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HETEROCYCLIZATION OF ALLYL β - IODOETHERS IN 1,4-DIOXANE DERIVATIVES**G.M. Talybov, S.A. Musaeva**

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Abstract: Alkoxyiodination of 1-vinyl-4-organylbenzenes with 2-methyl-3-buten-1-ol and crystalline iodine in the presence of clinoptilolite (NaK) $_4\text{CaAl}_6\text{Si}_{30}\text{O}_{72}$ leads to allyl β -iodoethers in high yields which in the presence of heteropolyacids are converted into substituted 1,4 -dioxane.

Keywords: allyl β - iodoethers, 1,4-dioxane derivatives, alkoxyiodination.

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Introduction

Alkoxyiodination of alkenes with propenol and iodine in the presence of HgO is a rational method for obtaining allyl β -iodoethers [1, 2]. We found that replacing the latter with clinoptilolite (NaK) $_4\text{CaAl}_6\text{Si}_{30}\text{O}_{72}$ facilitates the process with the participation of a safer and non-toxic catalyst. We used *para*-substituted styrene as substituted alkenes the alkoxyhalogenation of which gives aromatic β -iodoethers with a yield of up to 80.2 % (1-3). The hydrolysis of the C-I bond in compounds (1-3) promotes their conversion into monoallyl esters of 1,2-diols which, when heated in an aqueous solution of phosphomolybdicheteropoly acid, form products of intermolecular cyclization of aryl-substituted 1,4-dioxanes (4-6), structural analogs of which are effective inhibitors of acid corrosion of metals in an aggressive environment [3-5].

Regioselective alkoxyiodination of the double bond of *para*-substituted styrene is manifested in the presence of signals of methylene protons of compounds (1-3) at 3.28 dd (1H, J=8.3, 5.8, CH₂I) and 3.41 dd (1H, J = 8.3, 5.8, CH₂I) in the ¹H NMR spectra of the reaction products, as well as the presence in the IR spectra of an absorption band of stretching vibrations of the C-I bond in the region of 545-

560 cm⁻¹. Intramolecular O - H addition to the double bond of the allyl group in compounds (1-3) also proceeds regioselectively, as evidenced by the signals of methyl groups bonded to the 1,4-dioxane ring in the NMR spectra at $\delta = 1.09$ d (3H, CH₃, J = 6.9 Hz) [6.7].

In the IR spectra of the obtained compounds, stretching vibrations of the carbon-halogen bond, both C-Br (3,6) and C-I (1-3) bonds, are observed in the region of 850 and 550 cm⁻¹ and 690-515 cm⁻¹, respectively [8]

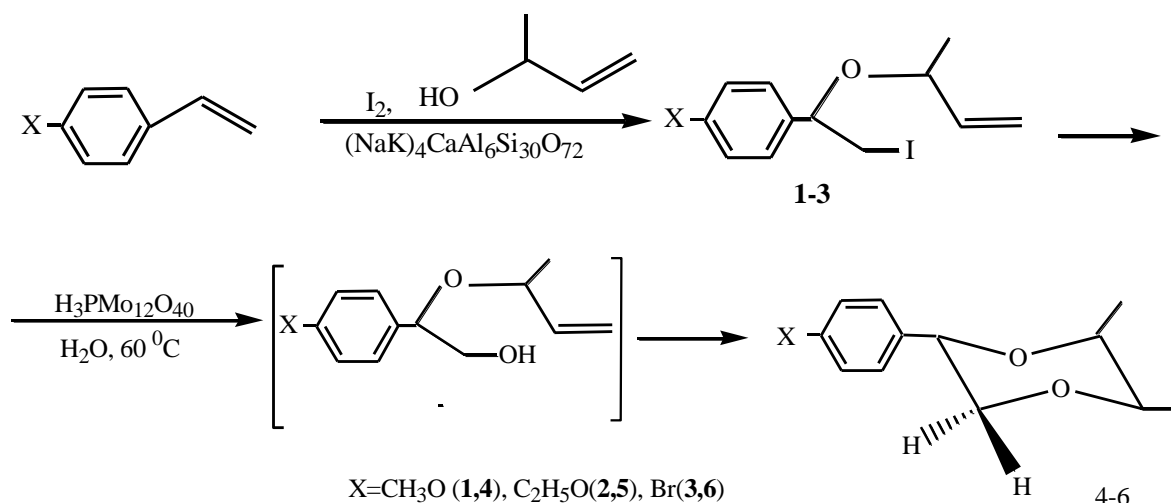
Stretching vibrations of the C-O-C bond group of 1,4-dioxane molecules is a strong band in the region of 1150-1085 cm⁻¹ caused by antisymmetric stretching vibrations of C-O-C, usually appearing at about 1125 cm⁻¹. The band of symmetric stretching vibrations of the C-O-C group in the six-membered ring absorbs 1170-1114 cm⁻¹.

The most intense bands in the benzene nucleus' IR spectra are observed at low frequencies between 900 and 675 cm⁻¹. These strong absorption bands arise due to out-of-plane deformation vibrations of the C-H bond of the cycle. The bands of in-plane vibrations appear within the range of 1300-1400 cm⁻¹. Skeletal vibrations, including vibrations of the

C-C cycle, have absorption in the region of 1600-1585 and 1500-1400 cm^{-1} . The bands of stretching C-H vibrations in aromatic compounds are observed between 3100 and 3000 cm^{-1} .

The presence in the structures of compounds (4-6) of an asymmetric carbon atom in position 2 in the adjacent methylene protons of the heterocyclic ring belonging to AB

systems, as well as being diastereotopic, i.e. magnetically nonequivalent, appear in the ^1H NMR spectrum as two singlet signals at 3.45 dd (1H, CH, $J = 8.1, 6.9$ Hz) and 3.65 dd (1H, CH, $J = 8.1, 6.9$ Hz) for 4, 3.46 dd (1H, CH, $J = 8.1, 6.9$ Hz) and 3.64 dd (1H, CH, $J = 8.1, 6.9$ Hz) for 5, 3.44 dd (1H, CH, $J = 8.1, 6.8$ Hz), 3.63 dd (1H, CH, $J = 8.1, 6.8$ Hz) for 6, respectively.



Owing to the asymmetric carbon atom in position 2, the adjacent protons of the methylene groups of the 1, 4-dioxane ring in position 3 contribute to their appearance in the form of two singlet signals in compounds (4-6).

The data of elemental analysis also confirmed the structure of obtained iodoethers (1-3) and substituted heterocycles (4-6).

Experimental part

IR spectra of compounds in a thin layer and KBr pellets were recorded on a Specord 75 IR instrument. NMR spectra of substances in SDSI3 solution were recorded on a Bruker SF-300 instrument (300.134 MHz), internal standard-HMDS.

1- [1- (But-3-en-2-yloxy) -2-iodoethyl] -4-methoxybenzene (1). To a cooled ($-5 \pm 0^\circ\text{C}$) and actively stirred mixture of 14 g (0.25 mol) 2-methyl-3-buten-1-ol and 33.2 g (0.25 mol) 4-methoxyphenylstyrene was added 2.6 g of clinoptilolite $(\text{NaK})_4\text{CaAl}_6\text{Si}_{30}\text{O}_{72}$, then portions (1 g) of 31.5 g (0.12 mol) of finely ground crystalline iodine. The stirring continued at room temperature for another 3-4 hours. Then the mixture was filtered; the filtrate washed with $\text{Na}_2\text{S}_2\text{O}_3$ solution, and extracted with ether. The

extract was dried with CaCl_2 . The ether was removed in a rotary evaporator, the residue was recrystallized. Obtained: 54.2 g (68%) of substance (I) with b.t. 137-138 $^\circ\text{C}$ (1 mm Hg), d_4^{20} 1.646, n_D^{20} 1.5712. IR (ν , cm^{-1}): 560, 850, 1270, 1340-1360, 1515, 1630, 1640, 3010, 3080 cm^{-1} . NMR ^1H (ν , ppm): 1.08 d (3H, CH₃, $J = 6.8$ Hz), 3.24-3.40 m (1H, CH), 3.81 s (3H, CH₃), 3.89 dd (1H, CH, $J = 12.5, 5.0$ Hz), 3.98 dd (1H, CH, $J = 12.5, 5.0$ Hz), 4.43 dd (1H, CH, $J = 8.0, 5.0$ Hz), 5.18 dd (1H, CH, $J = 10.0, 1.0$ Hz), 5.27 dd (1H, CH, $J = 17.0, 1.0$ Hz), 5.85-5.98 m (1H, CH), 6.89 d (2H, C₆H₂, $J = 9.0$ Hz), 7.24 d (2H, C₆H₂, $J = 9.0$ Hz). ^{13}C NMR (δ , ppm): 10.9, 55.3, 69.9, 80.5, 114.0, 117.4, 127.8, 131.9, 134.9, 134.4, 159.6. Found: %: C

C 47.08; H 5.24; I 38.25. $C_{13}H_{17}O_2I$. Calculated: %: C 47.00; H 5.16; I 38.20.

Allyl iodoethers (II, III) were obtained similarly.

1- [1- (But-3-en-2-yloxy) -2-iodoethyl] -4-ethoxybenzene (2). The yield is 80.2 %. b.p. 143-144 ° C (1 mm Hg), d_4^{20} 1.5653, n_D^{20} 1.5782, M_{rD} 70.46, calc. 69.93. IR (ν , cm^{-1}): 545, 850, 1270, 1360, 1515, 1630, 1640, 3010, 3080 cm^{-1} . NMR 1H (δ , ppm): 1.07 d (3H, CH_3 , $J = 6.8$ Hz), 1.18 t (3H, CH_3 , $J = 7.2$ Hz), 3.28 dd (1H, $J = 8.3$, 5.8, CH_2I), 3.41 dd (1H, $J = 8.3$, 5.8, CH_2I), 3.84 dd (1H, CH, $J = 12.5$, 5.0 Hz), 3.96 dd (1H, H_2C , $J = 14.2$, 7.2 Hz), 3.98 dd (1H, CH, $J = 12.5$, 5.0 Hz), 4.43 dd (1H, CH, $J = 8.0$, 5.0 Hz), 5.18 dd (1H, CH, $J = 10.0$, 1.0 Hz), 5.24 dd (1H, CH, $J = 17.0$, 1.0 Hz), 5.83-5.96 m (1H, CH), 6.84 d (2H, C_6H_2 , $J = 9.0$ Hz), 7.25 d (2H, C_6H_2 , $J = 9.0$ Hz). ^{13}C NMR (δ , ppm): 9.9, 25.1, 54.3, 69.4, 80.2, 113.4, 118.6, 126.9, 130.7, 133.6, 133.4, 161.6. Found, %: C 48.42; H 5.67; I 36.64. $C_{14}H_{19}O_2I$. Calculated, %: C 48.57; H 5.53; I 36.66.

1- [1- (But-3-en-2-yloxy) -2-iodoethyl] -4-bromobenzene (3). Yield 67.2 %. m.p. 78-79 ° C (from ethanol). IR (ν , cm^{-1}): 558, 670, 840, 1270, 1360, 1515, 1630, 1640, 3010, 3080 cm^{-1} . NMR 1H (δ , ppm): 1.08 d (3H, CH_3 , $J = 6.8$ Hz), 3.28 dd (1H, $J = 8.3$, 5.8, CH_2I), 3.41 dd (1H, $J = 8.3$, 5.8, CH_2I), 3.96 dd (1H, CH, $J = 12.5$, 5.0 Hz), 4.48 dd (1H, CH, $J = 8.3$, 5.8 Hz), 5.17 dd (1H, CH, $J = 10.0$, 1.0 Hz), 5.27 dd (1H, CH, $J = 17.0$, 1.0 Hz), 5.84-5.99 m (1H, CH), 6.94 d (2H, C_6H_2 , $J = 9.0$ Hz), 7.34 d (2H, C_6H_2 , $J = 9.0$ Hz). ^{13}C NMR (δ , ppm): 10.9, 55.3, 69.9, 80.5, 114.0, 117.4, 127.8, 131.9, 134.9, 134.4, 159.6. Found, %: C 37.64; H 3.65; Br 21.11; I 33.39. $C_{12}H_{14}BrIO$. Calculated, %: C 37.82; H 3.70; Br 20.97; I 33.30.

2- (4-Methoxyphenyl) -5,6-dimethyl-1,4-dioxane (4). 15.9 g (0.05 mmol) of compound (1) in 3 ml of THF was added over 30 minutes to a stirred magnetic stirrer mixture consisting of 1.2 g of $H_3PMo_{12}O_{40}$ and 10 ml of water. The temperature of the mixture was gradually raised to 50-60 ° C and kept for 1 hour. After cooling, the mixture was washed

with a solution of soda (0.05 mol) and $Na_2S_2O_3$, extracted with ether, and dried with $MgCO_3$. After vacuum distillation, 6.64 g (69.2 %) of substance (4) with b.p. 89-90 ° C (1 mm Hg), d_4^{20} 1.3464, n_D^{20} 1.5595 were isolated. IR (ν , cm^{-1}): 3008, 1310, 1170, 1125, 675. 1H NMR (δ , ppm): 1.09 d (3H, CH_3 , $J = 6.9$ Hz), 1.11 d (3H, CH_3 , $J = 6.8$ Hz), 3.45 dd (1H, CH, $J = 8.1$, 6.9 Hz), 3.65 dd (1H, CH, $J = 8.1$, 6.9 Hz), 3.80 s (3H, CH_3), 4.20 dd (1H, CH, $J = 8.4$, 6.9 Hz), 4.97 t (1H, CH, $J = 6.9$ Hz), 5.13 dd (1H, CH, $J = 8.1$, 6.9 Hz), 6.85-6.89 m (2H, C_6H_2), 7.23-7.29 m (2H, C_6H_2). ^{13}C NMR (δ , ppm): 17.9, 33.3, 42.6, 43.8, 55.2, 75.5, 79.7, 113.5, 126.7, 135.6, 158.5. Found, %: C 70.37; H 8.12; O 22.16. $C_{13}H_{18}O_3$. Calculated, %: C 70.24; H 8.16; O 21.59.

Substituted dioxanes were obtained in a similar way (5, 6).

2- (4-Ethoxyphenyl) -5,6-dimethyl-1,4-dioxane (5). Yield is 87.2 %. b.p. 94-95 ° C (1 mm Hg), d_4^{20} 1.2860, n_D^{20} 1.5602. IR (ν , cm^{-1}): 3078, 1350, 1169, 1124, 674. 1H NMR (δ , ppm): 1.09 d (3H, CH_3 , $J = 6.9$ Hz), 1.12 d (3H, CH_3 , $J = 6.8$ Hz), 1.18 t (3H, CH_3 , $J = 7.5$ Hz), 2.36-2.50 m (1H, CH), 3.46 dd (1H, CH, $J = 8.1$, 6.9 Hz), 3.64 dd (1H, CH, $J = 8.1$, 6.9 Hz), 3.75 q (2H, CH_2 , $J = 7.5$ Hz), 4.20 dd (1H, CH, $J = 8.4$, 6.9 Hz), 4.97 dd (1H, CH, $J = 6.9$ Hz), 6.85-6.89 m (2H, C_6H_2), 7.23-7.29 m (2H, C_6H_2). ^{13}C NMR spectrum (δ , ppm): 16.9, 25.4, 33.3, 42.6, 43.8, 55.2, 75.5, 79.7, 113.5, 126.7, 135.6, 158.5. Found, %: C 71.22; H 8.51. $C_{14}H_{20}O_3$. Calculated, %: C 71.16; H 8.53.

2- (4-Bromophenyl) -5,6-dimethyl-1,4-dioxane (6). Yield is 80.2 %. B.p. 111-112 ° C (1 mm Hg), d_4^{20} 1.6304, n_D^{20} 1.512. IR (ν , cm^{-1}): 3060, 1398, 1168, 1123, 676. 1H NMR (δ , ppm): 1.07 d (3H, CH_3 , $J = 6.9$ Hz), 1.13 d (3H, CH_3 , $J = 6.8$ Hz), 2.36-2.50 m (1H, CH), 3.44 dd (1H, CH, $J = 8.1$, 6.8 Hz), 3.63 dd (1H, CH, $J = 8.1$, 6.8 Hz), 4.20 dd (1H, CH, $J = 8.4$, 6.9 Hz), 4.97 dd (1H, CH, $J = 6.9$ Hz), 5.14 dd (1H, CH, $J = 8.1$, 6.9 Hz), 6.85-6.89 m (2H, C_6H_2), 7.23-7.29 m (2H, C_6H_2). ^{13}C NMR (δ , ppm): 16.9, 32.3, 41.6, 54.2, 73.5, 77.7, 112.5, 125.7, 133.6, 157.5. Found, %: C 52.82; H 5.88; Br 29.21. $C_{12}H_{16}BrO_2$. Calculated, %: C 52.77; H 5.91; Br 29.32.

Results and discussion

1. Alkoxyiodination of 1-vinyl-4-organylbzenes with 2-methyl-3-buten-1-ol and crystalline iodine leads to allyl-iodoethers in high yields.
2. Synthesized allyl β -iodoethers in the presence of heteropolyacids are converted into substituted 1,4-dioxanes.

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ALLİL β -YODEFİRLƏRİNİN 1,4-DİOKSANLARIN TÖRƏMƏLƏRİNƏ HETEROTSİKLİZASİYASI

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Klinoptilolit $(NaK)_4CaAl_6Si_3O_{72}$ iştirakında 1-vinil-4-üzvibenzolların 2-metil-3-buten-1-ol və kristallik yod ilə alkoksiyodlaşdırılması yüksək çıxımla və heteropoliturşuların iştirakında 1,4-dioksanın törəmələrinə çevrilən allil β -yodefirlərinin alınmasına gətirib çıxarır.

Açar sözlər: allil β -yodefirləri, 1,4-dioksanın törəmələri, alkoksiyodlaşdırılma.

**ГЕТЕРОЦИКЛИЗАЦИЯ АЛЛИЛОВЫХ β -ЙОДЭФИРОВ
В ПРОИЗВОДНЫХ 1,4-ДИОКСАНОВ**

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Алкоксидирование 1-винил-4-органилбензолов 2-метил-3-бутен-1-олом и кристаллическим йодом в присутствии клиноптилолита $(\text{NaK})_4\text{CaAl}_6\text{Si}_{30}\text{O}_{72}$ приводит к получению аллиловых β -йодэфиров с высоким выходом, которые в присутствии гетерополикислот превращаются в замещенные 1,4-диоксана.

Ключевые слова: аллиловые β -йодэфиры, производные 1,4-диоксана, алкоксидирование.