 s for compound **IIIb** and 3.10 d for compound **Vb**).

3450 cm^{-1}) and 2-propynyl (~2130 and 3300 cm^{-1}) groups. The conversion of the initial oxiranes **Ia** and **Ib** was estimated from the integral intensity of the epoxy ring signals [δ 3.08–3.10 m (1H, OCH), 2.73–2.74 d.d and 2.55–2.56 q (2H, OCH$_2$)] and/or of the hydroxy groups (δ 2.84–2.89 s) in the ^{1}H NMR spectra. The reaction with oxirane **Ib** was also monitored by TLC.
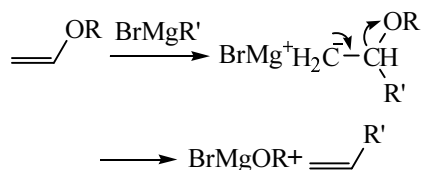
Reaction conditions, yields, and characteristics of the products obtained from oxiranes **I** and 2-propynyl-magnesium bromide (**IIa**) are presented in Table 1.

The results obtained are in general consistent with the published data [5–7, 10]. Under conditions we studied two competing reaction pathways occur providing alongside the normal reaction product, 1-[2-(vinyloxy)-ethoxy]- and 1-(allyloxy)-5-hexyn-2-ol (**IIIa and IIIb**), the corresponding secondary bromohydrin, 1-[2-(vinyl-oxy)ethoxy]- and 1-(allyloxy)-3-bromo-2-propanol (**Va** and **Vb**). The structure of initial oxirane **I** exerts stronger influence on the products ratio (namely, on the reaction pathway) than on their overall yield. The highest content (~86–96%) of 5-hexyn-2-ol **III** in the products mixture was obtained in reaction of ~1.8-fold molar excess of 2-propynylmagnesium bromide (**IIa**) with oxirane **Ia** (Table 1, runs nos. *1* and *4*). The comparison of results

of runs nos. *1* and *4* shows that the reaction carried out in the presence of catalytic quantities of CuBr favors increase in the products mixture of 1-[2-(vinyloxy)ethoxy]-5-hexyn-2-ol (**IIIa**) (up to 96%) but negatively influences the overall yield reducing it from 85 to 57%. A part of the substance was probably lost in the course of the flash-chromatography on Al_2O_3 (aimed at removal of CuBr traces), for in a similar run without additional purification with the help of Al_2O_3 the yield of the reaction products was virtually quantitative (Table 1, run no. *5*). In all experiments reported in Table 1 (runs nos. *1–5*) the content in the mixture of 5-hexyn-2-ol **IIIa** was 1.4–23 times greater than that of 3-bromo-2-propanol **Va**.

Under conditions used in our experiments we did not observe any decomposition of the vinyloxy group in reactions of oxirane **Ia** with 2-propynylmagnesium bromide (**IIa**) and the other organomagnesium compounds used in this study and considered further; it was however known [47] that the action of the Grignard reagents caused the cleavage of vinyl ethers into the corresponding alkoxides and olefins.

$$\underset{}{=}\!\!/^{OR} \xrightarrow{BrMgR'} BrMg^+H_2\bar{C}\!-\!\underset{R'}{\overset{OR}{\underset{|}{CH}}}$$

$$\xrightarrow{} BrMgOR + \underset{}{=}\!\!/^{R'}$$

The reaction with oxirane **Ib** of 2-propynylmagnesium bromide (**IIa**) taken in ~1.1–1.4-fold molar excess also furnished a mixture of two compounds, 5-hexyn-2-ol **IIIb** and 3-bromo-2-propanol **Vb** (Table 1, runs nos. *6–9*), but their relative amounts notably differed from the ratio of compounds **IIIa** and **Va** obtained under similar conditions (Table 1, run nos. *1–5*). The maximum content of 1-(allyloxy)-5-hexyn-2-ol (**IIIb**) in the distillation products reached 66% and was obtained in a single run (Table 1, run no. *6*). In other cases 5-hexyn-2-ol **IIIb** formed in amount equal to or less than that of the corresponding 3-bromo-2-propanol **Vb** (Table 1, run nos. *7–9*). The overall yield of products in reaction carried out in the presence of CuBr remained unchanged [in contrast to the analogous reaction of reagent **IIa** with oxirane **Ia** (Table 1, run no. *4*)], but unexpectedly the ratio of products significantly changed in favor of 3-bromo-2-propanol **Vb** whose content grew up to 66% (Table 1, run no. *9*). The greater content of 3-bromo-2-propanol in the reaction products obtained from reagent **IIa** with oxirane **Ib** may to a certain extent originate

from the lower temperature (10°C) of the work-up of the reaction complex than in the runs with oxirane **Ia**.

The results obtained do not suggest any sound conclusion on a correlation between the process parameters studied and the relative yield of 5-hexyn-2-ols **III** and the corresponding 3-bromo-2-propanols **V**. The data presented in Table 1 show that the runs carried out under quite similar conditions furnish products with bromine content according to the elemental analysis varying from 5.1 to 20.9% (run nos. *1–3*) or from 1.5 to 11.3% (experiments with CuBr, runs nos. *4* and *5*) for oxirane **Ia**, and from 13.8 to 22.6% (runs nos. *6* and *7*) for oxirane **Ib**. The content of the corresponding 3-bromo-2-propanol (calculated from the analysis data) varies respectively from 14 to 60% and from 4.2 to 31.8% for oxirane **Ia** and from 33.6 to 55% for oxirane **Ib**.

According to the published data [22, 48] 2-propynyl-magnesium halides react with electrophiles as a rule predominantly or exclusively in the allene form $H_2C=C=CHMgX$ affording allene and/or acetylene derivatives depending on the electrophile character. In our case allenols **VIa** and **VIb** might arise. The latter may also result from a prototropic isomerization of 5-hexyn-2-ols **III**. However an allene fragment did not give rise either to the absorption bands in the IR spectra or to any signals in the NMR spectra of the reaction products. On the contrary, the acetylene structure of these compounds is confirmed by the presence of absorption bands at 2120–2130 (C≡C) and 3280–3300 (H–C≡) cm^{-1} in the IR spectra and of signals at 1.89–1.96 t (1H, HC≡) and 2.33–2.34 t (2H, $CH_2C≡$) ppm in the ^{1}H NMR spectra.

IIIa, IIIb   **VIa, VIb**

$R = H_2C=CHOCH_2CH_2$ (**a**), $H_2C=CHCH_2$ (**b**).
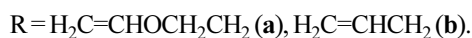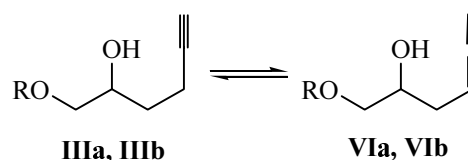
Only in the runs carried out in the presence of CuBr (Table 1, run nos. *4*, *5*, *9*) the reaction mixture contained insignificant amounts (no more than 5%) of allene derivatives. Then in the IR spectrum a characteristic absorption band of allene fragment appeared in the region 1950 cm^{-1} with the corresponding weak peaks at δ 5.44 d ($CH_2=$) and 6.72 t (CH=) ppm in the ^{1}H NMR spectra.

The addition of allenylmagnesium bromide (2.5 M solution in Et_2O) the carbohydrate derivatives of

Table 2. Reaction conditions [molar ratio oxirane **I** phenylethynylmagnesium bromide (**IIb**) 1:1–1.2, THF] and yields of 1-[2-(vinyloxy)ethoxy]- (**IVa**) and 1-(allyloxy)- (**IVb**) -5-phenyl-4-pentyn-2-ols, 1-[2-(vinyloxy)ethoxy]- (**Va**) and 1-(allyloxy)- (**Vb**) -3-bromo-2-poppanols and 2-methyl-4-(3-phenyl-2-poppynyl)- (**VIII**) and 2-methyl-4-(bromomethyl)- (**IX**) -1,3,6-trioxocanes

Run no.	Oxirane (I), mol	RMgBr (IIb), mol	Temperature, °C	Time, h	Reaction products before distillation, %				Reaction products after distillation, %			
					yield	ethynyl-benzene[a]	IV[a]	V[a]	IV	V	VIII	IX
1	0.10 (**Ia**)	0.10	20	1	57	56	–	44	–	65		traces
2	0.05 (**Ia**)	0.05	25	2	72	50	–	50	–	52	–	<5
3	0.10 (**Ia**)	0.12	45	0.5	78	20	5	75	–	–	–	–
4	0.10 (**Ia**)	0.10	50–55[c]	4	60	36	14	50	–	33	11	11
5	0.10 (**Ia**)	0.12	50–55[c]	2	87	10	10	80	–	75	12[d]	10[d]
6	0.10 (**Ib**)	0.12	50–55[c]	4	65	45	15	40	35	50	–	–
7[e]	0.10 (**Ib**)	0.12	35	2	56	50	10	40	25	50	–	–

[a] Compounds content was calculated from the ^{1}H NMR spectra (from the integral intensity of signals from OH groups).

[b] Reaction products were not distilled.

[c] The reaction mixture was additionally kept for 16 h at 20°C.

[d] 1,3,6-Trioxocanes **VIII** and **IX** (1–1.5:2.5) were distilled together. The yield was calculated from the ^{1}H NMR spectrum and from the bromine content.

[e] Reaction was carried out in Et$_2$O.

spirocyclic oxiranes (Et$_2$O, –78°C, 1 h) was also reported [10] to afford acetylenic derivatives: either exclusively 4-pentyn-1-ol (yield 55–98%) or a mixture of 4-pentyn-1-ol (46%) and the corresponding bromohydrin (43%) depending on the oxirane structure.

In a vacuum distillation 5-hexyn-2-ols **III** and 3-bromo-2-propanols **V** give azeotrope mixtures boiling in a narrow temperature range (Table 1). The structure of compounds synthesized was confirmed by IR, ^{1}H and ^{13}C NMR spectra. In the ^{1}H NMR spectrum the hydroxy group of compounds **III** appears as a singlet at 2.84–2.89 ppm whereas the signal of OH in compound **V** is observed as a doublet in a weaker field, at 3.09–3.10 ppm.

The synthesis of phenylethynylmagnesium bromide (**IIb**) (from ethynylbenzene and ethylmagnesium bromide) and its reaction with oxirane **I** leading to 1-[2-(vinyloxy)ethoxy]- (**IVa**) and 1-(allyloxy)- (**IVb**) -5-phenyl-4-pentyn-2-ols and -3-bromo-2-propanols **V** were carried out in THF. The reagents ratios used were 1–1.2:1. The solution of oxirane **I** in THF was added dropwise to the solution of phenylethynylmagnesium bromide (**IIb**) in THF at room temperature, and then the stirring was continued for 0.5–16 h at 20–55°C. The decomposition of the reaction complex was performed with aqueous ammonium chloride.

The reaction progress was monitored by IR and ^{1}H NMR spectra of the reaction mixtures. Alongside the

$R = H_2C=CHOCH_2CH_2$ (**a**), $H_2C=CHCH_2$ (**b**).
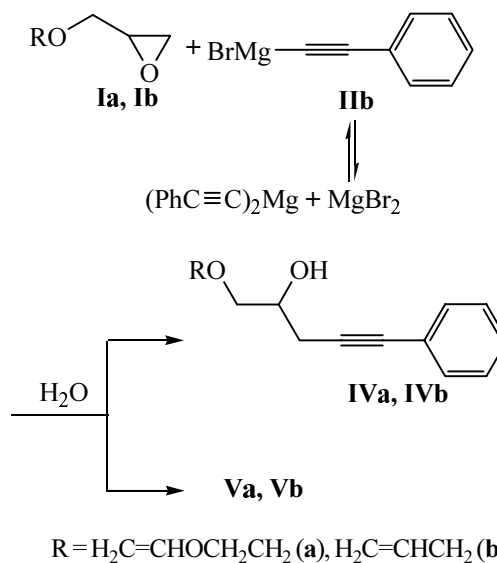
absorption band at 3000 cm^{-1} corresponding to the stretching vibrations of the C–H bond in the epoxy ring the absorptions of the internal C≡C bond (~2230 cm^{-1}) and of O–H bond (3400–3450 cm^{-1}) also were used as diagnostic bands.

Conditions of reactions between oxiranes **I** and phenylethynylmagnesium bromide (**IIb**) and their results are compiled in Table 2.

As seen from Table 2, in contrast to reaction of oxirane **I** with 2-propynylmagnesium bromide (**IIa**) the

only or the main (up to 80%) product of the reaction with phenylethynylmagnesium bromide (**IIb**) is 3-bromo-2-propanol **V**. In reaction of equimolar amounts of oxirane **Ia** and phenylethynylmagnesium bromide (**IIb**) at 20–25°C for 1–2 h no formation of 5-phenyl-4-pentyn-2-ol **IVa** was observed, and the only reaction product was 3-bromo-2-propanol **Va** (Table 2, runs nos. *1* and *2*). In the other runs 5-phenyl-4-pentyn-2-ol **IV** was detected in the reaction products in the amount of 5–15%. It should be noted that in the majority of the experiments the reaction mixture after work-up contained considerable amount of ethynylbenzene (up to 55%). The change of the 2-(vinyloxy)ethyl group for allyl in oxirane **Ib** did not considerably alter the pattern of its reaction with phenylethynylmagnesium bromide (**IIb**).

The results obtained caused by the different reactivity of 2-propynylmagnesium bromide (**IIa**) (Grignard reagent) and phenylethynylmagnesium bromide (**IIb**) (Iotsich reagent) in reaction with oxiranes **I** are well consistent with the known fact of the considerably higher activity of propargyl type carbanions –C–C≡C in the reactions with electrophiles as compared to that of acetylene carbanions –C≡C [21].

5-Phenyl-4-pentyn-2-ol **IVb** we succeeded to isolate by vacuum distillation in a virtually pure state [the impurity of 1-(allyloxy)-3-bromo-2-propanol (**Vb**) did not exceed 4% (Table 2, run no. *6*)]. The reaction mixture containing 5-phenyl-4-pentyn-2-ol **IVa** and the corresponding derivative of 3-bromo-2-propanol **Va** behaved differently. The presence in the structure of these compounds of a highly reactive vinyloxy group prone to electrophilic addition with proton-donor compounds and functions [37] resulted in proceeding (in the course of vacuum distillation) of a thermally induced intramolecular acetaliz-ation involving the hydroxy and vinyloxy groups to form oxygen-containing macrocycles. The intramolecular cyclization of compound **IVa** gave previously unknown 2-methyl-4-(3-phenyl-2-propynyl)-1,3,6-trioxocane (**VIII**) as a diastereomer mixture. The compound contained in the side chain a reactive acetylene fragment.

The cyclization providing a possibility to obtain in a high yield previously unknown 1,3,6-trioxacanes and 1,3,6,9-tetraoxacycloundecenes (a mixture of *d,l*- and *meso*-diastereomers)we carried out for the first time by an example of 1-[ω-(vinyloxy)alkoxy]-3-(OR)-2-propanols prepared from 2-[ω-(vinyloxy)alkoxy]-methyloxiranes, including oxirane **Ia**, and the appropriate alcohols ROH [R = HC≡CCH₂, H(CF₂)ₙCH₂, *n* = 2–8]. The cyclization occurred in the presence of the catalytic

quantity (~0.5–1 wt%) of CF_3CO_2H (Et_2O, 33–34°C, 7–20 h) [38].

Alongside compound **IVa** bromohydrin **Va** also suffered the thermal acetalization in the course of the vacuum distillation readily converting into the previously unknown 2-methyl-4-(bromomethyl)-1,3,6-trioxocane (**IX**) (a mixture of diastereomers). Compound **IX** might prove to be a unique starting substance for building up various molecular ensembles, containing rare and highly active trioxocane rings.

The distillation of compounds **IVa** and **Va** was not accompanied by formation via intermolecular oligo-merization of open-chain acetal structures of "head-to-tail" type as evidenced by the lack in the IR and NMR spectra of the absorption bands and signals belonging to hydroxy and vinyloxy groups.

Note that the distillation of mixtures of 1-[2-(vinyl-oxy)ethoxy]-5-hexyn-2-ol (**IIIa**) with bromohydrin **Va** did not induce the intramolecular cyclization.

The structure of compounds **VIII** and **IX** was confirmed by IR and NMR spectra. The acetal fragment gave rise to signals at δ_H 1.37 d (Me), 4.88 q (OCHO), and δ_C 20.70, 20.78 (Me) and 99.66, 99.87 (OCHO) ppm. The splitting of the acetal and other signals in ¹³C NMR spectra was due to the existence of the compounds as diastereomers mixtures.

Bringing into the reaction with 2-[2-(vinyloxy)-ethoxy]methyloxirane (**Ia**) of the simplest Iotsich reagent, ethynylmagnesium bromide (THF, 20°C, 1 h) resulted in exclusive formation of the derivative of 3-bromo-2-propanol **Va** in a 67% yield (oxirane **Ia** conversion 87%) in agreement with the reduced reactivity of carbanions generated from the terminal acetylenes (acetylene-magnesium compounds are considerably more inert than alkyl- and arylmagnesium derivatives [4]).

A successful synthesis of 1-[2-(vinyloxy)ethoxy]-4-pentyn-2-ol (**X**) was performed formerly via alkali metals acetylides [39–41].

1-Alkoxy-3-bromo-2-propanols **V** prepared by us are of obvious synthetic (not only as precucsors of cyclic ethers) and practical interest since the halohydrins, among them 1-alkoxy-3-halo-2-propanols, find various application, in particular, for drug synthesis, for agricultural chemicals, and cheap liquid crystals [49]. One way of a target preparation of bromohydrins is the opening of the oxirane ring effected by metal chlorides ($AlCl_3$, $ZnCl_2$) or concn. HCl [49], complexes of titanium tetraisopropoxide [Ti(OPr-*i*)₄] with the Grignard reagents [50] or haloids

(I_2, Br_2) [51]. However neither of the known methods is not fit for preparation, for example, of 1-[2-(vinyloxy)-ethoxy]-3-bromo-2-propanol (**Va**) contain-ing in the structure a functional group CH_2=CHO sensitive to the acid reagents.

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer Specord 75IR from thin films. ^1H and ^{13}C NMR spectra were registered on spectrometer Bruker DPX-400 [at operating frequencies 400 (^1H) and 100 MHz (^{13}C)] from~5–10% solutions of the samples in $CDCl_3$, internal reference HMDS.

All operations were carried out in an argon atmo-sphere. THF was purified first by dispersion of KOH and then by distillation over calcium hydride in the presence of benzophenone. Ethyl ether was dried by procedure from [52] and distilled before use. 2-[2-(Vinyloxy)ethoxy]methyloxirane (**Ia**) was synthesized from 2-vinyloxy-1-ethanol and 2-(chloromethyl)oxirane [53]. 3-Bromo-1-propyne was obtained from 2-propyn-1-ol, 2-propynylmagnesium bromide (**IIa**) was prepared by reacting magnesium with 3-bromo-1-propyne in Et_2O in the presence of $HgCl_2$, ethynyl- and phenylethynyl-(**IIb**) magnesium bromides were synthesized by treating in THF with ethylmagnesium bromide acetylene and ethynylbenzene respectively in keeping with procedures from [22]. The other reagents and solvents used in the study were commercial products.

Reaction of 2-propynylmagnesium bromide (IIa) with 2-[2-(vinyloxy)ethoxy]methyloxirane (Ia) (Table 1, runs nos. 1–5). *a*. To a solution of 110 mmol of 2-propynylmagnesium bromide (**IIa**) in 60 ml of Et_2O cooled to 0°C was added dropwise within ~40 min a solution of 60–80 mmol of oxirane **I** in ~5 ml of Et_2O keeping the reaction mixture temperature at 0–4°C. Then the cooling was removed, and after stirring for the time indicated in Table 1 the reaction mixture was poured into ~400 ml of water mixed with ice and acidified with HCl. The organic layer was separated, the water layer was extracted with ethyl ether, the combined organic solutions were washed with water, and dried over $MgSO_4$, the solvent was removed on a rotary evaporator, and the residue was distilled in a vacuum in the presence of a little hydroquinone.

b. To a solution of 110 mmol of 2-propynylmagnesium bromide (**IIa**) in 60 ml of Et_2O cooled to 0°C was added 0.5 g of finely ground powder of CuBr (the solution color changed from virtually black to dark-green), and then

within ~20 min was added dropwise a solution of 60 mmol of oxirane **Ia** in 10 ml of Et_2O, maintaining the reaction temperature at 0–4°C (the reaction mixture turned red-brown). Then the cooling was removed, and after stirring for 0,5 h more to the reaction mixture was added a solution of 20 g of NH_4Cl and 1.5 g of NaCN in 150 ml of water. The reaction products were extracted into ethyl ether, the combined organic solutions were dried over $MgSO_4$, the solution was passed through a small bed of neutral Al_2O_3, the solvent was removed under reduced pressure, and the residue was distilled. Yield of compound **IIIa** 2.9 g, bp 90–91°C (1 mm Hg), content of the main substance ~96% (NMR) (Table 1, run no. *4*). Run no. *5* (Table 1) was carried out similarly but without purification with Al_2O_3.

1-[2-(Vinyloxy)ethoxy]-5-hexyn-2-ol (IIIa). IR spectrum, cm^{-1}: 1620 (C=C), 2120 (C≡C), 3280 (H–C≡), 3450 (O–H). ^1H NMR spectrum, δ, ppm: 1.52 q (2H, C$\underline{H}_2$CH$_2$C≡), 1.89 t (1H, HC≡), 2.33 t (2H, CH$_2$C≡), 2.84 s (1H, OH), 3.37, 3.49 d.d.d (2H, OC$\underline{H}_2$CH), 3.68, 3.81 d.t (4H, OCH$_2$CH$_2$O), 3.91 m (1H, C$\underline{H}$OH), 4.00 d.d (1H, CH$_2$=, *cis*), 4.17 d.d (1H, CH$_2$=, *trans*), 6.43 d.d (1H, OCH=). ^{13}C NMR spectrum, δ, ppm: 14.63 ($\underline{C}$H$_2$C≡), 31.68 ($\underline{C}$H$_2$CH$_2$C≡), 67.14 ($\underline{C}$H$_2$OCH=), 67.18, 68.63 (HC≡, CHOH), 69.81 ($\underline{C}$H$_2$CH$_2$OCH=), 75.22 (O$\underline{C}$H$_2$CH), 83.92 (C≡), 86.90 (CH$_2$=), 151.55 (OCH=).

Reaction of 2-propynylmagnesium bromide (IIa) with 2-(allyloxymethyl)oxirane (Ib) (Table 1, runs nos. 6–9). *a*. To a solution of 50 mmol of 2-propynyl-magnesium bromide (**IIa**) in 40 ml of Et_2O cooled to 0°C was added dropwise 40 mmol of oxirane **Ib** maintaining the reaction temperature at –1...–0°C. Then the reaction mixture was warmed to 10°C and after analyzing the products by TLC (SiO_2, $CHCl_3$) the reaction mixture was poured into iced water acidified with HCl. The organic layer was separated, the water layer was extracted with ethyl ether, the combined organic solutions were washed with water and dried over K_2CO_3, the solvent was removed on a rotary evaporator. The residue (mobile yellow liquid) was distilled in a vacuum.

b. To a solution of 110 mmol of 2-propynylmagnesium bromide (**IIa**) in 50 ml of Et_2O was added 0.5 g of CuBr (the color of the solution changed from black to red), the mixture was cooled to 0°C, and 80 mmol of oxirane **Ib** was added dropwise maintaining the temperature at –1–0°C. Then the reaction mixture was warmed to 10°C and after analyzing the products by TLC (Silufol, Et_2O–benzene, 5:1) the reaction mixture was cooled to–5°C

and treated with a solution of 20 g of NH$_4$Cl and 1.5 g of NaCN in 150 ml of water. The organic layer was separated, the water layer was extracted with ethyl ether (4×70 ml), the combined organic solutions were washed with water and dried over K$_2$CO$_3$, the solution was passed through a small bed of neutral Al$_2$O$_3$, the solvent was removed on a rotary evaporator, and the residue was distilled in a vacuum.

1-(Allyloxy)-5-hexyn-2-ol (IIIb). IR spectrum, cm^{-1}: 1640 (C=C), 2130 (C≡C), 3300 (H–C≡), 3450 (O–H). ^{1}H NMR spectrum, δ, ppm: 1.65 q (2H, C$\underline{H}_2$CH$_2$C≡), 1.96 t (1H, HC≡), 2.34 t.d (2H, CH$_2$C≡), 2.89 br.s (1H, OH), 3.32, 3.44 q (2H, OC$\underline{H}_2$CH), 3.90 m (1H, C$\underline{H}$OH), 4.00 d (2H, OC$\underline{H}_2$CH=), 5.17 d.d.t (1H, CH$_2$=, *cis*), 5.26 d.d.t (1H, CH$_2$=, *trans*), 5.89 d.t (1H, CH=). ^{13}C NMR spectrum, δ, ppm: 14.81 (C$\underline{H}_2$C≡), 31.97 (C$\underline{H}_2$CH$_2$C≡), 68.79 (HC≡), 69.10 (CHOH), 72.30 (OC$\underline{H}_2$CH=), 74.28 (OC$\underline{H}_2$CH), 84.07 (C≡), 117.44 (CH$_2$=), 134.45 (CH=).

1-[2-(Vinyloxy)ethoxy]-5-phenyl-4-pentyn-2-ol (IVa) and 1-(allyloxy)-5-phenyl-4-pentyn-2-ol (IVb) (Table 2). *a.* To a solution of 50–120 mmol of phenylethynylmagnesium bromide (**IIb**) in 40 ml of THF at 4–23°C was added dropwise a solution of 50–100 mmol of oxirane **I** in 3–5 ml of THF. The temperature slowly rose to 29–42°C. The reaction mixture was heated at 45–55°C and stirred at this temperature for 0.5–4 h (Table 2), then was left overnight, and on the next day was treated with a water solution of NH$_4$Cl. The reaction products were extracted into ethyl ether, the combined organic solutions were washed with water, dried over MgSO$_4$, the solvent was removed on a rotary evaporator, and the residue was distilled in a vacuum. Yields of the products are reported in Table 2.

b. Compound **IVb** was prepared in a similar way but in the ethyl ether medium. The reaction conditions and yields of the products are given in Table 2 (run no. *7*).

1-[2-(Vinyloxy)ethoxy]-5-phenyl-4-pentyn-2-ol (IVa). IR spectrum, cm^{-1}: 1620, 1640 (C=C), 2230 (C≡C), 3450 (O–H). ^{1}H NMR spectrum, δ, ppm: 2.65 d.d (2H, CH$_2$C≡), 2.81 d (1H, OH), 3.45, 3.49 d.d.d (2H, OC$\underline{H}_2$CH), 3.72 t (2H, OCH$_2$C$\underline{H}_2$O), 3.75 m (1H, C$\underline{H}$OH), 3.83 t (2H, OC$\underline{H}_2$CH$_2$O), 4.01 d.d (1H, CH$_2$=, *cis*), 4.17 d.d (1H, CH$_2$=, *trans*), 6.45 m (1H, OCH=), 7.24–7.40 m (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 24.48 (C$\underline{H}_2$C≡), 67.30 (OC$\underline{H}_2$CH$_2$O), 69.07 (CHOH), 70.03 (OCH$_2$C$\underline{H}_2$O), 72.78 (OC$\underline{H}_2$CH), 82.78 (PhC≡), 85.66 (CH$_2$C≡), 87.11 (CH$_2$=), 127.96–132.18 (C$_{arom}$), 151.69 (OCH=).

1-(Allyloxy)-5-phenyl-4-pentyn-2-ol (IVb). Colorless fluid, bp 136–138°C (1 mm Hg), n_D^{20} 1.5503. IR spectrum, cm^{-1}: 1480, 1590 (Ph), 1640 (C=C), 2230 (C≡C), 3400 (O–H). ^{1}H NMR spectrum, δ, ppm: 2.63 d.d (2H, CH$_2$C≡), 3.00 br.s (1H, OH), 3.48, 3.59 q (2H, OC$\underline{H}_2$CH), 3.96 m (1H, C$\underline{H}$OH), 4.00 d.t (2H, OC$\underline{H}_2$CH=), 5.17 d.d.t (1H, CH$_2$=, *cis*), 5.25 d.d.t (1H, CH$_2$=, *trans*), 5.88 d.d.t (1H, CH=), 7.23–7.45 m (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 24.56 (C$\underline{H}_2$C≡), 69.15 (CHOH), 72.36 (OC$\underline{H}_2$CH=), 73.03 (OC$\underline{H}_2$CH), 82.72 (PhC≡), 85.82 (CH$_2$C≡), 117.38 (CH$_2$=), 127.91, 128.26, 131.67 (C$_{arom}$), 134.50 (CH=). Found, %: C 77.62; H 7.46. C$_{14}$H$_{16}$O$_2$. Calculated, %: C 77.75; H 7.46.

1-[2-(Vinyloxy)ethoxy]-3-bromo-2-propanol (Va). To a solution of 100 mmol of ethynylmagnesium bromide in 60 ml of THF at 2–4°C was added within 30 min by small portions 100 mmol of oxirane **Ia**. The reaction mixture was warmed to 20°C within 1 h and was stirred for 1 h more at 20°C (TLC monitoring). The reaction mixture was poured in 300 ml of water solution of NH$_4$Cl. The reaction products were extracted into ethyl ether, the combined organic solutions were dried over MgSO$_4$, the solvent was removed on the rotary evaporator. We obtained as a residue 17.1 g of viscous orange fluid containing 91% of compound **Va**. IR spectrum, cm^{-1}: 660 (C–Br), 1610, 1640 (C=C), 3110 (OCH=), 3450 (O–H). ^{1}H NMR spectrum, δ, ppm: 3.09 d (1H, OH), 3.46, 3.49 d.d.d (2H, OC$\underline{H}_2$CH), 3.62 d (2H, CH$_2$Br), 3.74 t (2H, OCH$_2$C$\underline{H}_2$O), 3.80 t (2H, OC$\underline{H}_2$CH$_2$O), 3.95 m (1H, C$\underline{H}$OH), 4.01 d.d (1H, CH$_2$=, *cis*), 4.18 d.d (1H, CH$_2$=, *trans*), 6.47 q (1H, OCH=). ^{13}C NMR spectrum, δ, ppm: 34.91 (CH$_2$Br), 67.29 (OC$\underline{H}_2$CH$_2$O), 69.91 (CHOH), 69.98 (OCH$_2$C$\underline{H}_2$O), 72.82 (OC$\underline{H}_2$CH), 87.12 (CH$_2$=), 151.73 (OCH=).

1-(Allyloxy)-3-bromo-2-propanol (Vb). From 12 g of reaction products obtained from oxirane **Ib** and phenylethynylmagnesium bromide (**IIb**) (Table 2, run no. *6*) alongside 4-pentyn-2-ol **IVb** was isolated by vacuum distillation 4.75 g of compound **Vb**, colorless liquid, bp 66–70°C (1 mm Hg), n_D^{20} 1.4892. IR spectrum, cm^{-1}: 670 (C–Br), 1640 (C=C), 3400 (O–H). ^{1}H NMR spectrum, δ, ppm: 3.10 d (1H, OH), 3.28, 3.44 q (2H, OC$\underline{H}_2$CH), 3.52 d (2H, CH$_2$Br), 3.95 q (1H, C$\underline{H}$OH), 4.01 d (2H, OC$\underline{H}_2$CH=), 5.17 d.d.t (1H, CH$_2$=, *cis*), 5.25 d.d.t (1H, CH$_2$=, *trans*), 5.86 d.d.t (1H, CH=). ^{13}C NMR spectrum, δ, ppm: 35.09 (CH$_2$Br), 69.94 (CHOH), 71.54 (OC$\underline{H}_2$CH), 72.38 (OC$\underline{H}_2$CH=), 117.55 (CH$_2$=), 134.33 (CH=). Found, %: C 36.81; H 5.49; Br 39.88. C$_6$H$_{11}$BrO$_2$. Calculated, %: C 36.95; H 5.68; Br 40.96.

2-Methyl-4-(3-phenyl-2-propynyl)-1,3,6-tri-oxocane (VIII). The distillation of reaction products (run no. *4*, Table 2) besides the main fraction, 3-bromo-2-propanol **Va**, yielded two more fractions possessing similar NMR spectra (distinguished by different ratio of the integral intensities of the identical signals) but with unlike boiling temperature and refraction indices. I fraction, bp 150–155°C (2 mm Hg), n_D^{20} 1.5190, contained ~30% of trioxocane **VIII** and ~70% of trioxocane **IX**. II fraction , bp 190–198°C (2 mm Hg), n_D^{20} 1.5572, contained ~81% of trioxocane **VIII** and ~19% of trioxocane **IX**. IR spectrum, cm^{-1}: 2990 (Me). ^{1}H NMR spectrum, δ, ppm, for compound **VIII**: 1.37 d (3H, Me), 2.43–2.69 m (2H, CH$_2$C≡), 3.24–3.75 m (7H, 2CH$_2$O, OCH$_2$CH), 4.88 q (1H, OCHO), 7.25–7.51 m (5H, Ph). ^{13}C NMR spectrum, δ, ppm, for compound **VIII**: 20.69, 20.78 (Me), 23.60, 23.84 (CH$_2$C≡), 64.14, 64.18, 68.86, 69.13, 69.19, 70.95, 71.04, 72.75 (2OCH$_2$, OCH$_2$CH), 79.87, 80.77 (C≡C), 98.89, 98.78 (OCHO), 127.88–131.68 (C$_{arom}$).

2-Methyl-4-(bromomethyl)-1,3,6-trioxocane (IX). From 5 g of 1-[2-(vinyloxy)ethoxy]-3-bromo-2-propanol **Va** obtained by reaction of ethynylmagnesium bromide with oxirane **Ia** was isolated by distillation 3 g of compound **IX** as a colorless liquid, bp 105–106°C (1 mm Hg), n_D^{20} 1.4996. IR spectrum, cm^{-1}: 655 (C–Br), 2980 (Me). ^{1}H NMR spectrum, δ, ppm: 1.33 d (3H, Me), 3.53–3.67 narrow.m (8H, 2CH$_2$O, OCH$_2$CH, CH$_2$Br), 3.95 m (1H, CHCH$_2$Br), 4.88 q (1H, OCHO). ^{13}C NMR spectrum, δ, ppm: 20.01, 20.09 (Me), 33.27, 33.47 (CH$_2$Br), 63.77, 63.96, 70.94, 71.58, 71.77, 73.36, 73.41 (2OCH$_2$, OCH$_2$CH), 99.57, 99.76 (OCHO). Found, %: C 38.77; H 6.10; Br 35.14. C$_7$H$_{13}$BrO$_3$. Calculated, %: C 37.35; H 5.82; Br 35.50.

REFERENCES

1. Dmitrieva, L.L., Nikitina, L.P., Albanov, A.I., Nedolya, N.A*., Zh. Org. Khim.,* 2005, vol. 41, p. 1462.
2. Normant, H., *Organometallic Chemistry (Plenary and Section Lectures Presented at the Fifth International Conference on Organometallic Chemistry),* 16–22 August, 1971 Moscow. Grignard, V., *C. r.,* 1900, vol. 130, p. 1233.
3. Wakefield, B.J., *Best Synthetic Methods. Organo-magnesium, Methods in Organic Synthesis,* New York: Academic Press, 1995, 249 p.; Ioffe, S.T. and Necmeya-nov, A.N., *Metody elementoorganicheskoi khimii. Magnesium, berillii, kal'tsii, strontsii, barii* (Methods of Organoelemental Chemistry. Magnesium, Beryllium, Calcium, Strontium, Barium), Moscow: Izd. Akad. Nauk SSSR, 1963, 561 p.; Kharasch, M.S. and Reinmuth, O., *Grignard Reactions of Nonmetallic Substances*, New York: Prentice-Hall, Inc., 1954, 1384 p.
4. Bergel'son, L.D., *Reaktsii i metody issledovaniya organicheskikh soedinenii* (Reaction and Methods of Investigation of Organic Compounds), Moscow: GNTI Khim. Lit., 1956, p. 7; Iotsich, Zh.I., *Zh. Ros. Khim. Obshch.,* 1906, vol. 38, p. 252; 1903, vol. 35, p. 431; 1902, vol. 34, pp. 101, 242.
5. Likhar, P.R., Kumar, M.P., and Bandyopadhyay, A.K*., Tetrahedron Lett.,* 2002, vol. 43, p. 3333; Mitani, M. and Iwaki, T*., J. Chem. Research (S),* 1998, 498; Jakob, B., Voss, G., and Gerlach, H*., Tetrahedron: Asymmetry.,* 1996, vol. 7, p. 3255; Larock, R.C., *Comprehensive Organic Trans-formations. A Guide to Functional Group Preparations,* New York: VCH, Publishers Inc., 1989, 1160 p.; Nutzel, K., *Meth. Org. Chem. (Houben-Weyl),* vol. 13/2a, 1973, p. 343; Malinovskii, M.S., *Okisi olefinov i ikh proizvodnye* (Oxides of Olephins and Their Derivatives), Moscow: Goskhim-izdat, 1961, p. 326.
6. Schaap, A. and Arens, J.F., *Rec. Trav. Chim.,* 1968, vol. 87, p. 1249.
7. Hambrecht, J., Straub, H., and Miller, E., *Chem. Ber.,* 1974, vol. 107, p. 2985; Zderic, J.A. and Limon, D.C*., J. Am. Chem. Soc.,* 1960, vol. 82, p. 2304; Knight, J.A. and Diamond, J.H*., J. Org. Chem.,* 1959, vol. 24, p. 400; Normant, H., German Patent 1049861, 1957–1959; *Chem. Abstr.,* 1959, p. 14561; Schlubach, H.H., Wolf, V., Justus, W., and Kohncke, C.A., *Lieb. Ann.,* 1950, vol. 568, p. 141; New-man, M.S. and Wotiz, J.H*., J. Am. Chem. Soc.,* 1949, vol. 71, p. 1292; Nazarov, I.N. and Torgov, I.V., *Izv. Akad. Nauk SSSR,* 1947, p. 495.
8. Danehy, J.P., Vogt, R.R., and Nieuwland, J.A*., J. Am. Chem. Soc.,* 1935, vol. 57, p. 2327; 1934, vol. 56, p. 2790; Faucou-nau, L. *C. r.,* 1934, vol. 199, p. 605; *Chem. Abstr.,* 1934, vol. 28, p. 7245.
9. Takisawa, Y., Kono, N., Saito, K., and Yamachika, H., US Patent 4958033, 1990; *Ref. Zh. Khim.,* 1991, 21N14 P.
10. Weyershausen, B., Nieger, M., and Dotz, K.H*., J. Organo-metal. Chem.,* 2000, vol. 602, p. 37.
11. Alexakis, A., Marek, I., Mangeney, P., and Normant, J.F*., Tetrahedron,* 1991, vol. 47, p. 1677; *Tetrahedron Lett.,* 1989, vol. 30, pp. 2391, 2387; Cahiez, G., Alexakis, A., and Normant, J.F., *Synthesis,* 1978, p. 528; Vermeer, P., Mei-jer, J., de Graaf, C., and Schreurs, H., *Rec. Trav. Chim.,* 1974, vol. 93, p. 46.
12. Shorygin, P.P., Isagulyants, V.I., Guseva, A., Polyakova, K., and Osipova, V., *Ber.,* 1931, vol. 64, p. 2585.
13. Roblin, R., Davidson, D., and Bogert, M*., J. Am. Chem. Soc.,* 1935, vol. 57, p. 151.
14. German Patent 423544, 1926; *Chem. Abstr.,* 1926, vol. I, p. 3635.
15. Fukumoto, T. and Yamamoto, A., Japan Patent 1-249736, 1989; *Ref. Zh. Khim.,* 1991, 1N14P.
16. Bonini, C., Chiummiento, L., Lopardo, M.T., Pullez, M., Colobert, F., and Solladie, G*., Tetrahedron Lett.,* 2003, vol. 44, p. 2695.

17. Takano, S., Moriya, M., Iwabuchi, Y., and Ogasawara, K.*, Tetrahedron Lett*., 1989, vol. 30, p. 3805.

18. Ribas, I. and Tapia, E., *Anales Soc. Espan. Fis. Quim*., 1932, vol. 30, p. 944; Boyd, D.R. and Vineall, G.J.C.*, J. Chem. Soc*., 1929, p. 1622; Ribas, I., *Anales Soc. Espan. Fis. Quim*., 1928, vol. 26, p. 122.

19. *The Chemistry of Functional Groups. Supplement E: The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and Their Sulphur Analogues*, Patai, S., New York: J. Wiley & Sons, 1980, part 1, p. 1; Monick, J.A., *Alcohols. Their Chemistry, Properties and Manufacture*, New York: Reinhold, 1968.

20. Pohlki, F. and Doye, S., *Chem. Soc. Rev*., 2003, vol. 32, p. 104; Chen, J.-T., *Coord. Chem. Rev*., 1999, pp. 190–192, 1143; *Modern Acetylene Chemistry*, Stang, P.J. and Diederich, F., New York: VCH, 1995, 506 p.; *The Chemistry of the Carbon-Carbon Triple Bond*, Patai, S., New York: J. Wiley & Sons, 1978, 1094 p.; *Chemistry of Acetylenes*, Viehe, H.G., New York: 1969, 1298 p.

21. Brandsma, L., *Best Synthetic Methods. Synthesis of Acetylenes, Allenes, and Cumulenes: Methods and Techniques,* New York: Elsevier Academic Press, 2004, 469 p.; *Meth. Org. Chem. (Houben-Weyl)*, 1993, 1313 p.

22. Brandsma, L., *Studies in Organic Chemistry. 34. Preparative Acetylenic Chemistry,* Amsterdam: Elsevier, 1988, 321 p.; Brandsma, L. and Verkruijsse, H., *Preparative Polar Organometallic Chemistry*, Berlin: Springer-Verlag, 1987, vol. 1, 240 p.

23. Ohno, H., Toda, A., Fujii, N., Takemoto, Y., Tanaki, T., and Ibuka, T.*, Tetrahedron, 2000*, vol. 56, p. 2811; Marshall, J.A. and Wang, X.J.*, J. Org. Chem*., 1991, vol. 56, p. 4913; Johnson, A.W., *The Chemistry of Acetylenic Compounds,* vol. 1, *Acetylenic Alcohols,* Arnold & Co., 1946.

24. Brandsma, L., Vasilevsky, S.F., and Verkruijsse, H.D., *Application of Transition Metal Catalysts in Organic Synthesis*, New York: Springer-Verlag, 1998, 335 p.

25. Fallis, A.G. and Forgione, P.*, Tetrahedron, 2001*, vol. 57, p. 5899; Forgione, P., Wilson, P.D. and Fallis, A.G.*, Tetrahedron Lett*., 2000, vol. 41, p. 17; Gabriele, B., Salerno, G., de Pascali, F., Costa, M., and Chiusoli, G.P.*, J. Org. Chem*., 1999, vol. 64, 7693; Dalla, V. and Pale, P., *New J. Chem*., 1999, vol. 23, p. 803; Gilchrist, T.L.*, J. Chem. Soc*., *Perkin Trans. I*, 1998, p. 615.

26. Derien, S., Ropartz, L., Le, Paih, J., and Dixneuf, P.H.*, J. Org. Chem.,* 1999, vol. 64, p. 3524.

27. Nedolya, N.A., Brandcma, L., and Tolmachev, S.V.*, Zh. Org. Khim.,* 2002, vol. 38, p. 948; Nedolya, N.A., Brandcma, L., Tolmachev, S.V., and Albanov, A.I.*, Khim. Geterotsikl. Soedin.,* 2001, p. 394; Brandcma, L., Nedolya, N.A., and Trofimov, B.A.*, Izv. Akad. Nauk, Ser. Khim*., 2000, p. 1645.

28. Tokunaga, M., Ota, M., Haga, M.-A., and Wakatsuki, Y.*, Tetrahedron Lett*., 2001, vol. 42, p. 3865.

29. Guan, H.-P., Tang, X.-Q., Luo, B.-H., and Hu, C.-M., *Synthesis*, 1997, p. 1489.

30. Nedolya, N.A., Brandcma, L., Shlyakhtina, N.I., and Fedorov, S.V.*, Khim. Geterotsikl. Soedin.,* 2002, p. 707; Nedolya, N.A., Schlyakhtina, N.I., Klyba, L.V., Ushakov, I.A., Fedorov, S.V., and Brandsma, L.*, Tetrahedron Lett*., 2002, vol. 43, p. 9679.

31. Jeong, I.-Y., Lee, W.S., Goto, S., Sano, S., Shiro, M., and Nagao, Y.*, Tetrahedron, 1998*, vol. 54, p. 14437.

32. Marson, C.M. and Campbell, J., *Tetrahedron Lett*., 1997, vol. 38, p. 7785.

33. Hiroi, K. and Kato, F.*, Tetrahedron, 2001*, vol. 57, p. 1543; Braverman, S., Pechenick, T., and Zafrani, Y.*, Tetrahedron Lett*., 2001, vol. 42, p. 1391; Condon-Gueugnot, S., and Linstrumelle, G.*, Tetrahedron, 2000*, 56, 1851; Tomita, I., Ubukata, M., and Endo, T., *React. Func. Polym.*, 1998, vol. 37, p. 27.

34. Brandsma, L. and Nedolya, N.A., *Synthesis*, 2004, p. 735; Golubev, A.S., Sergeeva, N.N., Hennig, L., Kolomiets, A.F., and Burger, K.*, Tetrahedron, 2003*, vol. 59, p. 1389; Ma, S. and Wang, G.*, Tetrahedron Lett*., 2002, vol. 43, p. 5723; Ogawa, A., Sakagami, K., Shima, A., Suzuki, H., Komiya, S., Katano, Y., and Mitsunobu, O.*, Tetrahedron Lett*., 2002, vol. 43, p. 6387; Bates, R.W. and Satcharoen, V., *Chem. Soc. Rev*., 2002, vol. 31, p. 12.

35. Song, Y., Okamoto, S. and Sato, F.*, Tetrahedron Lett*., 2002, 43, 8635; Mukai, C., Sugimoto, Y., Miyazawa, K., Yamaguchi, S. and Hanaoka, M.*, J. Org. Chem*., 1998, vol. 63, p. 6281.

36. Aoyagi, S., Hasegawa, Y., Hirashima, S. and Kibayashi, C.*, Tetrahedron Lett*., 1998, vol. 39, p. 2149.

37. Gorbovoi, P.M., Zagrichuk, G.Ya., Baranovskii, V.S., Nedolya, N.A. and Grishchuk, B.D.*, Zh. Obshch. Khim.,* 2000, vol. 70, p. 1872; Nedolya, N.A., *Doctoral Sci. (Chem.) Dissertation*, Irkutsk, 1998, 52 p.

38. Nikitina, L.P., Dmitrieva, L.L., Albanov, A.I., Nedolya, N.A. and Brandcma, L.*, Zh. Org. Khim.,* 2003, vol. 39, p. 1459; Nedolya, N.A., Zinov'eva, V.P., Shlyakhtina, N.I., Albanov, A.I. and Brandcma, L.*, Khim. Geterotsikl. Soedin.,* 2002, p. 1605.

39. Atavin, A.S., Trofimov, B.A., Vyalykh, E.P. and Golovanova, N.I.*, Zh. Org. Khim.,* 1969, vol. 5, p. 842; Shostakovskii, M.F., Atavin, A.S., Vyalykh, E.P. and Trofimov, B.A., USSR Inventor's Certificate Patent 327880, 1968; *SSSR Byull. Izobr*., 1969, no. 9.

40. Atavin, A.S., Shostakovskii, M.F., Vyalykh, E.P. and Trofimov, B.A.*, Zh. Org. Khim.,* 1970, vol. 6, p. 222.

41. Trofimov, B.A., *Geteroatomnye proizvodnye atsetilena* (Heteroatomiv Derivatives of Acetylene), Moscow: Nauka, 1981, 320 p.

42. Grobelny, Z., Stolarzewicz, A., Morejko-Buz, B., Maercker, A., Krompiec, S., and Bieg, T., *J. Organometal. Chem*., 2003, vol. 672, p. 43; Munavalli, S., Rohrbaugh, D.K., Rossman, D.I., McMahon, L.R., and Durst, H.D.*, J. Organometal. Chem*., 1999, vol. 587, p. 160; Skupin, R. and

Haufe, G.*, J. Fluorine Chem.*, 1998, vol. 92, p. 157.

43. Price, C.C. and Halpern, B.D.*, J. Am. Chem. Soc.*, 1951, vol. 73, p. 818; Cason, J. and Winans, W.R.*, J. Org. Chem.*, 1950, vol. 15, p. 139; Dice, J.R., Watkins, T.E. and Schuman, H.L.*, J. Am. Chem. Soc.*, 1950, vol. 72, p. 1738.

44. Sobotka, H. and Stynler, F.E.*, J. Am. Chem. Soc.*, 1950, vol. 72, p. 5139; Vaughan, T.H., Spahr, R.J. and, Nieuwland, J.A.*, J. Am. Chem. Soc.*, 1933, vol. 55, p. 4206; Hiers, G.S. and Adams, R.*, J. Am. Chem. Soc.*, 1926, vol. 48, p. 2385.

45. Huston, R.C. and Agett, A.H.*, J. Org. Chem.*, 1941, vol. 6, p. 123.

46. Malinovskii, M.S., Volkova, E.E. and Morozova, N.M.*, Zh. Obshch. Khim.,* 1949, vol. 19, p. 114; Frank, R.L., Adams, C.E., Allen, R.E., Gander, R. and Smith, P.V., *J. Am. Chem. Soc.*, 1946, vol. 68, p. 1365; Cohen, A., Cook, J.W., Hewett, C.L. and Girard, A., *J. Chem. Soc.*, 1934, p. 653.

47. Brandsma, L. and Arens, J.F., The *Chemistry of Functional Groups. The Chemistry of the Ether Linkage*, Patai, S., New York: J. Wiley & Sons, Interscience Publishers, 1967, p. 553; Parham, W.E. and Motter, R.F.*, J. Am. Chem. Soc.*, 1959, vol. 81, p. 2146; Hill, C.M., Prigmore, R.M., and Moore, G.J.*, J. Am. Chem. Soc.*, 1955, vol. 77, p. 352.

48. Darnault, G., Saquet, M., and Thuiller, A., *Chem. Ind. (London)*, 1983, p. 391; Hopf, H., Bohm, I., and Kleinschroth, J., *Org. Synth.*, 1981, vol. 60, p. 42; Prevost, C., Gaudemart, M., Miginiac, L., Bardone-Gaudemar, F., and Andrac, M., *Bull. Soc. Chim.,* 1959, p. 679.

49. Umedzava, D. and Furukhasi, K., Japan Patent 1275543, 1988–1989; *Ref. Zh. Khim.,* 1991, 9N25P.

50. Sosnovskii, G.M. and Astapovich, I.V., *Vestsi Akad. Nauk BSSR, Ser. Khim. Nauk*, 1990, p. 55; *Ref. Zh. Khim.,* 1991, 24Zh164.

51. Alvarez, E., Nunez, M.T., and Martin, V.S.*, J. Org. Chem.*, 1990, vol. 55, p. 3429.

52. Gordon, A.J. and Ford, R.A., *The Chemist's Companion*, New York: Wiley, 1972.

53. Trofimov, B.A., Stankevich, V.K., Belozerov, L.E., Kukharev, B.F., Klimenko, G.R., Nedolya, N.A., Kharitonov, V.I., Popov, A.D., Tyun'kov, O.V., and Moshchenko, Yu.A., USSR Inventor's Certificate 129208, 1984; *SSSR Byull. Izobr.,* 1984, no. 46.