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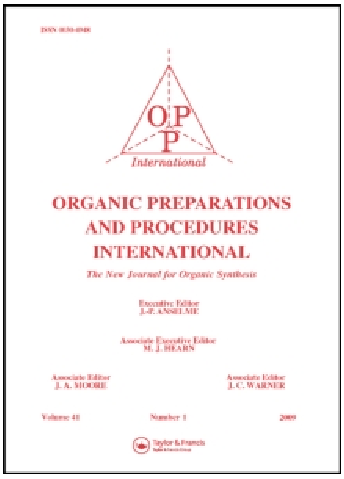

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SUGAR 1,3,4-OXADIAZOLES VII. CYCLIZATION OF ACETATES OF SUGAR AROYLHYDRAZONES USING LEAD TETRAACETATE

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ORGANIC PREPARATIONS AND PROCEDURES INT. 15(5), 329-333 (1983)

SUGAR 1,3,4-OXADIAZOLES VII.[1] CYCLIZATION OF ACETATES OF SUGAR AROYLHYDRAZONES USING LEAD TETRAACETATE

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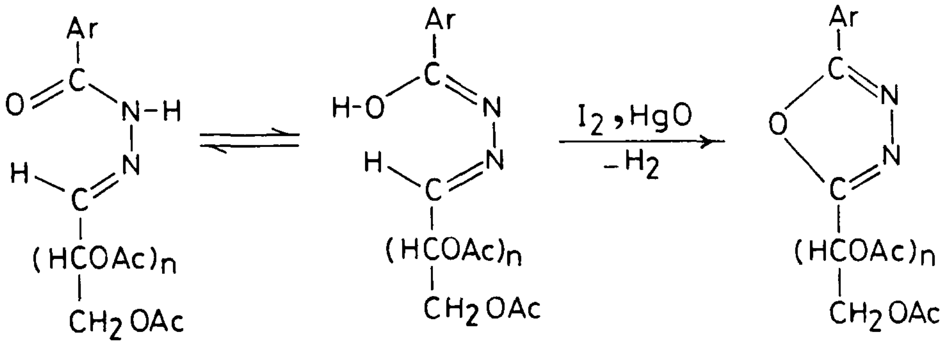
The first saccharide 1,3,4-oxadiazole derivatives (3) were prepared in our laboratory by the oxidative cyclization of acetates of aldehydo-sugar aroylhydrazone (1) with iodine and yellow mercuric oxide in dry ether.[2-4] The reaction is believed to take place *via* abstraction of the methine and of the enolized aroylhydrazido group hydrogens by iodine (2).



1 2 3

As a result of our search for new reagents to accomplish this oxidative cyclization, it was found that treatment of 2,3,4,5,6-penta-0-acetyl aldehydo-D-galactose benzoylhydrazone (4a) with lead tetraacetate in dry dichloromethane at 0°, gave a crystalline product which showed 0-acetyl group absorption

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band at 1740 cm^{-1}; the amide band of the parent compound (4a) at 1690 cm^{-1} was absent in the infrared spectrum of the oxidation product. This suggested that the product might be the same 1,3,4-oxadiazole derivative obtained on oxidative cyclization of the same hydrazone (4a) with iodine and yellow mercuric oxide.[3] Direct proof for this assumption was obtained when the two oxidation products as well as their infrared spectra were compared. The lead tetraacetate oxidation product was thus assigned the structure of 2-(D-galacto-1,2,3,4,5-penta-O-acetyl-pentilol-1-yl)-5-phenyl-1,3,4-oxadiazole (5a).

This structure was confirmed by the ^1H NMR spectrometry which revealed signals of five O-acetyl groups at δ 2.02 (6H, s, 2 OAc), 2.05 (3H, s, OAc), 2.15 (3H, s, OAc), 2.20 (3H, s, OAc) and the ABX system of the C-6 methylene, which appeared

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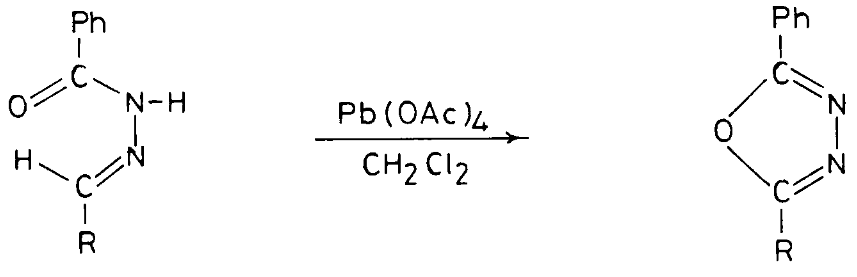

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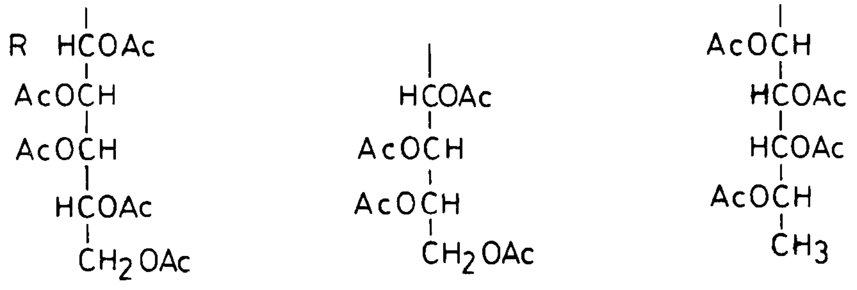

a

b

c

as two doublet of doublets, at δ 3.92, J_{AB}=12 Hz, J_{AX}=7 Hz, and δ 4.35, J_{BX}=5 Hz. The rest of the alkyl-chain hydrogens appeared between δ 5.4-6.3 (4H, m, 4CH); the phenyl hydrogens at δ 7.31-8.1 ppm (5H, m, C_6H_5). The imino proton of the parent hydrazone acetate (at δ 10.4 ppm) was absent in the mass spectrum of this product which showed typical acetoxyalkyl chain fragmentation, with successive breakdown at M^+, M-Ac, M-OAc, M-CHOAc, and so on, including major peaks at m/e 218 due to 2-(acetoxymethyl)-5-phenyl-1,3,4-oxadiazole, at 176 due to the 2-(hydroxymethyl) derivatives, and at 145 for 2-phenyl-1,3,4-oxadiazole. Important rearrangement peaks appeared at m/e 404 (due to cyclization of the M-(OAc + Ac) fragment to a furanoside derivative and subsequent loss of Ac and oAc (which afforded peaks at 360, 344 and 302) and its loss of the heterocycle moiety to give the peak at m/e 260. At lower mass, important peaks for Ac, Ph, and Hz were observed at 43, 77 and 105 respectively.

In order to test the generality of this reagent 2,3,4,5-tetra-0-acetyl-aldehydo-D-arabinose benzoylhydrazone (4b)[7] was also subjected to the above reaction, whereby the oxidation product was identical in every respect with 2-(D-arabino-1,2,-3,4-tetra-0-acetyl-tetrilol-1-yl)-5-phenyl-1,3,4-oxadiazole (5b) obtained on oxidation of (4b) with iodine and yellow mercuric oxide.[3] Application of the lead tetraacetate oxidative cyclization to deoxy sugar aroylhydrazone namely 2,3,4,5-tetraacetyl-aldehydo-L-fucose benzoylhydrazone (4c) also gave the expected 2-(6-deoxy-L-galacto-1,2,3,4-tetra-0-acetylpentilol-1-yl)-5-phenyl-1,3,4-oxadiazole (5c).[4]

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EXPERIMENTAL

Melting points were determined with a Kofler block and are uncorrected. The infrared spectra were recorded as KBr pellets on a Unicam SP 1025 or Pye Unicam SP 200 spectrophotometers. ^{1}H NMR spectra were carried out at 90 MHz with a Varian EM-390 spectrometer in $CDCl_3$ containing 1% tetramethylsilane as an internal standard. The mass spectrum was performed on a Hitachi-Perkin Elmer RMU-6 mass spectrometer. The homogeneity of the product was checked by tlc on Silica Gel plates (layer thickness 0.25 mm) and the spots were detected by spraying with anisaldehyde-sulfuric acid-ethanol (1:1:18 v/v) (Ref. 9) followed by heating the chromatograms on a hot plate for a few minutes. Evaporation under diminished pressure, with an outside bath temperature kept below 45°.

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2-(D-Galacto-1,2,3,4,5-penta-0-acetylpentilol-1-yl)-5-phenyl-1,3,4-oxadiazole (5a).- A solution of 2,3,4,5-penta-0-acetyl-aldehydo-D-galactose benzoylhydrazone[5] (4a, 1g, 3.56 mmoles) in dry dichloromethane (40 ml) was cooled to 0° and treated with a solution of lead tetraacetate (2 g) in dry dichloromethane (20 ml) and the mixture was stirred at 0° for 12 hrs. Ice-water (50 ml) was added to the mixture and the inorganic residue was filtered through a celite layer and washed with dichloromethane (20 ml). The organic layer of the filtrate was washed successively with a 30% solution of sodium hydrogensulfate, water, 20% sodium hydrogencarbonate solution and water, then dried over anhydrous sodium sulfate. Evaporation of the solvent gave a syrup which crystallized from methanol-water to give 0.6 g (60%) of 2-(D-galacto-1,2,3,4,5-penta-0-acetylpentilol-1-yl)-5-phenyl-1,3,4-oxadiazole (5a), mp. 82-83°, mixed mp. 83°[2], ν_{max}^{KBr} 980, 1385 (oxadiazole ring) and 1740 cm^{-1} (OAc). ^{1}H NMR δ 2.02 (6H, s, 2 OAc), 2.05 (3H, s, OAc), 2.15 (3H, s, oAc), 2.20 (3H, s, OAc), 3.92, 4.35 (2H, CH_2, J_{AB} 12Hz, J_{AY} 7Hz, J_{BX} 5Hz), 5.4-6.3 (4H, m, 4CH) and 7.3-8.1 ppm (5H, m, C_6H_5).

2-(D-Arabino-1,2,3,4-tetra-0-acetyltetrilol-1-yl)-5-phenyl-1,3,4-oxadiazole (5b).- This compound was prepared in 50% yield from 2,3,4,5-tetra-0-acetyl-aldehydo-D-arabinose benzoylhydrazone[5] (4b) as mentioned above for compound (5a), mp. and mixed mp. 105°,[3] ν_{max}^{KBr} 980, 1380 (oxadiazole ring) and 1740 cm^{-1} (OAc).

2-(6-Deoxyl-L-galacto-1,2,3,4-tetra-0-acetylpentilol-1-yl)-5-phenyl-1,2,3,4-oxadiazole (5c).- It was prepared in 52% yield from 2,3,4,5-tetra-0-acetyl-aldehyo-L-fucose benzoylhydrazone[4] (4c) as mentioned above for compound (5a), mp. and mixed mp. 157°,[4] ν_{max}^{Kbr} 780, 1385 (oxadiazole ring) and 1750 cm^{-1} (OAc).

REFERENCES

1. Part VI, M. A. M. Nassr, M. A. Taha, and M. A. E. Shaban, Carbohyrd. Res., In press.
2. M. H. El-Khadem, M. A. E. Shaban, and M. A. M. Nassr, ibid., 13, 470 (1970).
3. M. H. El-Khadem, M. A. E. Shaban, and M. A. M. Nassr, ibid., 23, 103 (1972).
4. M. A. E. Shaban and M. A. M. Nassr, Org. Prep. Proc. Int., 8, 107 (1976).
5. H. Zinner, J. Brock, B. Peter, and H. Shaukellis, J. prakt. Chem., 29, 101 (1965).
6. P. J. Dunphy, J. D. Kerr, J. F. Pennock and K. J. Whittle, Chem. Ind. (London), 154a (1966).

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