

SHORT  
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## New Aryl-substituted 1,4-Dioxanes Prepared from Propargyl Ethers of (Bromomethyl)(phenylalkyl)methanols.

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1,4-Dioxane and its derivatives (especially those with unsaturated substituents) are promising initial compounds for synthesis and efficient inhibitors of acid corrosion of metals [1, 2].

We formerly showed that the key stage in the synthesis of such heterocycles consisted in the intramolecular elimination of hydrogen halide from compounds containing in their structure a fragment of ( $\beta$ -haloethoxy)ethanol [3, 4].

Aiming at preparation of new aryl-1,4-dioxanes we carried out a synthesis of the key ethers I–IV. The procedure was three-stage and included isolation of the ethers as individual compounds followed by the hydrogen halide elimination in an ethereal suspension of potassium hydroxide, and by heterocyclization.

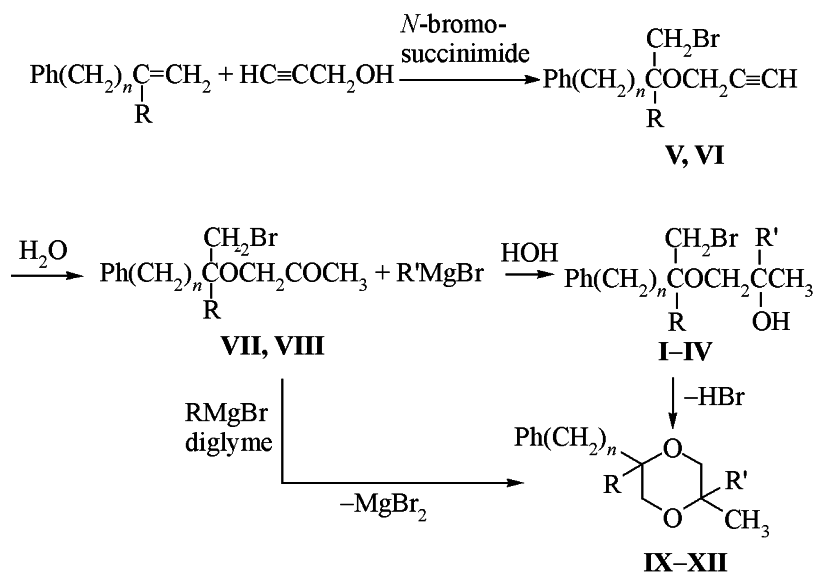
Propargyl ethers of (bromomethyl)(phenylalkyl)methanols V, VI were prepared by bromoalkoxyla-

tion of phenylalkene with propargyl alcohol and *N*-bromosuccinimide.

1,4-Dioxanes IX–XII are also formed at direct reaction of Grignard reagent with ethers of (bromomethyl)(phenylalkyl)methanols VII, VIII in diglyme circumventing the isolation of compounds I–IV.

The composition and structure of compounds obtained were confirmed by elemental analysis, IR and  $^1\text{H}$  NMR spectra.

**7-Benzyl-8-bromo-4-methyl-3-oxa-1-octyn-4-ol (I).** To a stirred Grignard reagent prepared from 5.95 g (0.05 mol) of propargyl bromide, 1.2 g (0.05 mol) of magnesium in 80 ml of ethyl ether in the presence of traces  $\text{HgCl}_2$  was added gradually at cooling to 0–5°C 13.6 g (0.05 mol) of ketone VII. The mixture was heated to 30°C for 3–4 h, then cooled and treated with 10% HCl. The water layer



R = H,  $n = 1$  (I, II, V, VII, IX, X); R =  $\text{CH}_3$ ,  $n = 0$  (III, IV, VI, VIII, XI, XII); R' =  $\text{CH}_2\text{C}\equiv\text{CH}$  (I, III, IX, XI),  $\text{C}_2\text{H}_5$  (II, IV, X, XII).

was extracted with diethyl ether, the extract was dried on  $\text{Na}_2\text{SO}_4$ . On removing the solvent the vacuum distillation of the residue provided 11.2 g (72%) of alcohol **I**, bp 148–149°C (*p*, 1 mm Hg),  $d_4^{20}$  1.2231,  $n_D^{20}$  1.5235,  $MR_D$  77.79, calc. 77.29. Found, %: C 57.42; H 6.08; Br 25.29.  $\text{C}_{15}\text{H}_{19}\text{BrO}_2$ . Calculated, %: C 57.89; H 6.15; Br 25.68.

Similarly were obtained compounds **II–IV**.

**6-Benzyl-7-bromo-3-methyl-5-oxaheptan-3-ol (II)**. Yield 75%, bp 138–139°C (*p*, 1 mm Hg),  $d_4^{20}$  1.2245,  $n_D^{20}$  1.5240,  $MR_D$  75.27, calc. 74.77. Found, %: C 55.35; H 6.95; Br 26.14.  $\text{C}_{14}\text{H}_{21}\text{BrO}_2$ . Calcd., %: C 55.82; H 7.03; Br 26.53.

**8-Bromo-4,7-dimethyl-7-phenyl-6-oxa-1-octyn-4-ol (III)** – Yield 48%, bp 112–113°C (*p*, 1 mm Hg),  $d_4^{20}$  1.2658,  $n_D^{20}$  1.5448,  $MR_D$  77.71, Calcd. 77.21. Found, %: C 57.56; H 6.02; Br 25.45.  $\text{C}_{15}\text{H}_{19}\text{BrO}_2$ . Calculated, %: C 57.89; H 6.15; Br 25.68.

**7-Bromo-3,6-dimethyl-6-phenyl-5-oxaheptan-3-ol (IV)** Yield 52%, bp 108–109°C (*p*, 1 mm Hg),  $d_4^{20}$  1.2650,  $n_D^{20}$  1.5442,  $MR_D$  75.19, Calcd. 74.69. Found, %: C 55.53; H 7.00; Br 26.39.  $\text{C}_{14}\text{H}_{21}\text{BrO}_2$ . Calculated, %: C 55.82; H 7.03; Br 26.53.

**5-Benzyl-6-bromo-4-oxa-1-hexyne (V)**. To an equimolar mixture of 38 g (0.32 mol) of allylbenzene and 18 g (0.32 mol) of propargyl alcohol cooled to –5°C was gradually added at stirring 26 g (0.32 mol) of *N*-bromosuccinimide maintaining the temperature of the reaction mixture below 0°C. The stirring was continued for 3 h at room temperature, the formed succinimide was removed by filtration, to the residue was added a solution of 15 g of NaOH in 100 ml of water, the product was extracted into ethyl ether, and the extract was dried on  $\text{CaCl}_2$ . On removing the ether the residue was subjected to vacuum distillation to afford 38.9 g (67%) of ether **V**, bp 106–107°C (*p*, 1 mm Hg),  $d_4^{20}$  1.3091,  $n_D^{20}$  1.5540,  $MR_D$  61.94, calc. 61.44. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 680 (C–Br), 1100 (C–O–C), 2110 and 3310 (C≡CH), 1515, 1620, 3040, 3080, 3100 ( $\text{C}_6\text{H}_5$ ). Found, %: C 56.43; H 5.02; Br 31.42.  $\text{C}_{12}\text{H}_{13}\text{BrO}$ . Calculated, %: C 56.92; H 5.14; Br 31.62.

**6-Bromo-5-methyl-5-phenyl-4-oxa-1-hexyne (VI)** was similarly prepared in 74% yield, mp 76°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 660 (C–Br), 1100 (C–O–C), 2100 and 3300 (C≡C–H).  $^1\text{H}$ NMR spectrum,  $\delta$ , ppm: 1.65 s (3H,  $\text{CH}_3$ ), 2.45 t (1H, ≡CH), 3.45 s (2H,  $\text{CH}_2\text{Br}$ ), 4.01 d (2H,  $\text{OCH}_2\text{C}\equiv$ ), 7.45 m (5H,  $\text{C}_6\text{H}_5$ ). Found, %: C 56.25; H 5.05; Br 31.15.  $\text{C}_{12}\text{H}_{13}\text{BrO}$ . Calculated, %: C 56.94; H 5.18; Br 31.57.

**5-Benzyl-6-bromo-4-oxa-2-hexanone (VII)**. To a stirred mixture heated to 60°C containing 0.65 g of  $\text{HgO}$ , 1 ml of concn.  $\text{H}_2\text{SO}_4$ , and 23.5 ml of water was gradually added at stirring 12.6 g (0.05 mol) of compound **V**. The mixture was boiled for 6 h at 60–65°C, extracted with ethyl ether, the water layer was saturated with NaCl and again extracted with ethyl ether. The combined organic solutions were dried on  $\text{Na}_2\text{SO}_4$ , the solvent was removed, and the residue was subjected to vacuum distillation to obtain 7.7 g (57%) of compound **VII**, bp 116–117°C (*p*, 3 mm Hg),  $d_4^{20}$  1.3440,  $n_D^{20}$  1.5480,  $MR_D$  64.04, calc. 63.54. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 675 (C–Br), 1100 (C–O–C), 1725 (C=O), 1515, 1620, 3040, 3080, 3100 ( $\text{C}_6\text{H}_5$ ). Found, %: C 53.02; H 5.10; Br 29.05.  $\text{C}_{12}\text{H}_{15}\text{BrO}_2$ . Calculated, %: C 53.14; H 5.54; Br 29.52.

**6-Bromo-5-methyl-5-phenyl-4-oxa-2-hexanone (VIII)** was similarly prepared in 57% yield, bp 88–90°C (*p*, 1 mm Hg),  $d_4^{20}$  1.3696,  $n_D^{20}$  1.5632,  $MR_D$  64.32, calc. 63.92. Found, %: C 53.01; H 5.25; Br 29.17.  $\text{C}_{12}\text{H}_{15}\text{BrO}_2$ . Calculated, %: C 53.15; H 5.58; Br 29.47.

**5-Benzyl-2-methyl-2-propargyl-1,4-dioxane (IX)**. (a) To a stirred suspension of 4.44 g KOH in 80 ml of ethyl ether was added 9.33 g (0.03 mol) of alcohol **I**, and the mixture was heated at reflux for 4 h. Then it was treated with water, the ether layer was separated and dried on  $\text{MgSO}_4$ . On removing the ether the residue was distilled in a vacuum to furnish 5.5 g (79%) of compound **IX**, bp 142–143°C (*p*, 1 mm Hg),  $d_4^{20}$  1.0449,  $n_D^{20}$  1.5318,  $MR_D$  68.28, calc. 67.78. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1100 (C–O–C), 2100 and 3330 (C≡C–H), 1515, 1620, 3040, 3080, 3100 ( $\text{C}_6\text{H}_5$ ).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 2.1 t (1H, ≡CH), 2.6 d (2H,  $\text{CH}_2\text{C}\equiv$ ), 3.00 m (2H,  $\text{CH}_2$ ), 3.20–3.75 m [4H, ( $\text{CH}_2\text{O}$ ) $_2$ ], 7.3 m (5H,  $\text{C}_6\text{H}_5$ ). Found, %: C 78.11; H 7.45.  $\text{C}_{15}\text{H}_{18}\text{O}_2$ . Calculated, %: C 78.23; H 7.88.

(b) To a stirred Grignard reagent prepared from 5.9 g of propargyl bromide, 1.2 g of magnesium in 50 of anhydrous diglyme at cooling to 0°C was gradually added 13.5 g (0.05 mol) of ether **III**. The mixture was heated at stirring to 75–80°C for 4 h, then cooled to room temperature, treated with water, and the product was extracted into ethyl ether. The extract was dried with  $\text{Na}_2\text{SO}_4$ . On removing the solvent the vacuum distillation of the residue furnish 5.3 g (46%) of compound **IX**.

Substituted dioxanes **X–XII** were similarly obtained by procedure (a).

**5-Benzyl-2-methyl-2-ethyl-1,4-dioxane (X)**: Yield 80%, bp 136°C (*p*, 1 mm Hg),  $d_4^{20}$  1.0136,  $n_D^{20}$

1.5170,  $MR_D$  65.76, calc. 65.26. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1100 (C–O–C), 2100 and 3330 (C $\equiv$ C–H), 1515, 1640, 3080, 3100 (C<sub>6</sub>H<sub>5</sub>). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.85–1.45 m (5H, CH<sub>3</sub>CH<sub>2</sub>), 3.00 m (2H, CH<sub>2</sub>), 3.20–3.75 m (4H, (CH<sub>2</sub>O)<sub>2</sub>), 7.35 m (5H, C<sub>6</sub>H<sub>5</sub>). Found, %: C 76.05; H 9.02. C<sub>14</sub>H<sub>20</sub>O<sub>2</sub>. Calculated, %: C 76.33; H 9.15.

**2,5-Dimethyl-2-propargyl-5-phenyl-1,4-dioxane (XI)** Yield 70%, bp 118–119°C (*p*, 1 mm Hg),  $d_4^{20}$  1.0771,  $n_D^{20}$  1.5516,  $MR_D$  68.28,  $E_{\text{calc}}$  67.78. Found, %: C 78.12; H 7.65. C<sub>15</sub>H<sub>18</sub>O<sub>2</sub>. Calculated, %: C 78.23; H 7.88.

**2,5-Dimethyl-5-phenyl-2-ethyl-1,4-dioxane (XII)**: Yield 75%, bp 102–103°C (*p*, 1 mm Hg),  $d_4^{20}$  1.0368,  $n_D^{20}$  1.5312,  $MR_D$  65.76,  $E_{\text{calc}}$  65.26. Found, %: C 76.18; H 9.07. C<sub>14</sub>H<sub>20</sub>O<sub>2</sub>. Calculated, %: C 76.33; H 9.15.

The organomagnesium synthesis in diglyme afforded compounds **X–XII** in 40–50% yield.

IR spectra were recorded on spectrophotometers UR-20 and Specord 75 IR from thin films or KBr

pellets. <sup>1</sup>H NMR spectra were registered on spectrometer Bruker SF-400 (400.134 MHz) from solutions in CDCl<sub>3</sub>, internal reference HMDS.

## REFERENCES

1. Karaev, S.F., Garaeva, Sh.V., and Mamedov, F.V., *Khimiya geteroatomnykh propargil'nykh soedinenii* (Chemistry of Propargyl Compounds Containing Heteroatoms), Moscow: Khimiya, 1993.
2. Karaev, S.F., Mekhtieva, V.Z., Agaev, N.M., and Dzharchieva, S.S., Abstracts of Papers, *Vserossiiskaya nauchno-prakticheskoi konf. "Razrabotka, proizvodstvo i primenenie khimicheskikh reagentov dlya neftyanoi i gazovoi promyshlennosti"* (Development, Production, and Application of Chemical Reagents for Petrochemical Industry), Moscow, 2002.
3. Karaev, S.F., Talybov, G.M., and Khabib Rakhman, Tukhi, *Zh. Org. Khim.*, 1993, vol. 29, p. 421.
4. Nurieva, U.G., Talybov, G.M., and Karaev, S.F., Abstracts of Papers, *Vth Bakinskaya Mezhdunarodn. Mamedalievskaya Neftekhim. Konf* (V Mamedaliev Petrochemical Baku Conf.), 2002, Baku, p. 91.