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LETTERS TO THE EDITOR

Synthesis and Some Transformations of Cyclic Acetals of Propargyl Aldehyde

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Abstract—Dehydrobromination of 2-(1,2-dibromoethyl)-1,3-dioxocyclanes with sodium amide in liquid ammonia provided cyclic acetals of propargyl aldehyde. Reactions of the resulting compounds with nitrile oxides and diazomethane afforded the corresponding isoxazole and pyrazole derivatives.

Keywords: cyclic acetals of propargyl aldehyde, 1,3-dipolar cycloaddition, isoxazoles, pyrazoles, dehydrobromination

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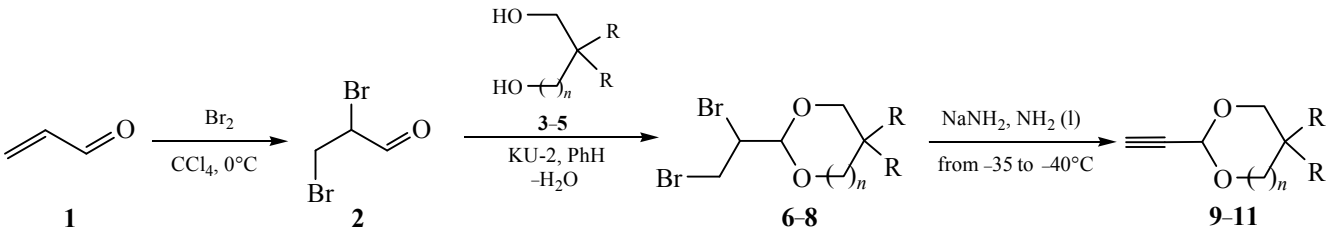
N- and *N*,*O*-containing heterocycles are widely used in the chemistry of biologically active and medicinal products [1–3]. Previously we have described the synthesis of 1,2,3-triazoles containing the cycloacetal fragment [4]. Continuing these studies we obtained 1,3-dioxacyclanes containing pyrazole and isoxazole moieties from propargyl aldehyde derivatives.

The commercially available acrolein **1** was converted to 2,3-dibromopropionic aldehyde **2**, which was condensed with glycols **3**–**5** to form cyclic acetals **6**–**8**. The reactions were carried out at 35–40°C using the cation exchanger KU-2-8 as the acid catalyst of acetalization, which allowed obtaining the target heterocycles **6**–**8** in a 60–70% yield. An alternative way is the addition of molecular bromine to 2-vinyl-1,3-dioxacyclanes which proceeds unselectively due to the parallel destruction of heterocycles. The yield of the target dibromoacetals **6**–**8** in this case did not exceed 30%, and their isolation and purification involve additional difficulties.

The dehydrobromination of compounds **6**–**8** with alkali in ethanol, which was carried out according to the known procedure [5], occurred only at temperatures above 70°C to give the target acetals **9**–**11** in a 25% yield due to a number of side processes. Therefore we carried out the dehydrobromination by sodium amide in liquid ammonia (from –35 to –40°C) according to the procedure [6]. The reaction was completed in 2.5–3 h. The yield of the desired products **9**–**11** was 45–60% (Scheme 1).

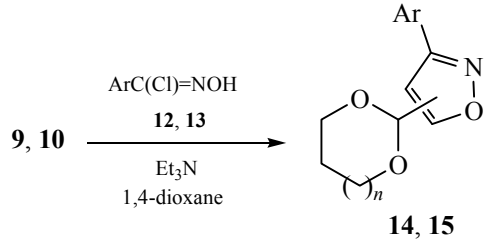
In the ^{1}H NMR spectra of compounds **9**–**11** there were the singlets of the proton at the triple bond (2.5–2.6 ppm) as well as the signals of the CH^2 proton of the 1,3-dioxocyclane fragment (5.4–5.9 ppm). The signals of the other ring protons were registered in a

Scheme 1.



R = H, *n* = 0 (**3**, **6**, **9**); R = H, *n* = 1 (**4**, **7**, **10**); R = Me, *n* = 1 (**5**, **8**, **11**).

Scheme 2.



Ar = *p*-Cl (**12**), *p*-MeO (**13**), *p*-Cl, *n* = 0 (**14**); Ar = *p*-MeO, *n* = 1 (**15**).

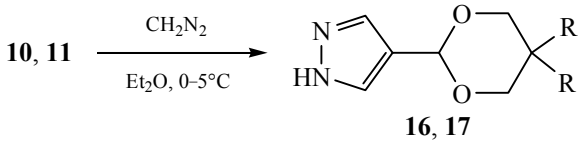
range of 3.7–4.2 ppm. The ^{13}C NMR spectra contained the signals at 73 and 80 ppm characteristic of the ethynyl group as well as the signals of the ring carbon atoms (~64 ppm for compounds **9**–**11** and ~25 ppm for dioxanes **10** and **11**). The signal of the C^2 atom was shifted to a weak field (89–92 ppm) due to the electron-acceptor effect of the oxygen atoms as well as of an ethynyl substituent. The spectrum of compound **11** contained two signals at 22.3 and 22.6 ppm corresponding to equatorial and axial methyl groups.

Further we involved alkyne-1,3-dioxacyclanes **9** and **10** into the reaction of 1,3-dipolar cycloaddition with arylnitrile oxides generated *in situ* from the corresponding benzhydroxymoyl chlorides **12** and **13** in dioxane solution at room temperature. The addition of 4-chlorophenylnitrile oxide to alkyne **9** proceeded regioselectively resulting in 3-(4-chlorophenyl)-5-(1,3-dioxolan-2-yl)isoxazole **14** in 70% yield (Scheme 2). The reaction of 4-methoxyphenylnitrile oxide with alkyne **10** led to the formation of a mixture of 4- and 5-substituted isoxazoles **15**. In all cases the cycloaddition was accompanied by dimerization of nitrile oxides; however, according to GC-MS data, the content of furoxane impurities in the target products **14** and **15** did not exceed 3–5%.

Regioselective cycloaddition of diazomethane to alkynes **10** and **11** (48 h, 5–7°C) furnished 4-(1,3-dioxocyclan-2-yl)pyrazoles **16** and **17** in yields of 81 and 66%, respectively (Scheme 3). Their structure was confirmed by ^{1}H NMR method. In the resonance region of pyrazole protons only one singlet was present about 7.7 ppm corresponding to the magnetically equivalent atoms H^3 and H^5. In the ^{13}C NMR spectra the carbon atoms attached to these protons resonated at 132 ppm.

Acetals of analogous heterocyclic aldehydes we have previously obtained starting from alkyl- or phenylacetylenes [4, 7]. However this approach for the synthesis of propargyl derivatives of **9**–**11** proved to be unsuitable.

Scheme 3.



R = H (**16**), R = Me (**17**).

In summary, we developed an effective method for the synthesis of substituted isoxazoles and pyrazoles starting from the cyclic acetals of propargyl aldehyde.

Acrolein (Aldrich) was distilled before use. Benzhydroxymoyl chlorides were synthesized by chlorination of the corresponding aldoximes with *N*-chlorosuccinimide in DMF by the procedure described in [8] and recrystallized from petroleum ether 40/70. An ether solution of diazomethane was prepared from *N*-nitroso-*N*-methylurea.

2,3-Dibromopropionic aldehyde (2). To a solution of 37.4 g (0.66 mol) of acrolein **1** in 100 mL of CCl_4 while cooling with a mixture of ice and salt (0°C) a solution of 108.8 g (0.67 mol) of bromine in 75 mL of CCl_4 was added. The solvent was distilled off and the residue was distilled in a vacuum. Yield 112 g (80%), colorless liquid, bp 81–83°C (15 mmHg) {bp 79°C (11 mmHg) [9]}. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.71 d.d (1H, CH_2, J_{HH} = 5.0, 10.8 Hz), 3.84 t (1H, CH_2, J_{HH} = 10.3 Hz), 4.54 d.d.d (1H, CH, J_{HH} = 3.0, 5.0, 10.3 Hz), 9.33 d (1H, CHO, J_{HH} = 3.5 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 27.09 (CH_2), 48.98 (CH), 182.17 (CHO).

2-(1,2-Dibromoethyl)-1,3-dioxolane (6). A mixture of 40.0 g (0.185 mol) of 2,3-dibromopropionic aldehyde **2**, 18.3 g (0.295) mol of ethylene glycol **3**, 190 mL of benzene, and 0.6 g of cationite KU-2-8 was heated with stirring until the distillation of water was completed, after which the cation resin was filtered off. Benzene was distilled off in a vacuum, and the residue was distilled in a vacuum. Yield 34 g (71%), colorless viscous liquid, bp 110–115°C (7 mmHg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.71–3.86 m [2H, $BrC\underline{H}_2$·(Br)CH], 3.95–4.03 m (2H, $H^{4,5}$), 4.05–4.17 m (2H, $H^{4,5}$), 4.26 d.d.d [1H, $BrCH_2(Br)C\underline{H}$, J_{HH} = 3.0, 6.10, 8.1 Hz], 5.23 d (1H, H^2, J_{HH} = 3.1 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 31.5 [$Br\underline{C}H_2(Br)CH$], 52.8 [$BrCH_2$·(Br)$\underline{C}$H], 66.0 ($C^{4,5}$), 102.1 (C^2). Mass spectrum, *m*/*z* (I_{rel}, %): 259 (0.5) $[M]^+$, 73 (100) $[M - BrCH_2BrCH]^+$.

2-(1,2-Dibromoethyl)-1,3-dioxane (7) was prepared similarly from 23.0 g of aldehyde **2** and 9.2 g of diol **4**.

Yield 20.5 g (71%), colorless viscous liquid, bp 164–167°C (23 mmHg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.39 d (1H, H^5, J_{HH} = 13.6 Hz), 2.04–2.24 m (1H, H^5), 3.67–3.96 m [4H, $H^{4,6}$ + $BrC\underline{H}_2(Br)CH$], 4.09–4.28 m [3H, $H^{4,6}$ + $BrCH_2(Br)C\underline{H}$], 4.81 d (1H, H^2, J_{HH} = 2.8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 25.5 (C^5), 31.8 [$Br\underline{C}H_2(Br)CH$], 51.4 [$BrCH_2(Br)\underline{C}H$], 67.2 ($C^{4,6}$), 99.0 (C^2). Mass spectrum, *m*/*z* (I_{rel}, %): 273 (1.5) $[M - H]^+$, 87 (100) $[M - BrCH_2BrCH]^+$.

2-(1,2-Dibromoethyl)-5,5-dibromoethyl-1,3-dioxane (8) was prepared similarly from 10.2 g of aldehyde **2** and 6.0 g of diol **5**. Yield 9.1 g (64%), colorless viscous liquid, crystallizing during storage, bp 144–148°C (11 mmHg), mp 52–54°C {mp 55–57°C [5]}. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.77 s (3H, Me^{eq}), 1.24 s (3H, Me^{ax}), 3.54 d.d (2H, $H^{4,6}$, J_{HH} = 3.5, 11.1 Hz), 3.71 d.d (2H, $H^{4,6}$, J_{HH} = 3.3, 8.1 Hz), 3.76 t [1H, $BrC\underline{H}_2(Br)CH$, J_{HH} = 5.7 Hz], 3.86 d.d [1H, $BrC\underline{H}_2(Br)CH$, J_{HH} = 8.4, 10.5 Hz], 4.20 d.d.d [1H, $BrCH_2(Br)C\underline{H}$, J_{HH} = 2.7, 5.7, 8.2 Hz], 4.73 d (1H, H^2, J_{HH} = 2.4 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.6(Me^{eq}), 23.0(Me^{ax}), 30.4 (C^5), 31.6 [$Br\underline{C}H_2(Br)CH$], 51.9 [$BrCH_2(Br)\underline{C}H$], 77.2 ($C^{4,6}$), 98.7 (C^2). Mass spectrum, *m*/*z* (I_{rel}, %): 301 (2.8) $[M - H]^+$, 115 (100) $[M - BrCH_2BrCH]^+$.

2-Ethynyl-1,3-dioxolane (9). *a.* To a solution of 56.0 g (1 mol) of KOH in 320 mL of anhydrous EtOH was added dropwise with stirring 88.0 g (0.34 mol) of compound **6**, then the reaction mixture was heated to 65°C, stirred for 15 min, and cooled to 10°C. The precipitated KBr was filtered off on a Buchner funnel, washed with 20 mL of anhydrous EtOH, and the filtrate was boiled under stirring for an additional 8 h. After cooling the reaction mixture was poured into 1700 mL of water, 50 mL of acetic acid, and extracted with CH_2Cl_2 (3 × 100 mL). The extract was dried with Na_2SO_4, the solvent was distilled off on a water bath. The residue was distilled in a vacuum. Yield 6.31 g (19%), colorless liquid with a characteristic odor, bp 66–67°C (58 mmHg). IR spectrum, ν, cm^{-1}: 3280 (C≡C–H), 2115 (C≡C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.54 s (1H, HC≡C), 3.77–3.88 m (4H, $H^{4,5}$), 5.46 s (1H, H^2). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 63.9 ($C^{4,5}$), 73.3 (H$\underline{C}$≡C), 79.1 (HC≡$\underline{C}$), 91.9 (C^2). Mass spectrum, *m*/*z* (I_{rel}, %): 97 (100) $[M - H]^+$.

b. To a solution of sodium amide prepared by dissolving 10.8 g (0.47 mol) of sodium metal in 150 mL of liquid ammonia was added dropwise 21.1 g (0.081 mol) of dibromide **6** while stirring within 30 min at from –35 to –40°C. The reaction mixture was stirred for 2 h, after which 21 g of crystalline NH_4Cl was added in portions, and ammonia was removed. Next, 100 mL of diethyl ether was added to the solid residue. The mixture was stirred thoroughly. The resulting ether solution was decanted. The operation was repeated three times, after which the residue was gently poured into 100 mL of ethanol and 600 mL of water. The resulting solution was extracted twice with diethyl ether; the extract was dried with calcined K_2CO_3 and combined with ether extracts. The solvent was distilled off, and the residue was distilled in a vacuum. Yield 3.45 g (41%).

2-Ethynyl-1,3-dioxane (10) was prepared similarly by the procedure *b* from 18.5 g of dibromide **7**. Yield 4.1 g (55%), colorless liquid with a characteristic odor, bp 169–174°C (760 mmHg). IR spectrum, ν, cm^{-1}: 3277 (C≡C–H), 2118 (C≡C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.58–1.68 m (1H, $H^5{}_{eq}$), 1.73–1.90 m (1H, $H^5{}_{ax}$), 2.60 s (1H, HC≡C), 3.73–3.82 m (2H, $H^{4,6}$), 4.09–4.18 m (2H, $H^{4,6}$), 5.86 s (1H, H^2). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 25.4 (C^5), 64.6 ($C^{4,6}$), 74.0 (H$\underline{C}$≡C), 78.3 (HC≡$\underline{C}$), 89.8 (C^2). Mass spectrum, *m*/*z* (I_{rel}, %): 111 (100) $[M - H]^+$.

5,5-Dimethyl-2-ethynyl-1,3-dioxane (11) was prepared similarly by the procedure *b* from 8.2 g of dibromide **8**. Yield 1.5 g (40%), colorless liquid with a menthol odor, bp 64–65°C (45 mmHg). IR spectrum, ν, cm^{-1}: 3272 (C≡C–H), 2113 (C≡C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.95 s (3H, Me^{eq}), 1.04 s (3H, Me^{ax}),2.59 s (1H, HC≡C), 3.43 d (2H, $H^{4,6}$, J_{HH} = 11.2 Hz), 3.78 d (2H, $H^{4,6}$, J_{HH} = 11.2 Hz), 5.34 s (1H, H^2). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 22.3 (Me^{eq}), 22.6 (Me^{ax}), 30.5 (C^5), 68.2 ($C^{4,6}$), 74.0 (HC≡$\underline{C}$), 78.3 (H$\underline{C}$≡C), 89.8 (C^2). Mass spectrum, *m*/*z* (I_{rel}, %): 139 (4) $[M - H]^+$.

3-(4-Chlorophenyl)-5-(1,3-dioxolan-2-yl)isoxazole (14). To a solution of 98 mg (1 mmol) of compound **10** and 190 mg (1 mmol) of 4-chloro-*N*-hydroxybenzimidoyl chloride in 1 mL of 1,4-dioxane was added with stirring 0.16 mL (1.15 mmol) of triethylamine. After 20 h the reaction mixture was poured with stirring into 10 g of ice. The crystalline product was filtered off, washed with 5 mL of water, and dried in air. Yield 176 mg (70%), colorless crystals, mp 73–75°C (aq. EtOH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.07–4.19 m (4H, $H^{4,5}$), 6.12 s (1H, H^2), 6.61 s (1H, H^4), 7.44 d (2H, H_{Ar}, J_{HH} = 8.8 Hz), 7.74 d (2H, H_{Ar}, J_{HH} = 8.4 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 65.5

($C^{4,5}$), 96.5 (C^2), 100.5 (C^4), 128.2, 129.3, 129.6, 136.2, 161.2, 170.0. Found, %: C 57.10; H 4.12. $C_{12}H_{10}ClNO_3$. Calculated, %: C 57.27; H 4.01.

3-(4-Methoxyphenyl)-5(4)-(1,3-dioxan-2-yl)isoxazole (15) was prepared similarly from 112 mg of alkyne **10** and 186 mg of benzhydroxymoyl chloride **13**. Yield 183 mg (70%, regioisomers mixture), colorless crystals, mp 54–56°C (aq. EtOH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.51 d (1H, H^5, J_{HH} = 13.8 Hz), 2.17–2.35 m (1H, H^5), 3.85 s (3H, MeO), 4.01 t (2H, $H^{4,6}$, J_{HH} = 11.6 Hz), 4.29 d.d (2H, $H^{4,6}$, J_{HH} = 11.4, 4.0 Hz), 5.74 c (H^2, 5-isomer), 6.64 s (H^2, 4-isomer), 6.97 d (2H, H_{Ar}, J_{HH} = 8.3 Hz), 7.28 s (1H, isoxazole), 7.48 s (1H, isoxazole), 7.75 d (2H, H_{Ar}, J_{HH} = 8.4 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 25.6 (C^5), 55.4 (MeO), 67.3 ($C^{4,6}$), 95.0 (C^2, dioxane, 5-isomer), 95.7 (C^4, isoxazole, 5-isomer), 99.9 (C^2, dioxane, 4-isomer), 114.4 (C_{Ar}), 114.5 (C^4, isoxazole, 4-isomer), 121.39 (C_{Ar}), 128.29 (C_{Ar}). Found, %: C 64.18; H 5.84. $C_{14}H_{15}NO_4$. Calculated, %: C 64.36; H 5.79.

4-(1,3-Dioxan-2-yl)-1*H*-pyrazole (16). To 112 mg (1 mmol) of compound **10** was added 3 mL of a 0.45 M solution of diazomethane in diethyl ether with ice cooling. The mixture was kept at 5–7°C for 48 h, then the crystals were filtered off and dried. Yield 133 mg (87%), colorless crystals, mp 98–100°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.36–1.50 m (1H, H^5), 2.05–2.35 m (1H, H^5), 3.87–4.05 m (2H, $H^{4,6}$), 4.12–4.31 m (2H, $H^{4,6}$), 5.60 s (1H, H^2), 7.64 s (2H, $H^{3,5}$), 9.91 s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 25.7 (C^5), 67.1 ($2C^{4,6}$), 96.9 (C^2), 120.8 (C^4), 131.7 ($2C^{3,5}$). Mass spectrum, *m*/*z* (I_{rel}, %): 153 (82) $[M - H]^+$, 124 (10), 95 (100). Found, %: C 54.33; H 6.58. $C_7H_{10}N_2O_2$. Calculated, %: C 54.54; H 6.54.

4-(5,5-Dimethyl-1,3-dioxan-2-yl)-1*H*-pyrazole (17) was prepared similarly from 140 mg of compound **11**. Yield 120 mg (66%), colorless crystals, mp 160–161°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.79 s (3H, Me^{eq}), 1.27 s (3H, Me^{ax}), 3.60 d (2H, $H^{4,6}$, $^2J_{HH}$ = 10.8 Hz), 3.73 d (2H, $H^{4,6}$, $^2J_{HH}$ = 10.8 Hz), 5.51 s (1H, H^2), 7.69 s (2H, $H^{3,5}$), 10.92 s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.9 (Me^{eq}), 23.0 (Me^{ax}), 30.2 (C^5), 77.4 ($2C^{4,6}$), 96.7 (C^2), 120.5 (C^4), 131.8 ($2C^{3,5}$). Mass spectrum, *m*/*z* (I_{rel}, %): 181 (39) $[M - H]^+$, 152 (5), 113 (5), 97 (100). Found, %: C 59.60; H 7.55. $C_9H_{14}N_2O_2$. Calculated, %: C 59.32; H 7.74.

^{1}H and ^{13}C NMR spectra of the solutions in $CDCl_3$ were recorded on a Bruker AM300 spectrometer at operating frequencies of 300 and 75 MHz, respectively, using TMS as an internal reference. IR spectra were recorded on a FSM-1201 instrument with Fourier transform; spectra of the liquid samples were obtained from a thin layer between the KBr pellets; spectra of the solids were recorded from KBr pellets. Mass spectra of electron ionization (70 eV) were recorded on a Shimadzu GCMS-QP2010 Ultra chromatography-mass spectrometer. The sample was introduced through a Rtx-5MS capillary column containing 5% diphenyl- and 95% dimethylpolysiloxane as a stationary phase (*l* 30 m). Purity of the resulting compounds was monitored by TLC on Sorbfil plates (eluent ethyl acetate–petroleum ether mixture in various ratios), as well as by GC method on a Crystallux 4000M chromatograph with a flame ionization detector and a ZB-1 column (stationary phase 100% polydimethylsiloxane, column length 50 m, internal diameter 0.25 mm, fixed phase film thickness 0.5 μm).

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