Synthesis of N-(D-aldopyranosyl)-N′-(2,4,6-trichlorophenyl)-hydrazines and their conversion to 1,2-diaza-1,3-butadiene derivatives

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Facile conversion of N-(D-aldopyranosyl)-N′-(2,4,6-trichlorophenyl)-hydrazines to 1,2-diaza-1,3-butadiene derivatives under the conditions is described of acetic anhydride only.

Keywords: N-(D-aldopyranosyl)-N′-(2,4,6-trichlorophenyl)-hydrazines

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The versatility of sugar hydrazones and the inherent functionality in their derivatives make them valuable enantiomerically pure synthons for the synthesis of nucleosides, acyclo nucleosides and heterocyclic compounds.[1–5] Hydrazines and hydrazones exhibit important biological activities such as inhibiting oxidases, redox and mitochondrial systems as well as possessing antiviral and antimicrobial activities. As a part of a program directed towards the synthesis of effective anti-hepatits B viral agents (HBV)[10,11] the synthesis and reactions of some sugars hydrazones possessing the 2,4,6-trichlorophenyl group have been studied. Treatment of D-glucose (**1**) with three molar equivalent of 2,4,6-trichlorophenylhydrazine (**3**) did not afford the expected bishydrazone **4**, but instead the monohydrazone[12] **5**, was obtained. Compound **5** was also obtained from the equimolar condensation of **1** and **3**. Similarly, D-galactose (**2**) was converted to the respective monohydrazone[12] **6**. The ^{1}H and ^{13}C NMR data of **5** and **6** in solutions of DMSO-d_6 showed that both compounds exist in the cyclic hydrazine forms **9** and **10**, respectively. Acetylation of **9** and **10** with acetic anhydride in pyridine afforded the corresponding tetra-O-acetyl derivatives **11** and **12**. Compound **16** was isolated as a minor product from the acetylation of **10**. Per-O-acetyl derivatives of acyclic sugar arylhydrazones undergo base (pyridine) catalysed elimination of the C-2 acetoxy group as acetic acid with the formation of sugar 1,2-diaza-1,3-butadiene derivatives.[16–19] A similar elimination took place within compounds **9** and **10** but with boiling acetic anhydride to give (1*E*, 3*E*)-4-(tetra-O-acetyl-D-arabino- and D-lyxo-tetritol-1-yl)-1-(2,4,6-trichlorophenyl)-1,2-diaza-1,3-butadiene **15** and **16**, respectively. Furthermore treatment of **11** with boiling acetic anhydride afforded **15**. This is the first example of such an elimination in the presence of acetic anhydride without pyridine. Treatment of **9** with acetic anhydride -trifluoroacetic acid afforded (**17**).

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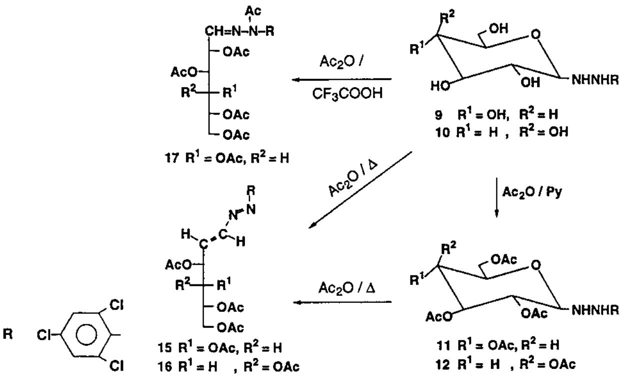

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