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SHORT COMMUNICATIONS

Monosaccharide Dimethylhydrazones

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It has been demonstrated that in reaction between monosaccharides with phenylhydrazine depending on the reagents ratio form individual hydrazones, or ozazones, or mixtures of cyclic and acyclic compounds [1–5]. As a part of systematic investigation of unsymmetrical dimethylhydrazine reactions with halovinyl ketones and haloacroleins [6, 7] we succeeded in preparation of dimethylhydrazones from some monosaccharides.

It was shown that 1,1-dimethylhydrazine was involved into reaction with D- and L-arabinose and D- and L-galactose at equimolar reagents ratio affording dimethylhydrazones of the corresponding aldoses **I** and **II** in 73 and 77% yields respectively.

$$\mathrm{HOCH_2(CHOH)}_n\mathrm{CH{=}O + NH_2N(CH_3)_2}$$

$$\longrightarrow \mathrm{HOCH_2(CHOH)}_n\mathrm{CH{=}NN(CH_3)_2}$$

$$\textbf{I, II}$$

$$n = 3\ (\textbf{I}),\ 4\ (\textbf{II}).$$

The reaction occurs with a heat evolution and does not require a catalyst. Even at 3-fold excess of 1,1-dimethylhydrazine form no hydrazones or monohydrazones of α-ketoaldehydes that might arise in case of aldoses oxidation with the hydrazine, whereas the dehydration of monosaccharides into ketoaldehydes in reaction with excess phenylhydrazine affording further the ketoaldehydes diphenylhydrazones is well known [2].

The structure of compounds **I** and **II** was established using ^{1}H, ^{13}C NMR and IR spectra. The composition was confirmed by elemental analyses. In the IR spectra of dimethylhydrazones **I** and **II** a wide weak band in the region 1640 cm^{-1} should be mentioned that corresponds to the stretching vibrations of the C=N bond.

The ^{1}H and ^{13}C NMR spectra of compounds **I** and **II** are fairly characteristic because of the presence of CH=N and $\mathrm{N(CH_3)_2}$ groups. The protons from these groups give rise in the ^{1}H NMR spectra to a doublet and a singlet respectively, and in the ^{13}C NMR spectra appear the corresponding carbon signals belonging to the azomethine and dimethylamine groups with the chemical shifts of 138.72, 138.86 and 43.15, 42.83 ppm respectively. Besides the spectra contain the carbon signals of the carbohydrate skeleton.

Compounds **I** and **II** are colorless crystalline substances, soluble in water, ethanol, dimethyl sulfoxide, but insoluble in hydrocarbons. They may be applied as synthons in organic synthesis and as initial compounds for building up previously unknown hybrid chiral ligands. The reactions of other carbohydrates with dimethylhydrazine and the chemical transformations of hydrazones synthesized are under investigation.

Arabinose dimethylhydrazone (I). In 10 ml of water was dissolved 1.52 g (0.01 mol) of L- or D-arabinose, and to the solution was added 0.6 g (0.76 ml, 0.01 mol) of 1,1-dimethylhydrazine. The temperature of the reaction mixture increased by 3°C. The solution obtained was left standing for 1 h and then it was diluted with 10 ml of ethanol. On evaporating the solvents the residue was recrystallized from anhydrous ethanol. The yield of the target hydrazone was 1.41 g (73%), mp 88–90°C. IR spectrum, ν, cm^{-1}: 1600 (C–N), 1640 (C=N), 2860, 2910, 2940, 2960 (CH), 3410 (OH). ^{1}H NMR spectrum, δ, ppm: 6.61 d (1H, CH=N, ^3J 5.9 Hz), 2.65 s [6H, $\mathrm{N(CH_3)_2}$]. ^{13}C NMR spectrum, δ, ppm: 138.72 (C^1), 74.11 (C^2), 71.69, 71.06 (C^3/C^4) (alternative assignment of signals), 63.84 (C^5), 43.15 (C^6). Found, %: C 42.91; H 8.78; N 12.22. $\mathrm{C_7H_{16}N_2O_4}$. Calculated, %: C 43.74; H 8.39; N 14.57.

Galactose dimethylhydrazone (II). Likewise from 1.8 g (0.01 mol) of D- or L-galactose and 0.6 g of dimethylhydrazine was obtained 1.72 g (77%) of galactose dimethylhydrazone (II), mp 96–100°C. IR spectrum, ν, cm^{-1}: 1600 (C–N), 1640 (C=N), 2870, 2940, 2960 (CH), 3370 (OH). ^{1}H NMR spectrum, δ, ppm: 6.81 d (1H, CH=N, ^3J 5.8 Hz), 2.68 s [6H, N$(CH_3)_2$]. ^{13}C NMR spectrum, δ, ppm: 138.86 (C^1), 72.72 (C^2), 70.65, 70.18 (C^3/C^4) (alternative assignment of signals), 69.45 (C^5), 63.34 (C^6), 42.83 (C^7). Found, %: C 42.04; H 8.45; N 9.15. $C_8H_{18}N_2O_5$. Calculated, %: C 43.24; H 8.11; N 12.61.

IR spectra were recorded on spectrophotometer Specord IR 75 from samples prepared as KBr pellets. ^{1}H and ^{13}C NMR spectra were registered from solutions in DMSO-d_6 on spectrometer Varian VXR-500S at operating frequencies 500 (^{1}H) and 125.5 MHz (^{13}C). ^{13}C NMR spectra with the wide-band decoupling from protons were registered with the relaxation interval 2.5 s, pulse 90°. Chromium(III) acetylacetonate was used as relaxation agent (0.02 mol/l).

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