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Dedicated to Full Member of the Russian Academy of Sciences
B.A. Trofimov on his 70th anniversary

Vinylation of Hydroxy-Containing Cyclic Formaldehyde Acetals with Acetylene

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Abstract—Nucleophilic addition of alcohols having cyclic acetal fragments to acetylene smoothly occurs under relatively mild conditions (KOH, 100–125°C, 1–2 h, initial acetylene pressure 11–12 atm) to give the corresponding vinyl ethers in 80–83% yield.

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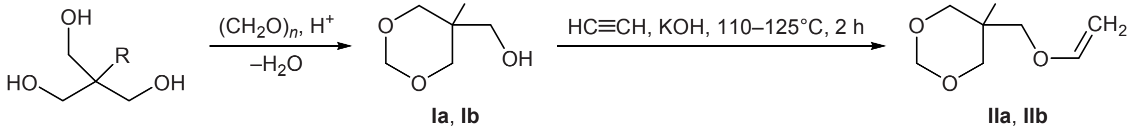
Development of the chemistry of cyclic acetals is stimulated by wide occurrence of cyclic acetal fragments in natural compounds [1], extensive use of acetal protection in the chemistry of carbohydrates [2] and steroids [3], and strong and versatile physiological activity. Of particular importance are cyclic acetals possessing other functional groups, e.g., hydroxy. Such compounds have found application in the manufacture of plasticizers for poly(vinyl chloride) resins [4, 5], in building construction [6], and as components of diesel fuels [7]. Furthermore, cyclic acetals derived from glycerol are used in perfumery, cosmetics (as carriers ensuring transdermal delivery of biologically active components) [8], medicine, and veterinary (as solvents for the preparation of parenteral formulations) [9]. Increased interest in functionalized 1,3-dioxacycloalkanes is also explained by their accessibility: they are readily synthesized from large-scale triols and carbonyl compounds [10]. Moreover, a known problem is utilization of dioxane alcohols formed as by-products in the manufacture of isoprene (~100 kg per ton of isoprene) [4]. A convenient approach to modification of cyclic acetals containing reactive hydroxy groups is based on their vinylation with acetylene, which leads to promising functionalized vinyl ethers.

Published data on vinyl ethers containing a cyclic acetal fragment are limited: only the corresponding carbohydrate derivatives were mainly reported [11]. It was also noted that nucleophilic addition of glycerol to acetylene in superbasic catalytic systems [12] could give rise to both 1,2,3-tris(vinyloxy)propane and 4-vinyloxymethyl-2-methyl-1,3-dioxolane, depending on the conditions [13].

Direct vinylation of alcohols having an acetal fragment with acetylene was described only for hydroxy derivatives of 2-substituted 1,3-dioxanes [14]. The reaction was carried out under severe conditions (KOH, 160–170°C, 1.5–2 h) at an initial acetylene pressure of 16 atm, and the yield of the corresponding vinyl ethers was 60–75% [14].

The present study was aimed at developing an efficient procedure for the vinylation of hydroxy-containing cyclic formaldehyde acetals. As substrates we used 5-alkyl-5-hydroxymethyl-1,3-dioxanes and isomeric acetals derived from formaldehyde and glycerol.

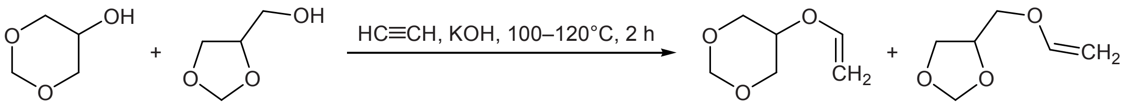
Scheme 1.



Ia, **Ib** **IIa**, **IIb**

R = Me (**a**), Et (**b**).

Scheme 2.



III **IV** **V** **VI**

5-Alkyl-5-hydroxymethyl-1,3-dioxanes **Ia** and **Ib** were found to react with acetylene at an initial pressure of 12 atm (10 wt % of KOH, 110–125°C, 2 h) to produce the corresponding vinyl ethers **IIa** and **IIb** (82 and 80%, respectively; Scheme 1). Initial hydroxymethyl dioxanes **Ia** and **Ib** were synthesized from paraformaldehyde and 2-hydroxymethyl-2-methyl- and -2-ethylpropane-1,3-diols, respectively.

Mild reaction conditions, high yields of vinyl ethers **IIa** and **IIb**, and complete conversion of alcohols **Ia** and **Ib** indicate that the latter are considerably more reactive than primary alkanols in nucleophilic addition to acetylene. For example, heptan-1-ol reacts with acetylene under analogous conditions (initial acetylene pressure 12–13 atm, 10 wt % of KOH, 110–115°C, 4 h) to give heptyl vinyl ether in a poor yield (27%) [15]. The reactions with unbranched primary alkanols are more effective at 135–150°C.

Relatively facile vinylation was also observed in the reaction of acetylene with cyclic acetals derived from formaldehyde and glycerol. A mixture of isomeric 1,3-dioxan-5-ol (**III**) and 1,3-dioxolan-4-ylmethanol (**IV**) at a ratio of ~1.5 : 1 reacted with acetylene at an initial pressure of 11 atm (10 wt % of KOH, 100–120°C, 1–2 h) to produce 5-vinyloxy-1,3-dioxane (**V**) and 4-vinyloxymethyl-1,3-dioxolane (**VI**) in an overall yield of 83% (Scheme 2). The ratio of vinyl ethers **V** and **VI** was the same as the ratio of initial alcohols **III** and **IV**, indicating their comparable reactivities though compound **III** has a secondary hydroxy group while the hydroxy group in **IV** is primary.

A probable reason for the observed unusually facile nucleophilic addition to acetylene of alcohols having cyclic acetal fragments, as compared to unbranched alkanols, is chelation of alkali metal cation by two oxygen atoms of the substrate; as a result, KOH ion pair becomes separated to a stronger extent and hence hydroxide ion becomes more reactive. Activation of anions via creation of intrinsic superbasicity was proposed for the first time in [12, 16] in the vinylation of oligo(ethylene glycols). Therefore, it might be expected that, e.g., 2-methoxyethanol should react with acetylene in the presence of alkali metal hydroxides more effectively than unsubstituted aliphatic alcohols. In fact, under comparable conditions (10 wt % of KOH, 115–120°C, 2 h), the yield of 1-methoxy-2-vinyloxyethane was greater by ~25–30% than the yield of heptyl vinyl ether.

Vinyl ethers **IIa**, **IIb**, and **V**/**VI** (isomer mixture) are colorless transparent liquids with a slight pleasant odor; they are readily soluble in most organic solvents and sparingly soluble in water. Their structure was confirmed by spectral and analytical data.

Thus the results of the present study showed that the presence of a cyclic acetal fragment in alkanols facilitates their nucleophilic addition to acetylene, ensuring preparation of the corresponding vinyl ethers under relatively mild conditions in high yield. The products can be used as monomers for the synthesis of water-soluble polyvinyl alcohol derivatives via polymerization and subsequent removal of acetal protection.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Bruker DPX-400 instrument (400.13 MHz for ^{1}H and 100.62 MHz for ^{13}C) using $CDCl_3$ as solvent; the chemical shifts were measured relative to the solvent signals. The IR spectra (400–4000 cm^{-1}) were obtained from thin films (neat) on a Bruker IFS-25 spectrometer. GLC analysis was performed on an Agilent 6890N chromatograph.

1,3-Dioxan-5-ol (**III**) and 1,3-dioxolan-4-ylmethanol (**IV**) (mixture of isomers at a ratio of ~1.5 : 1), 2-hydroxymethyl-2-methylpropane-1,3-diol (Aldrich), and 2-ethyl-2-hydroxymethylpropane-1,3-diol (BASF) were commercial products.

5-Methyl-1,3-dioxan-5-ylmethanol (Ia). *p*-Toluenesulfonic acid monohydrate, 0.45 g (0.002 mol), was added to a suspension of 36.0 g (0.3 mol) of 2-hydroxymethyl-2-methylpropane-1,3-diol and 9.0 g (0.3 mol) of paraformaldehyde in 80 ml of toluene, and the mixture was heated under reflux in a flask equipped with a Dean–Stark trap (~3.5 h). When the reaction was complete (water no longer separated), 0.25 g of anhydrous sodium carbonate was added to neutralize the catalyst, the solvent was removed on a rotary evaporator, and the residue was distilled under reduced pressure to isolate 33.5 g (85%) of compound

Ia as a colorless liquid, bp 76–78°C (4 mm), n_D^{20} = 1.4586; published data [14]: bp 90–92°C (5 mm), n_D^{20} = 1.4605. IR spectrum, ν, cm^{-1}: 3438 s (OH); 2957 s, 2851 s (CH_2, CH_3); 2767 s, 2698 m (OCH_2O); 1458 s, 1397 m, 1340 m, 1310 m, 1276 m (CH_2, CH_3, OH); 1226 s (COC); 1166 s, 1096 s, 1034 s (OCH_2O), 959 m, 935 m, 920 m (ring); 787 m (CH_2), 668 m, 561 w, 497 w, 434 w (COC, ring). ^1H NMR spectrum, δ, ppm: 4.93 d and 4.64 d (1H each, 2-H, ^2J = 5.9 Hz), 3.82 d and 3.41 d (2H each, 4-H, 6-H, ^2J = 11.2 Hz), 3.67 s (2H, CH_2O), 2.88 s (1H, OH), 0.81 s (3H, Me). ^{13}C NMR spectrum, δ_C, ppm: 93.93 (C^2), 72.89 (C^4, C^6), 65.41 (CH_2), 35.63 (C^5), 17.44 (Me). Found, %: C 54.29; H 9.27. $C_6H_{12}O_3$. Calculated, %: C 54.53; H 9.15.

5-Ethyl-1,3-dioxan-5-ylmethanol (Ib). A suspension of 52.8 g (0.39 mol) of 2-ethyl-2-hydroxymethylpropane-1,3-diol, 12.0 g (0.4 mol) of paraformaldehyde, and 0.6 g (0.003 mol) of *p*-toluenesulfonic acid monohydrate in 100 ml of tetrahydrofuran was heated under reflux until the mixture became homogeneous (3 h). Anhydrous sodium carbonate, 0.25 g, was added to neutralize the catalyst, the solvent was removed on a rotary evaporator, and the residue was distilled under reduced pressure to isolate 53.8 g (93%) of compound **Ib** as a colorless liquid, bp 92–94°C (5 mm), n_D^{20} = 1.4641. IR spectrum, ν, cm^{-1}: 3449 s (OH); 2967 s, 2930 s, 2882 s, 2857 s (CH_2, CH_3); 2765 s, 2698 m (OCH_2O); 1477 s, 1457 s, 1400 sh, 1387 m, 1341 m, 1310 m, 1254 m (CH_2, CH_3, OH); 1230 s, 1218 m (COC); 1198 m, 1167 s, 1141 sh, 1101 s, 1033 s (OCH_2O); 987 m, 956 m, 925 s (ring), 884 m, 784 m, 774 m (CH_2), 663 m, 564 w, 520 w, 455 w, 442 w (COC, ring). ^1H NMR spectrum, δ, ppm: 4.92 d and 4.63 d (1H each, 2-H, ^2J = 6.0 Hz), 3.83 d and 3.45 d (2H each, 4-H, 6-H, ^2J = 11.5 Hz), 3.72 s (2H, CH_2O), 3.03 s (1H, OH), 1.28 q (2H, $C\mathbf{H}_2Me$, ^3J = 7.6 Hz), 0.82 t (3H, Me, ^3J = 7.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 94.05 (C^2), 71.86 (C^4, C^6), 62.05 (CH_2), 37.68 (C^5), 23.58 (5-CH_2), 6.81 (Me). Found, %: C 57.61; H 9.53. $C_7H_{14}O_3$. Calculated, %: C 57.51; H 9.65.

5-Alkyl-5-vinyloxymethyl-1,3-dioxanes IIa and IIb (*general procedure*). A 1-l steel rotating high-pressure reactor was charged with 0.18 mol of alcohol **Ia** or **Ib** and potassium hydroxide (10 wt %), acetylene was supplied to a pressure of 12 atm, and the mixture was heated for 2 h at 110–125°C. The products were isolated by vacuum distillation.

5-Methyl-5-vyniloxymethyl-1,3-dioxane (IIa). Yield 23.4 g (82%), bp 46-48°C (2 mm), n_D^{20} = 1.4508; published data [14]: bp 64–65°C (8 mm), n_D^{20} = 1.4550. IR spectrum, ν, cm^{-1}: 3118 w, 3044 w (CH=, CH_2=); 2963 sh, 2957 s, 2953 sh, 2848 s (CH_2, CH_3); 2767 m, 2698 w (OCH_2O); 1639 s, 1619 s (C=C); 1469 m, 1458 m, 1403 m, 1397 m (ring); 1372 m, 1318 s (CH=, CH_2=); 1285 w (ring); 1244 m, 1202 s (COC); 1167 s, 1099 s, 1076 s, 1036 s, 1018 s, 964 s, 949 s, 937 s, 923 s, 817 s, 700 m (COC, CH=, CH_2=, ring). ^1H NMR spectrum, δ, ppm: 6.46 d.d (1H, =CHO), 4.18 d.d (1H, =CH_{trans}, ^3J = 14.2, ^2J = 1.2 Hz), 3.94 d.d (1H, =CH_{cis}, ^3J = 6.6, ^2J = 1.2 Hz), 4.90 d and 4.63 d (1H each, 2-H, ^2J = 6.0 Hz), 3.83 d and 3.39 d (2H each, 4-H, 6-H, ^2J = 11.5 Hz), 3.72 s (2H, CH_2), 0.89 s (3H, Me). ^{13}C NMR spectrum, δ_C, ppm: 152.15 (OC=), 94.11 (C^2), 86.48 (CH=), 73.00 (C^4, C^6), 70.46 (=CH_2), 34.85 (C^5), 17.86 (Me). Found, %: C 60.60; H 9.09. $C_8H_{14}O_3$. Calculated, %: C 60.74; H 8.92.

5-Ethyl-5-vinyloxymethyl-1,3-dioxane (IIb). Yield 24.8 g (80%), bp 62–63°C (3 mm), n_D^{20} = 1.4541. IR spectrum, ν, cm^{-1}: 3118 w, 3044 w (CH=, CH_2=); 2969 s, 2936 s, 2889 sh, 2851 s (CH_2, CH_3); 2770 m, 2705 w (OCH_2O); 1637 s, 1617 s (C=C); 1477 s, 1463 s, 1402 m, 1384 m (ring); 1372 m, 1319 s (CH=, CH_2=); 1265 w (ring); 1236 m, 1202 s (COC); 1169 s, 1105 s, 1078 s, 1034 s, 1010 s, 961 s, 928 s, 894 s, 817 s, 775 m, 700 w (COC, CH_2=, ring). ^1H NMR spectrum, δ, ppm: 6.48 d.d (1H, =CHO), 4.22 d.d (1H, =CH_{trans}, ^3J = 14.4, ^2J = 1.9 Hz), 3.98 d.d (1H, =CH_{cis}, ^3J = 6.8, ^2J = 1.9 Hz), 4.93 d and 4.64 d (1H each, 2-H, ^2J = 5.9 Hz), 3.86 d and 3.46 d (2H each, 4-H, 6-H, ^2J = 11.7 Hz), 3.79 s (2H, CH_2), 1.33 q (2H, $C\mathbf{H}_2Me$, ^3J = 7.6 Hz), 0.80 t (3H, Me, ^3J = 7.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 152.11 (OC=), 94.27 (C^2), 86.44 (C=), 72.01 (C^4, C^6), 67.35 (OCH_2), 36.98 (C^5), 24.06 (5-CH_2), 6.90 (Me). Found, %: C 62.60; H 9.49. $C_9H_{16}O_3$. Calculated, %: C 62.77; H 9.36.

Vinyl ethers V and VI (mixture of isomers**).** A 1-l steel rotating high-pressure reactor was charged with 26.0 g (0.25 mol) of a ~1.5 : 1 mixture of compounds **III** and **IV** and 2.6 g (10 wt %) of potassium hydroxide, acetylene was supplied to a pressure of 12 atm, and the mixture was heated for 2 h at 100–110°C or for 1 h at 110–120°C. Vacuum distillation gave 26.9 g (83%) of a mixture of 5-vinyloxy-1,3-dioxane (**V**) and 4-vinyloxymethyl-1,3-dioxolane (**VI**) at a ratio of ~1.5 : 1 (according to the ^1H NMR data). bp 45–47°C (9 mm), n_D^{20} = 1.4510. IR spectrum, ν, cm^{-1}: 3117 w (CH=, CH_2=); 2983 m, 2926 m, 2857 s (CH_2), 2778 m (OCH_2O); 1638 s, 1619 s (C=C); 1478 m, 1446 m, 1403 m (ring), 1347 m, 1327 s (CH=, CH_2=); 1283 m (ring); 1225 m, 1200 s (COC), 1174 s, 1151 s, 1090 s, 1078 s, 1044 s, 1022 s, 980 s, 965 s, 825 s (COC, CH=, CH_2=, ring). ^1H NMR spectrum, δ, ppm: compound **V**: 6.34 d.d (1H, =CHO), 4.30 d.d (1H, $=CH_{trans}$, ^3J = 14.4, ^2J = 1.8 Hz), 4.09 d.d (1H, $=CH_{cis}$, ^3J = 6.6, ^2J = 1.8 Hz), 4.84 d and 4.76 d (1H each, 2-H, ^2J = 6.1 Hz), 4.03 m and 3.73 d.d (4H, 4-H, 6-H, ^2J = 11.8, ^3J = 5.6 Hz), 3.89 m (5-H); compound **VI**: 6.45 d.d (1H, =CHO), 4.18 d.d (1H, $=CH_{trans}$, ^3J = 14.3, ^2J = 1.8 Hz), 4.00 d.d (1H, $=CH_{cis}$, ^3J = 6.8, ^2J = 1.8 Hz), 5.02 s and 4.88 s (1H each, 2-H), 4.25 m (1H, 4-H), 3.95 m (2H, 5-H), 3.69 m (2H, OCH_2). ^{13}C NMR spectrum, δ_C, ppm: compound **V**: 149.47 (CH=), 93.21 (C^2), 88.87 (CH_2=), 68.20 (C^4, C^6), 65.91 (C^5); compound **VI**: 151.41 (CH=), 95.00 (C^2), 86.78 (CH_2=), 73.20 (C^4), 68.41 (C^5), 65.91 (CH_2). Found, %: C 55.38; H 7.87. $C_6H_{10}O_3$. Calculated, %: C 55.37; H 7.74.

Vinylation of 2-methoxyethanol. A 1-l steel rotating high-pressure reactor was charged with 22.4 g (0.29 mol) of 2-methoxyethanol and 2.2 g (10 wt %) of potassium hydroxide, acetylene was supplied to a pressure of 12 atm, and the mixture was heated for 2 h at 115–120°C. Distillation (105–115°C) gave 22.8 g of a substance containing 22% of unreacted 2-methoxyethanol (GLC). Yield of 1-methoxy-2-vinyloxyethane 17.8 g (60%).

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