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SYNTHESIS OF UNSATURATED SUGARS FROM TRANS-DIOL PRECURSORS AND THROUGH THIONOCARBONATE INTERMEDIATES

D. Horton and W. N. Turner
Chemistry Department
The Ohio State University, Columbus, Ohio 43210

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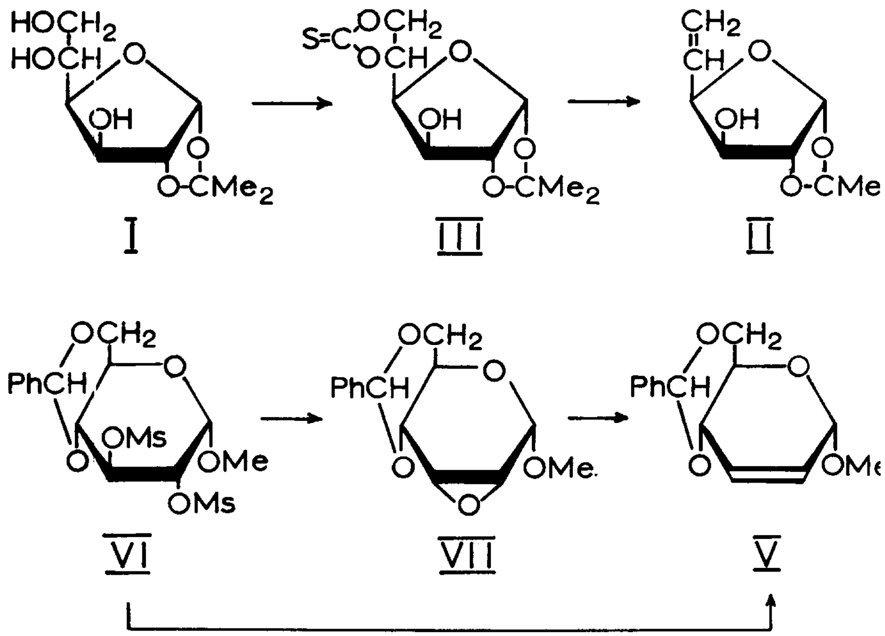
This communication demonstrates two reactions in carbohydrate systems which should be generally applicable under mild conditions for synthesis of the hitherto rather inaccessible unsaturated sugars, from selected trans, cis, or terminal vicinal diol groups in a sugar molecule. Conversion of the 5,6-diol group of 1,2-O-isopropylidene-α-D-glucofuranose (I) into the 5,6-alkene (II) was achieved by way of the 5,6-thionocarbonate (III), and indicates that the new alkene synthesis of Corey and Winter[1] may be of general utility for conversion of cis and terminal diol groups in carbohydrates into alkenes. The trans-diol group of methyl 4,6-O-benzylidene-α-D-glucopyranoside (IV) was converted into the 2,3-alkene (V), either by way of the 2,3-dimethanesulfonate (VI) of IV, or from the epoxide (VII) which can be prepared from VI by treatment with base.



A mixture of (I) (1 equiv.) and bis(imidazol-1-yl)thione[2] (1.2 equiv.) was refluxed in butanone for 4 hr. to give 1,2-O-isopropylidene-α-D-glucofuranose 5,6-thionocarbonate (III) in 85% yield. It was recrystallized from methanol as fine needles, m.p. 205-206°, $[\alpha]_D^{18}$ -17.3° (c 1, acetone); λ_{max}^{EtOH} 238 mμ (ε 12,300), 274 mμ (ε 3000); λ_{max}^{KBr} 2.95 (OH), 7.25 (CMe_2), 8.4 (C=S).[3] [Found: C, 45.70; H, 5.15; S, 12.08; mol. wt. (Rast). 235; Calcd. for $C_{10}H_{14}O_6S$: C, 45.78; H, 5.34; S, 12.22; mol. wt. 262]. Substance III was homogeneous (R_f 0.20, solvent A) by thin-layer chromatography[4], gave an n.m.r. spectrum in agreement with the assigned structure, and gave an optical rotatory dispersion spectrum in dioxane which showed a positive Cotton effect, with a peak at 320 mμ, an inflection at 315 mμ, and a trough at 305 mμ. The optical rotatory dispersion spectra of thionocarbonate derivatives such as III may be of value for configurational correlations in the carbohydrate field.

A solution of III in trimethyl phosphite was refluxed for 18 hr., evaporated, and the residue was sublimed at 100°/0.5 mm. The sublimate, yield 75%, was identical by infrared spectrum and by thin-layer chromatography[4] (R_f 0.35, solvent A) with an authentic sample of 5,6-dideoxy-1,2-O-isopropylidene-α-D-xylo-hexofuranos-5-ene[5] (II).

A solution of methyl 4,6-O-benzylidene-2,3-di-O-(methylsulfonyl)-α-D-glucopyranoside[6] (VI) in 1-butanol was refluxed for 3 hr. with an excess of potassium ethylxanthate, to give methyl 4,6-O-benzylidene-2,3-dideoxy-α-D-erythro-hexopyranosid-2-ene (V) in 65% yield, m.p. 120-122°, R_f 0.6 (solvent B)[4], identical in all respects with an authentic sample of V which had been prepared by a multi-step procedure[7]. Treatment of methyl 2,3-anhydro-4,6-O-benzylidene-α-D-allopyranoside (VII) with potassium ethylxanthate in refluxing 1-butanol similarly led to the formation of V in good yield, together with a side-product, m.p. 222-224°.

Some instances have been reported[8] in other systems, where alkylxanthate ion has converted epoxides into alkenes instead of the more usual trithiocarbonates.

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