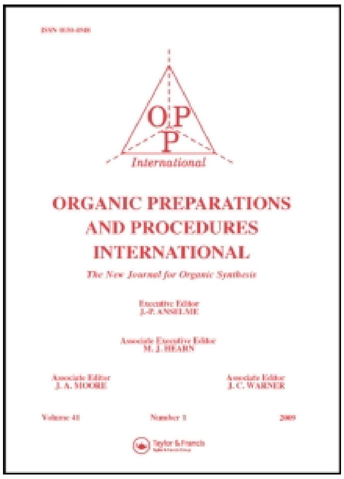

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SYNTHESIS OF METHYL 2,3,4-TRI-0-ACETYL-6-DEOXY-6-IODO-α-D-GLUCOPYRANOSIDE

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SYNTHESIS OF METHYL 2,3,4-TRI-O-ACETYL-6-DEOXY-6-IODO-α-D-GLUCOPYRANOSIDE

Submitted by
3/26/74

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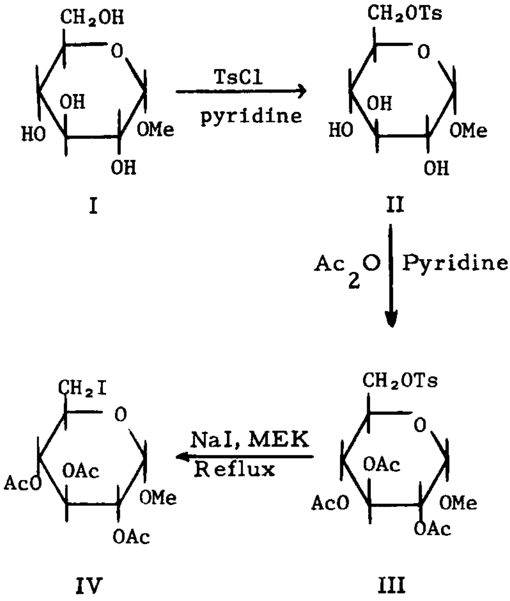
An improved synthesis of iodo sugar IV, an important precursor for the synthesis of naturally occurring amino nucleosides,[1,2] starts from I. Tosylation of I with tosyl chloride in pyridine[3,4] was followed by acetylation of the free hydroxyl groups on II with acetic anhydride added directly to the reaction mixture. Removal of volatile materials under reduced pressure afforded III[5,6] in excellent yield

(88%), which was reacted with sodium iodide in refluxing methyl ethyl ketone to give the title compound IV. Protecting the free hydroxyl groups of II by acetylation before the iodide displacement reaction reduced the loss of iodo sugar caused by decomposition. Hence, the modified method improved the overall yield of IV to 48% (based on I compared to less than 25%[1,2]).



EXPERIMENTAL

Melting points were taken on a Thomas-Hoover Unimelt apparatus and are corrected. The nmr spectra were run on a Varian A-60 spectrometer using TMS as internal standard. A Beckman IR-8 spectrophotometer was used to determine the ir spectra. Optical rotations were measured with a Standard Model D Keston Polarimetric Unit attached to a Beckman DU-2 Spectrophotometer.

Methyl 2,3,4-tri-O-acetyl-6-O-(p-toluenesulfonyl)-α-D-glucopyranoside (III). - To a solution of methyl α-D-glucopyranoside (500 g, 2.57 moles) in 2.5 l. of dry pyridine, was added at 0°, slowly, with stirring, a solution of p-toluenesulfonyl chloride (525 g, 2.75 moles) in 2 l. of dry pyridine. After stirring the reaction mixture for 2 days at room temperature, acetic anhydride (1.1 l.) was added and the solution was stirred for another 2 days at room temperature. The solvents were removed under reduced pressure, and the residual syrup was dissolved in chloroform. After washing with $KHCO_3$ and $NaHCO_3$ solutions and water, respectively, the chloroform solution was dried ($MgSO_4$) and the solvent removed under diminished pressure to afford compound III (1067 g, 88%) as a thick syrup which was used directly in the next step.

Methyl 2,3,4-tri-O-acetyl-6-deoxy-6-iodo-α-D-glucopyranoside (IV). - Compound III (131.9 g, 0.28 mole), sodium iodide (83.4 g, 0.57 mole) and 2 l. of methyl ethyl ketone were refluxed for 48 hrs. in a 5-l. round bottom flask, equipped with a mechanical stirrer and water cooled condenser. The precipitated sodium p-toluenesulfonate was removed by filtration. The filtrate was evaporated to dryness and the residue was dissolved in methylene chloride. The solution was washed with water, dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was crystallized from 95% ethanol. Recrystallization from the same solvent furnished compound IV (65.5 g, 55%) as white crystals, mp. 145-147°, lit.[1] mp. 149-150°; $[\alpha]_D^{26}$ + 121.4° (C,1,$CHCl_3$); ir (Nujol), 1749 (C=O), 1240 cm^{-1} (C-O); nmr ($CDCl_3$), δ4.98 (m,2,-CH_2I), 3.50 (s,3,-OCH_3), 2.10, 2.00 (s,9,3-OAc).

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AN IMPROVED SYNTHESIS OF 2-ETHYL-2-PHENYL-GLUTACONIMIDE

Submitted by
(4/16/74)

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It has been found that II can be obtained by dehydrohalogenation of I using sodium bicarbonate in dimethylsulfoxide in almost quantitative yield, making this procedure superior to the one previously reported (refluxing in collidine, 74% crude yield).[1]