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Condensation of Phenols and Alcohols with 1,2-Dichloroethyl-*gem*-dichlorocyclopropanes

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Abstract—Dichlorocarbenation of 3,4-dichlorobut-1-ene by Makosza method results in the stereoisomeric 1,2-dichloroethyl-*gem*-dichlorocyclopropanes in a 1:1 ratio. The reaction of the mixture of stereoisomeric *gem*-dichlorocyclopropanes with phenols and alcohols in dimethylsulfoxide in the presence of solid sodium hydroxide gives rise to the corresponding ketals containing the exocyclic double and triple bonds. In this case, the acetylene compounds dominate in the reaction products. The ratio of the reaction products containing the double and triple bonds depends on the nucleophile nature.

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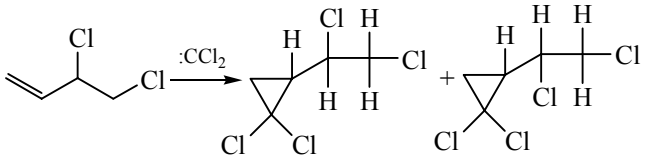
The chlorination of butadiene affords 3,4-dichlorobut-1-ene **I** in a high yield, which is widely used in organic synthesis [1].

We used compound **I** to obtain the stereoisomeric 1,2-dichloroethyl-*gem*-dichlorocyclopropanes **II** by the Makosza method [2].

The diastereoisomers **IIa** and **IIb** (1:1) were separated by vacuum distillation and characterized by the ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry.



I **IIa** **IIb**

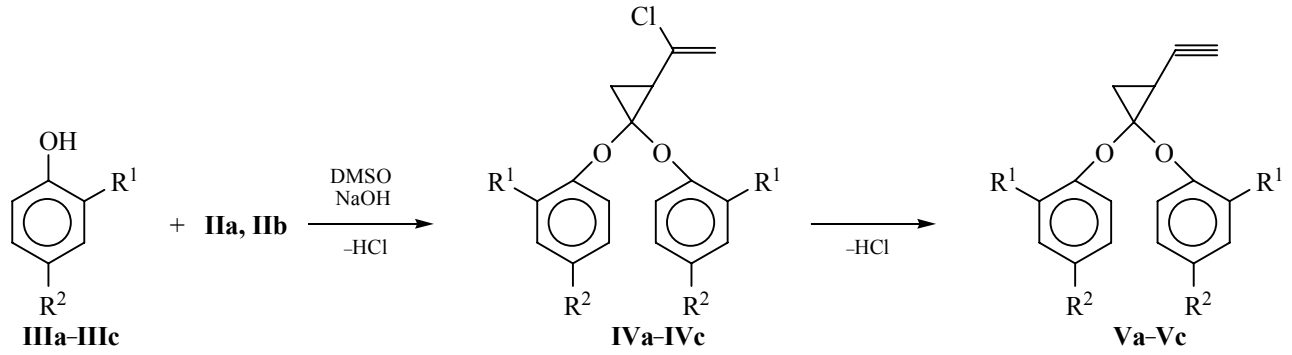
Thus, in the case of compound **IIa**, in the ^{1}H NMR spectrum the signal of the CH-proton of the cyclopropane ring is observed as a doublet of doublets of doublets at 2.5 ppm, with the spin-spin coupling constants $^3J_{3a-2}$ 7.7, $^3J_{3b-2}$ 10.4, $^3J_{2-1'}$ 9.4 Hz, whereas the signal of the similar proton in the spectrum of compound **IIb** appears at 2.05 ppm as a doublet of doublets of doublets with the coupling constants $^3J_{3b-2}$ 7.7, $^3J_{3a-2}$ 10.4, $^3J_{2-1'}$ 5 Hz. According to the literature data [3], the values of the spin-spin coupling constants of the CH-proton of the cyclopropane ring for compounds **IIa** (9.4 Hz) and **IIb** (5 Hz) indicate the *threo*- and *erythro*- configuration of compounds **IIa** and **IIb**, respectively

In the ^{13}C NMR spectra of **IIa** the signals of the carbon atoms of CHCl- and CH_2Cl-groups are in a weaker field at 60.54 and 47.96 ppm, than similar signals of the carbon atoms in the spectrum of compound **IIb** (60.27 and 47.48 ppm, respectively). The upfield shift of the signals of the carbon atoms in the spectrum of *erythro*-isomer indicates a stronger *syn*-interaction between the atoms of CHCl- and CH_2Cl-groups than in the *threo*-structure. On the contrary, the signals of the CH_2- and CH-carbon atoms of the cyclopropane ring in compound **IIb** are in a weaker field as compared with the signals of similar atoms in **IIa** (the chemical shifts of the CH_2- and CH-carbon atoms in the *erythro*- and *threo*-isomer are 28.07, 34.87 and 27.29, 34.45 ppm, respectively).

The resulting mixture of stereoisomeric *gem*-dichlorocyclopropanes **IIa** and **IIb** was we used in the *O*-alkylation of phenols **III** in dimethyl sulfoxide (DMSO) in the presence of solid NaOH.

The reaction is complete at room temperature within 15–20 min and results in ketals with the exocyclic double (**IVa**–**IVc**) and triple (**Va**–**Vc**) bonds.

The total yield of compounds **IV** and **V** equals 70–80% and is independent of the nature of the aromatic



IIIa–IIIc **IVa–IVc** **Va–Vc**

$R^1 = R^2 = H$ (**IIIa, IVa, Va**); $R^1 = CH_3$, $R^2 = H$ (**IIIb, IVb, Vb**); $R^1 = H$, $R^2 = Cl$ (**IIIc, IVc, Vc**).

reactant **IIIa**–**IIIc**. However, the nature and position of the substituent affect the ratio of the ethylene and acetylene structures (**IVa**–**IVc**/**Va**–**Vc**). In the reaction with phenol **IIIa** the yield of acetylene ketal **Va** is much higher, while in the reaction with *p*-chlorophenol **IIIc** the yield of the fully dehydrochlorinated product **Vc** is only 2-fold higher than that of the partially dehydrochlorinated product **IVc**. However, in the case of alcohols of linear structure [allyl (**VIa**) and butyl (**VIb**)] the total yield of similar ketals **VIIa**, **VIIb**, **VIIIa** and **VIIIb**) is much lower (20–30%).

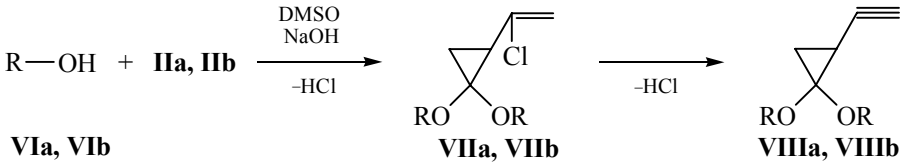
Phenol	Yield, %	
IIIa	6 (**IVa**)	71 (**Va**)
IIIb	15 (**IVb**)	58 (**Vb**)
IIIc	23 (**IVc**)	47 (**Vc**)

In this case, the acetylene product **VIII** dominates in the reaction products.

Earlier we mentioned the elimination of the hydrogen halides in phenylpolyhaloalkyl ethers in the study of the *O*-alkylation of phenols and alcohols with polyhaloalkanes. [4]

The individual compounds **IVa**–**IVc**, **Va**–**Vc**, as well as a mixture of isomers **VIa**, **VIb** and **VIIa**, **VIIb** were isolated by column chromatography from the reaction mixture of phenols **IIIa**–**IIIc** and alcohols **VIa**, **IVb** with the reagents **IIa**, **IIb**.

In the ^{1}H NMR spectrum of compound **IVc** the CH-proton of the cyclopropane ring is observed at 2.40 ppm as a doublet of doublets with the spin-spin coupling constants $^3J_{2-3a}$ 7.4, $^3J_{2-3b}$ 10.2 Hz. The *trans*-positioned CH_2-proton of the cyclopropane ring



VIa, VIb **VIIa, VIIb** **VIIIa, VIIIb**

R = CH_2=$CHCH_2$ (**VIa, VIIa, VIIIa**); C_4H_9 (**VIb, VIIb, VIIIb**).

appears as a doublet of doublets at 1.56 ppm (^2J 6.9, $^3J_{3a-2}$ 7.4 Hz), while the *cis*-positioned CH_2-proton appears as a doublet of doublets in a weak field at 1.75 ppm (^2J 6.9, $^3J_{3b-2}$ 10.2 Hz). The proton of the terminal double bond, which is *cis*-positioned relative to the chlorine atom, is observed as a doublet at 5.28 ppm (^2J 1.4 Hz), while the *trans*-positioned proton is observed as a doublet in a weak field (5.41 ppm, ^2J 1.4 Hz). A multiplet in the range of 7.08–7.27 ppm belongs to the protons of the aromatic ring. The structures of compounds **VIa**, **IVb**, **VIIa**, **VIIb** were identified in a similar way.

Alcohol	Yield, %	
VIa	4 (**VIIa**)	26 (**VIIIa**)
VIb	6 (**VIIb**)	14 (**VIIIb**)

The mass spectra of compounds **IVa**–**IVc** contains low-intensive peaks (<1%) of the molecular ions. The main decay directions are caused by eliminating the halogen ion and aryloxy radical. The most abundant

ions are $[ArOH]^{+\cdot}$ with *m*/*z* (83%), 108 (100%), 128/130 (100%) in the spectra of compounds **IVa**–**IVc**, respectively.

The ^{1}H NMR spectrum of compound **Vc** contains the CH-proton of the cyclopropane ring as a doublet of doublets of doublets at 2.11 ppm ($^3J_{2-3a}$ 6.9, $^3J_{2-3b}$ 10.5, $^4J_{2-2'}$ 2.2 Hz). The *trans*- positioned CH_2-proton of the cyclopropane ring appears as a doublet of doublets at 1.49 ppm (^2J 6.3, $^3J_{2-3a}$ 6.9 Hz), while the *cis*-positioned CH_2-proton is observed as a doublet of doublets in a weaker field at 1.70 ppm (^2J 6.3, $^3J_{2-3b}$ 10.5 Hz). A doublet signal at 1.98 ppm ($^4J_{2-2'}$ 2.2 Hz) belongs to the proton of the terminal triple bond. A multiplet at 7.05–7.27 ppm corresponds to the aromatic ring protons. The structures of compounds **Va**, **Vb**, **VIIIa**, **VIIIb** were identified in a similar way.

The mass spectra of compounds **Va**–**Vc** are characterized by the low-intensive peaks (≤ 1%). Acetylene ketals **Va**–**Vc** are capable of undergoing cleavage of the CH_2CO moiety from the ions produced with the release of aryloxy radical from the $M^{+\cdot}$ ion, and the peaks of these ions have a maximum intensity (100%) [*m*/*z* 115, 129, 149/151 for compounds **Va**–**Vc**, respectively]. Compounds **VIIa**, **VIIb**, **VIIIa**, **VIIIb** are characterized by the absence of the molecular peaks (<0.1%). The main decay direction is caused by the breaking of bonds with oxygen and the formation of oxonium ions, which then loose the olefin molecule from the second alkoxy group.

Thus, the diastereoisomeric 1,2-dichloroethyl-*gem*-dichlorocyclopropanes were obtained via the dichlorocarbenation by the Makosza method. The reactions of the obtained 1,2-dichloroethyl-*gem*-dichlorocyclopropanes with phenols and alcohols in DMSO are a convenient method of the synthesis of ketals of chlorovinyl- and ethynylcyclopropanes.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer (300.13 and 75.47 MHz, respectively) in $CDCl_3$ relative to internal TMS. The GC-MS analysis was performed on a Shimadzu GCMS-QP2010 Plus instrument (EI, 70 eV; an ion source temperature 200°C, the direct input temperature 40–290°C, the heating rate 12 deg min^{-1}). The GLC analysis was performed on a LKhM-8MD chromatograph equipped with a thermal conductivity detector, carrier gas helium (flow rate 1.5 l h^{-1}, the column length 2 m, 5% SE-30 on a Chromaton N-AW carrier). The TLC analysis was performed using Silufol plates (Merk) eluting with a hexane–AcOEt mixture, 98:2. The preparative separation was carried out by column chromatography on silica gel eluting with hexane with increasing ethyl acetate content of 5 to 100%.

General procedure of dihalocarbenation. To a mixture of 0.1 mol of 3,4-dichlorobut-1-ene **I**, 0.2 g of a phase transfer catalyst (catamine AB in 300 ml of chloroform) was added dropwise 320 g of 50% NaOH solution at 40°C under stirring within 6 h. Then the mixture was stirred for 2 h at the same temperature. The reaction mixture was washed with water until the neutral reaction. The extract was dried over calcined $MgSO_4$. The solvent was evaporated, and the residue was distilled in a vacuum.

(2*R)-1,1-Dichloro-2-[(1*S**)-1,2-dichloroethyl]-cyclopropane (IIa, *threo*-diastereomer)**. Yield 40%, colorless liquid, bp 96°C (2 mm Hg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.50 d.d (1H, C^3H_a, ^2J 7.4, ^3J 7.7), 1.88 d.d (1H, C^3H_b, ^2J 7.4, ^3J 10.4), 2.05 d.d. d (1H, C^2H, ^3J 7.7, ^3J 10.4, ^3J 9.4), 3.76–3.96 m (3H, $C^{1'}HCl$, $C^{2'}H_2Cl$). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 27.29 (C^3H_2), 34.45 (C^2H), 47.96 ($C^{2'}H_2Cl$), 58.48 (C^1Cl_2), 60.54 ($C^{1'}HCl$). Mass spectrum, *m*/*e* (I_{rel}, %): 206/208/210/212 (<1) $[M]^+$, 171/173/175 (1) $[M - Cl]^+$, 157/159/161 (5/4/1) $[M - CH_2Cl]^+$, 144 (12/11/3), 135 (11/8/1), 109/111/113 (100/61/10), 96/98/100 (15/10/3), 75/77 (48/15), 51 (15).

(2*R)-1,1-Dichloro-2-[(1*R**)-1,2-dichloroethyl]-cyclopropane (IIb, *erythro*-diastereomer).** Yield 40%, colorless liquid, bp 99°C (2 mm Hg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.50 d.d (1H, C^3H_a, ^2J 7.4, ^3J 7.7), 1.87 d.d (1H, C^3H_b, ^2J 7.4, ^3J 10.4), 2.05 d.d. d (1H, C^2H, ^3J 7.7, ^3J 10.4, ^3J 5.0), 3.75–3.94 m (3H, $C^{1'}HCl$, $C^{2'}H_2Cl$). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 28.07 (C^3H_2), 34.87 (C^2H), 47.48 ($C^{2'}H_2Cl$), 58.48 (C^1Cl_2), 60.27 ($C^{1'}HCl$). Mass spectrum, *m*/*e* (I_{rel}, %): 206/208/210/212 (<1) $[M]^+$, 171/173/175 (0.5) $[M - Cl]^+$, 157/159/161 (2/1/0.3) $[M - CH_2Cl]^+$, 144 (12/11/3), 135 (11/8/1), 109/111/113 (100/61/10), 96/98/100 (11/8/2), 75/77 (32/10), 51 (11).

Reaction of phenols IIIa–IIIc and alcohols VIa and VIb with a 1,2-dichloroethyl-*gem*-dichlorocyclopropanes IIa and IIb mixture. A mixture of 7.5 mmol of phenol **IIIa–IIIc** (or 12.5 mmol of alcohol **VIa** or **VIb**), 15 mmol of NaOH (or 25 mmol in the case of alcohols **VIa** or **VIb**) in 2.1 ml of DMSO was stirred at 55–60°C for 1 h. Then to the mixture

was added a solution of 2.5 mmol of **IIa** or **IIb** in 1 ml of DMSO at 20°C. The reaction mixture was diluted with 30 ml of water and extracted with chloroform. The organic layer was washed with 20 ml of 20% NaOH solution, then with water to pH 7, and dried over $MgSO_4$. Chloroform was evaporated in a vacuum. The residue was chromatographed on silica gel (100–400 μm, hexane–AcOEt, 98:2).

1,1'-[(2-(1-Chlorovinyl)cyclopropane-1,1-diyl)bis-(oxy)]dibenzene (IVa). Yield 6%, colorless liquid, R_f 0.31 (hexane–AcOEt, 98:2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.57 d.d (1H, C^3H_a, ^2J 6.6, ^3J 7.4), 1.77 d.d (1H, C^3H_b, ^2J 6.6, ^3J 10.5), 2.40 d.d (1H, C^2H, ^3J 7.4, ^3J 10.5), 5.30 d (1H, $=C^{2'}H_a$, ^2J 1.5), 5.41 d (1H, $=C^{2'}H_b$, ^2J 1.5), 6.97–7.28 m (10H, Ph). Mass spectrum, *m*/*e* (I_{rel}, %): 286/288 $[M]^+$ (<1), 251 $[M - Cl]^+$ (2), 193/195 $[M - PhO^{\cdot}]^+$ (19/5), 157 (63), 151/153 (50/21), 129 (60), 115 (72), 94 (83), 77 (100), 65 (22), 51 (49).

1,1'-[(2-Ethynylcyclopropane-1,1-diyl)bis(oxy)]-dibenzene (Va). Yield 71%, white crystals, mp 63–65°C, R_f 0.26 (hexane–AcOEt, 98:2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.52 d.d (1H, C^3H_a, ^2J 6.2, ^3J 7.0), 1.75 d.d (1H, C^3H_b, ^2J 6.2, ^3J 10.2), 2.01 d (1H, $\equiv C^{2'}H$, ^4J 2.1), 2.15 d.d.d (1H, C^2H, ^3J 7.0, ^3J 10.2, ^4J 2.1), 7.02–7.35 m (10H, Ph). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 16.03 (C^2H), 21.48 (C^3H_2), 66.5 ($\equiv C^{2'}H$), 80.26 ($C^{1'}\equiv$), 87.42 (C^1), 116.77, 117.22 (*ortho*-Ph), 122.59 (*para*-Ph), 129.27, 129.48 (*meta*-Ph), 155.60, 155.93 (Ph). Mass spectrum, *m*/*e* (I_{rel}, %): 250 $[M]^+$ (<1), 157 $[M - PhO^{\cdot}]^+$ (5), 156 $[M - PhOH]^+$ (3), 128 (26), 115 (100), 94 (28), 77 (29), 65 (9), 51 (8).

1,1'-[(2-(1-Chlorovinyl)cyclopropane-1,1-diyl)bis-(oxy)]bis(2-methylbenzene) (IVb). Yield 15%, white crystals, mp 65–67°C, R_f 0.37 (hexane–AcOEt, 98:2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.62 d.d (1H, C^3H_a, ^2J 6.8, ^3J 7.4), 1.87 d.d (1H, C^3H_b, ^2J 6.8, ^3J 10.2), 2.22 d (6H, CH_3), 2.43 d.d (1H, C^2H, ^3J 7.4, ^3J 10.2), 5.36 d (1H, $=C^{2'}H_a$, ^2J 1.4), 5.44 d (1H, $=C^{2'}H_b$, ^2J 1.4), 6.90–7.62 m (8H, Ph). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 16.21 (CH_3), 21.63 (C^3H_2), 32.65 (C^2H), 87.51 (C^1), 114.26 ($=C^{2'}H_2$), 115.16 (*ortho*-Ph), 122.08 (*para*-Ph), 126.57, 130.88 (*meta*-Ph), 127.65 (CH_3–C), 137.59 ($=C^{1'}Cl$), 154.22 (Ph). Mass spectrum, *m*/*e* (I_{rel}, %): 314/316 $[M]^+$ (<1), 279 $[M - Cl]^+$ (6), 207/209 $[M - PhO^{\cdot}]^+$ (25/8), 171 (26), 165/167 (63/21), 143 (26), 129 (42), 108 (100), 91 (59), 77 (15), 65 (31).

1,1'-[(2-Ethynylcyclopropane-1,1-diyl)bis(oxy)]-bis(2-methylbenzene) (Vb). Yield 58%, colorless liquid, R_f 0.32 (hexane–AcOEt, 98:2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.57 d.d (1H, C^3H_a, ^2J 6.3, ^3J 7.4), 1.85 d.d (1H, C^3H_b, ^2J 6.3, ^3J 10.3), 2.08 d (1H, $\equiv C^{2'}H$, ^4J 1.9), 2.20 d.d.d (1H, C^2H, ^3J 7.4, ^3J 10.3, ^4J 1.9), 2.28 s (3H, CH_3), 2.37 s (3H, CH_3), 6.98–7.57 m (8H, Ph). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 16.36, 16.42 (CH_3), 20.10 (C^3H_2), 32.65 (C^2H), 66.52 ($\equiv C^{2'}H$), 80.71 ($C^{1'}\equiv$), 86.94 (C^1), 114.71, 114.89 (*ortho*-Ph), 122.02 (*para*-Ph), 126.78, 126.90, 130.88 (*meta*-Ph), 126.72, 127.23 (CH_3–C), 153.77 (Ph). Mass spectrum, *m*/*e* (I_{rel}, %): 278 $[M]^+$ (<1), 171 $[M - PhO^{\cdot}]^+$ (6), 170 $[M - PhOH]^+$ (3), 142 (6), 129 (100), 108 (53), 91 (23), 77 (8), 65 (14).

1,1'-[(2-(1-Chlorovinyl)cyclopropane-1,1-diyl)bis-(oxy)]bis(4-chlorobenzene) (IVc). Yield 23%, colorless liquid, R_f 0.30 (hexane–AcOEt, 98:2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.56 d.d (1H, C^3H_a, ^2J 6.9, ^3J 7.4), 1.75 d.d (1H, C^3H_b, ^2J 6.9, ^3J 10.2), 2.40 d.d (1H, C^2H, ^3J 7.4, ^3J 10.2), 5.28 d (1H, $=C^{2'}H_a$, ^2J 1.4), 5.41 d (1H, $=C^{2'}H_b$, ^2J 1.4), 7.08–7.27 m (8H, Ph). Mass spectrum, *m*/*e* (I_{rel}, %): 354/356/358 $[M]^+$ (<1), 319/321/323 $[M - Cl]^+$ (5/3/0.6), 227/229/231 $[M - PhO^{\cdot}]^+$ (13/9/2), 191/193 (31/11), 185/187/189 (92/61/11), 163/165 (17/6), 149/151 (41/14), 128/130 (100/30), 111/113 (43/14), 99/101 (20/7), 75 (26), 63 (8).

1,1'-[(2-Ethynylcyclopropane-1,1-diyl)bis(oxy)]-bis(4-chlorobenzene) (Vc). Yield 47%, colorless liquid, R_f 0.27 (hexane–AcOEt, 98:2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.49 d.d (1H, C^3H_a, ^2J 6.3, ^3J 6.9), 1.70 d.d (1H, C^3H_b, ^2J 6.3, ^3J 10.5), 1.98 d (1H, $\equiv C^{2'}H$, ^4J 2.2), 2.11 d.d. d (1H, C^2H, ^3J 6.9, ^3J 10.5, ^4J 2.2), 7.05–7.27 m (8H, Ph). Mass spectrum, *m*/*e* (I_{rel}, %): 318/320/322 $[M]^+$ (1), 191/193 $[M - PhO^{\cdot}]^+$ (2/0.7), 190/192 $[M - PhOH]^+$ (2/0.7), 162/164 (6/2), 149/151 (100/32), 128/130 (44/14), 111/113 (14/5), 99/101 (5/2), 75 (9), 63 (3).

A mixture of 1,1-bis(allyloxy)-2-(1-chlorovinyl)-cyclopropane (VIIa) and **1,1-bis(allyloxy)-2-ethynyl-cyclopropane (VIIIa).** Yield 4 (**VIIa**) and 26% (**VIIIa**), colorless liquid, R_f 0.24 (hexane–AcOEt, 98:2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.88 d.d [1H, C^3H_a, ^2J 6.6, ^3J 7.2 (**VIIa**)], 1.18 d.d [1H, C^3H_a, ^2J 5.5, ^3J 6.4 (**VIIIa**); 1H, C^3H_b (**VIIa**)], 1.33 d.d [1H, C^3H_b, ^2J 5.5, ^3J 10.0 (**VIIIa**)], 1.76 d.d. d [1H, C^2H, ^3J 6.4, ^3J 10.0, ^4J 2.2 (**VIIIa**)], 1.91 d [1H, $\equiv C^{2'}H$, ^4J 2.2 (**VIIIa**)], 2.09 d.d [1H, C^2H, ^3J 7.2, ^3J 10.0

(**VIIa**)], 4.07–4.19 m [4H, CH_2–O (**VIIIa**)], 4.20–4.38 m [4H, CH_2–O (**VIIa**)], 5.10–5.35 m [4H, CH_2= (**VIIIa**); 4H, CH_2= (**VIIIa**), 2H, $=C^{2'}H_a$, $=C^{2'}H_b$ (**VIIIa**)], 5.82–6.04 m [2H, =CH (**VIIIa**); 2H, =CH (**VIIIa**)]. Mass spectrum (**VIIa**), *m*/*e* (I_{rel}, %): 214/216 (<0.1) $[M]^+$, 179 $[M - Cl]^+$ (3), 173/175 (3/1) $[M - C_3H_3^{\cdot}]^+$, 157/159 $[M - C_3H_5O^{\cdot}]^+$ (2/0.7), 155 (2), 151 (5), 137 (19), 131/133 (28/9), 127 (16), 121 (5), 117/119 (25/11), 115 (30), 113 (18), 109 (24), 97 (13), 95 (24), 93 (100), 91 (74), 88 (63), 81 (33), 79 (25), 77 (44), 75 (12), 67 (30), 65 (9), 55 (30), 53 (70), 42 (18). Mass spectrum (**VIIIa**), *m*/*e* (I_{rel}, %): 178 (<1) $[M]^+$, 137 $[M - C_3H_5^{\cdot}]^+$ (4), 121 $[M - C_3H_5O^{\cdot}]^+$ (6), 119 (12), 109 (24), 95 (27), 93 (20), 91 (100), 81 (64), 79 (66), 77 (84), 67 (48), 65 (21), 57 (6), 55 (98), 52 (64), 42 (18).

A mixture of 1,1-dibuthoxy-2-(1-chlorovinyl) cyclopropane (VIIb) and **1,1-dibuthoxy-2-ethynyl-cyclopropane (VIIIb).** Yield 6 (**VIIb**) and 14% (**VIIIb**), colorless liquid, R_f 0.27 (hexane–AcOEt, 98:2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.93 t (12H, CH_3), 1.10 d.d [1H, C^3H_a, ^2J 5.3, ^3J 6.3 (**VIIIb**)], 1.24 m [8H, $\underline{CH_2}$–CH_3 (**VIIb**, **VIIIb**); 8H, $\underline{CH_2}$–CH_2–CH_3 (**VIIb**, **VIIIb**); 1H, C^3H_b (**VIIIb**); 2H, C^3H_a, C^3H_b (**VIIb**); 1H, C^2H (**VIIIb**)], 1.87 d [1H, $\equiv C^{2'}H$, ^4J 2.3 (**VIIIb**)], 2.01 d.d [1H, C^2H, ^3J 7.0, ^3J 10.0 (**VIIb**)], 3.53–3.62 m (8H, $\underline{CH_2}$–O), 5.12 d [1H, $=C^{2'}H_a$, ^2J 1.3 (**VIIb**)], 5.23 d [1H, $=C^{2'}H_b$, ^2J 1.3 (**VIIb**)]. Mass spectrum (**VIIb**), *m*/*e* (I_{rel}, %): 246/248 $[M]^+$ (<0.1), 211 $[M - Cl]^+$ (<1), 210 $[M - HCl]^+$ (<1), 173/175 $[M - C_4H_9O^{\cdot}]^+$ (<1), 155 (20), 134/136 (6/2), 117/119 (6/2), 99 (100), 89 (7), 57 (42). Mass spectrum (**VIIIb**), *m*/*e* (I_{rel}, %): 210 $[M]^+$ (<1), 153 $[M - C_4H_8^{\cdot}]^+$ (3), 137 $[M - C_3H_5O^{\cdot}]^+$ (4), 135 (15), 107 (100), 83 (38), 81 (30), 79 (65), 74 (3).

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