LETTERS TO THE EDITOR

MUTAROTATION OF FRUCTOSE THIOSEMICARBAZONE AND ITS 4-SUBSTITUTED HOMOLOGS

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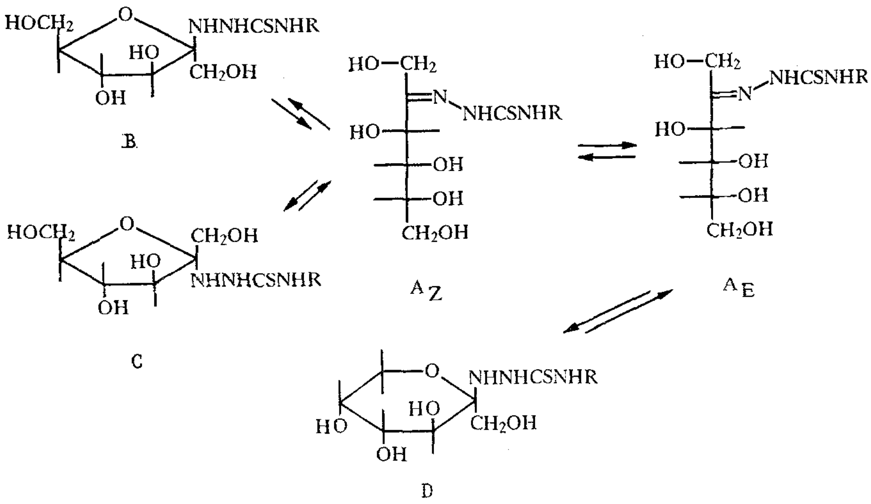
Some arylhydrazones [1] and semi- [2] and thiosemicarbazones [3, 4] of aldoses exhibit the ability to undergo ring-chain tautomerism with the participation of the pyranose form in the equilibrium. The simultaneous coexistence of furanose tautomers along with it has not been noted. From the widely known data on the mutarotation of carbohydrates, this property is most likely in the fructose hydrazone series, information regarding which is not available.



Ia R=H, b R=Me, c R=CH$_2$Ph

By prolonged refluxing of fructose with thiosemicarbazides in methanol we were able for the first time to synthesize thiosemicarbazones I-III (80-90% yields), which are viscous glassy substances that are homogeneous according to TLC data [elution with butanol—acetone—water (8:1:1)].

In solution in d$_6$-DMSO they form an equilibrium mixture of five tautomers, which gives rise to the appearance in the ^{13}C NMR spectra of five signals of the C=S carbon atoms. The signals of C=N bonds at 152.9 and 153.4 ppm in the ^{13}C NMR spectrum correspond to two stereoisomers of the linear hydrazone tautomer (A$_E$ and A$_Z$) of I. The furanose (B and C) forms of this compound have paired signals of carbon atoms at 94.3 and 81.6 ppm and at 95.9 and 81.9 ppm [the C$_{(2)}$ and C$_{(5)}$ atoms, respectively]. The pyranose tautomer gives rise to the appearance of signals of the C$_{(2)}$ atom at 90.3 ppm 90.8 ppm for the β-pyranose form of glucose thiosemicarbazone [3], 90.7 ppm for its 2,4-dinitrophenylhydrazone [1]). A similar pattern is also observed for solutions of II-III.

Since the A ⇄ B ⇄ C ⇄ D equilibrium is established in the course of a week, the reliability of the assignment of all of the signals of the tautomers (except for form D, the amount of which is no more than 5%) presents no difficulties if the spectra are recorded daily.

Compound I. ^{13}C NMR spectrum: form A: 177.4 and 177.9 (C=S), 152.9 and 153.4 (C=N), 72.1, 71.8, 71.3, 70.3, 63.5, 62.8, 61.3, 59.7; form B: 182.4 (C=S), 95.4 [C$_{(2)}$], 81.9 [C$_{(5)}$], 77.6, 74.6, 61.6, 61.0; form C: 182.1 (C=S), 94.3 [C$_{(2)}$], 81.6 [C$_{(5)}$], 76.7, 74.8, 63.5, 63.2; form D: 182.3 (C=S), 90.3 ppm [C$_{(2)}$].

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Compound II. ^{13}C NMR spectrum: form A: 178.0 and 177.6 (C=S), 152.8 and 152.3 (C=N), 71.8, 71.7, 71.5, 71.2, 64.0, 63.0, 61.2, 59.6; form B: 182.8 (C=S), 96.0 [$C_{(2)}$], 82.0 [$C_{(5)}$], 77.3, 74.7, 62.5, 61.2; form C: 182.5 (C=S), 94.4 [$C_{(2)}$], 81.6 [$C_{(5)}$], 77.1, 74.8, 64.0, 63.7; form D: 182.6 (C=S), 90.3 ppm [$C_{(2)}$]. The carbon atoms of the methyl groups give a signal at 30.9-31.1 ppm.

Compound III. ^{13}C NMR spectrum: form A: 177.9 and 177.4 (C=S), 153.2 and 152.7 (C=N), 71.5, 71.2, 70.9, 69.5, 63.9, 63.8, 61.2, 59.7; form B: 182.8 (C=S), 96.1 [$C_{(2)}$], 82.0 [$C_{(5)}$], 78.1, 74.8, 61.8, 61.2; form C: 182.4 (C=S), 94.4 [$C_{(2)}$], 81.7 [$C_{(5)}$], 77.0, 74.8, 63.8, 63.3; form D: 182.5 (C=S), 90.5 ppm. The carbon atoms of the CH_2 groups resonate at 47.0-47.2 ppm, while the carbon atoms of the benzene ring resonate at 127.5-139.6 ppm.

The amounts of the linear forms in the equilibrium range from 60% to 65%, as compared with 15-20% each for the furanose forms and no more than 5% for the pyranose form. Satisfactory results of elementary analysis for C, H, and N were obtained for I-III.

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UNUSUAL REACTION OF 2,4-DIMETHOXYBENZALDEHYDE AND 2-METHYLFURAN

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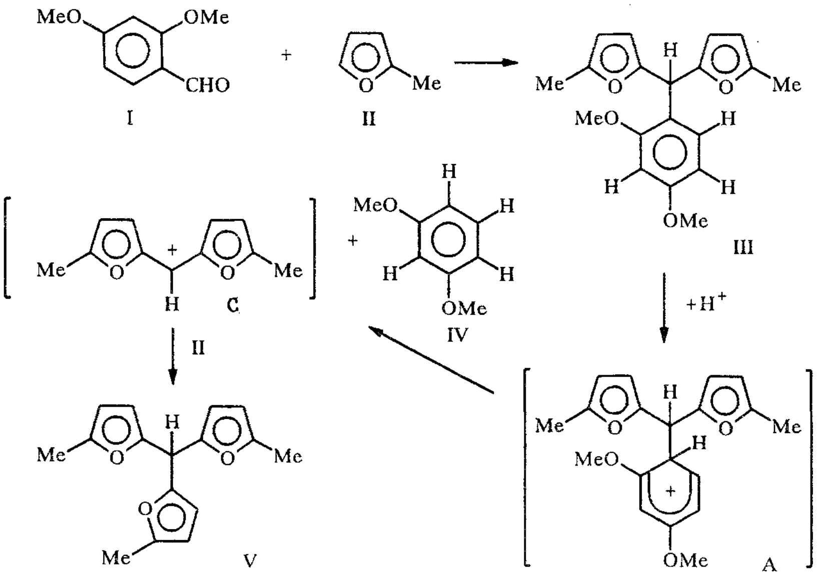
Cleavage of the C—C bond in polyarylmethanes has been known for a long time. This phenomenon was observed in superacid media by means of NMR spectroscopy [1], in concentrated sulfuric acid by means of UV spectroscopy [2], and preparatively using equimolar amounts of Friedel—Crafts catalysts [3].



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