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Preliminary communication

A new, stereospecific method for the synthesis of 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranosides

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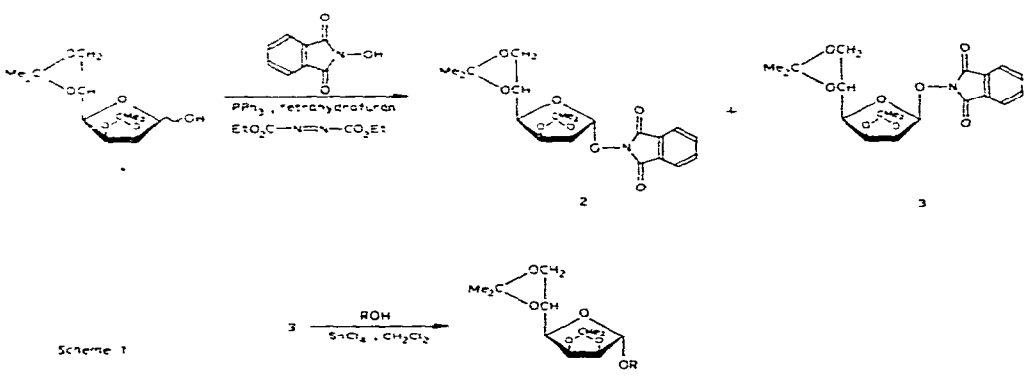
Glycosylation reactions have been effected with glycosyl halide derivatives[1,2], sugar 1,2-orthoesters[1], sugar 1-acetates[3], sugar 1-carbonates[4], sugar 1-sulfonates[5], sugar 1-(*N*-methylacetimidates)[6], glucosylisoureas[7], and 1-thioglycoside derivatives[8]. Although methods for the synthesis of 1,2-*trans*- and 1,2-*cis*-glycosides are well established, there is still a need for efficient and stereospecific condensation reactions leading to either α or β anomers.

We have been interested in the application of ready available[9] *N*-(glycosyloxy)-phthalimides, which have a potential good leaving-group, in the stereospecific synthesis of glycosides, and we now report on an efficient method for the preparation of 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranosides (4) from *N*-(2,3:5,6-di-*O*-isopropylidene-β-D-mannofuranosyloxy)phthalimide (3) and various alcohols in the presence of $SnCl_4$, as shown in Scheme 1.



Scheme 1

Compounds 2 and 3 were prepared as described earlier[9]. The β-anomer 3 (m.p. 146–147°) was condensed with methanol, ethanol, 2-propanol, *tert*-butyl alcohol, cyclohexanol, benzyl alcohol, and phenol severally in the presence of 30% of $SnCl_4$ in dichloromethane at room temperature for 24 h. The products, 2,3:5,6-di-*O*-isopropylidene-α-D-

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mannofuranosides 4, were isolated in yields of 66–76% by chromatography on silica gel (benzene–ether, 95:5), followed by distillation under reduced pressure. The physical constants and analytical data are recorded in Table I.

TABLE I

DATA FOR 2,3:5,6-DI-*O*-ISOPROPYLIDENE-α-D-MANNOFURANOSIDES[a] (4)

Product	*R*	*Yield (%)*	*B.p./Torr*[b] *or m.p. (degrees)*	$[\alpha]_D^{20}$ *(chloroform) (degrees)*	*Lit.*[10] $[\alpha]_D^{25}$ *(degrees)*	*^{1}H-N.m.r. data*[d] *($CDCl_3$) H-1, δ*
4a	Me	70	71/0.3	+49 (*c* 5.1)	+48.9	4.86 (s)
4b	Et	74	75/0.3	+48 (*c* 5.1)		4.95 (s)
4c	i-Pr	74	81/0.2	+54 (*c* 5.1)	+53.0	5.08 (s)
4d	t-Bu	66	89/0.3	+49 (*c* 1.4)	+49.4	5.30 (s)
4e	C_6H_{11}	76	102/0.2	+63 (*c* 5.1)		5.08 (s)
4f	$PhCH_2$	75	119/0.3 53–54	+81.5 (*c* 1.45)[c]	+78.3	5.09 (s)
4g	Ph	72	105/0.2 91–93	+115 (*c* 1.65)	+114.7	5.69 (s)

[a]All products gave satisfactory microanalyses (C, ±0.36%; H, ±0.36%). [b]Bath temperature. [c]In acetone. [d]Obtained with a Jeol JNM-4H-100 spectrometer at 100 MHz; values are in good agreement with those reported [10,11]

Each of the above reactions afforded the α anomer 4 only. The α anomer 2 did not react with methanol in the presence of $SnCl_4$ (30 mol%) during 24 h at room temperature. However, with a higher concentration of catalyst (100 mol%), 41% of the α-glycoside 4a could be obtained. Some 2 remained and the β anomer 3 was formed. Thus, 3 is formed first from 2 and then reacts to give 4a.

The reaction described offers a convenient and efficient approach to the stereospecific synthesis of α-furanosides.

REFERENCES

1 G. Wulff and G. Rohle, *Angew. Chem. Int. Ed. Engl.*, 13 (1974) 157–216.
2 R. U. Lemieux, K. B. Hendriks, R. V. Stick, and K. James, *J. Am. Chem. Soc.*, 97 (1975) 4056–4062.
3 B. Helferich and E. Schmitz-Hillebrecht, *Ber.*, 66 (1933) 378–383.
4 S. Inaba, M. Yamada, T. Yoshino and Y. Ishido, *J. Am. Chem. Soc.*, 95 (1973) 2062–2063.
5 S. Koto, Y. Hamada, and S. Zen, *Chem. Lett.*, (1975) 587–588.
6 J. R. Pougny, J.-C. Jacquinet, M. Nassr, D. Duchet, M.-L. Milat, and P. Sinaÿ, *J. Am. Chem. Soc.*, 99 (1977) 6762–6763.
7 K. Tsutsumi, Y. Kawai, and Y. Ishido, *Chem. Lett.*, (1978) 629–632.
8 T. Mukaiyama, T. Nakatsuko, and S. Shoda, *Chem. Lett.*, (1979) 487–490.
9 E. Grochowski and J. Jurczak, *Carbohydr. Res.*, 50 (1976) C15–C16.
10 R. A. Boigegrain, B. Castro, and B. Gross, *Bull. Soc. Chim. Fr.*, (1974) 2623–2627.
11 M. H. Randall, *Carbohydr. Res.*, 11 (1969) 173–178.