Preliminary Communication

New route for the synthesis of 3-deoxy-D-*erythro*-hexos-2-ulose★

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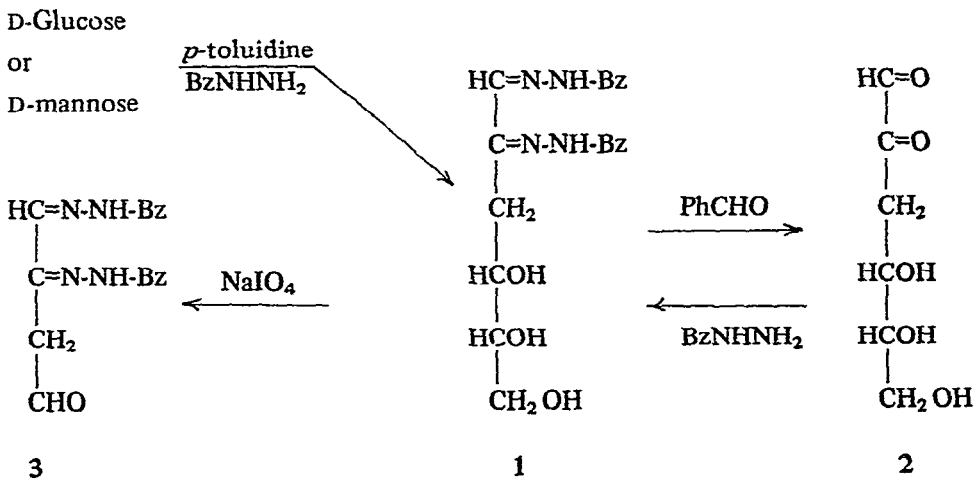
It is known[1] that aldoses are converted into 3-deoxy-aldos-2-uloses by prolonged heating with amines. We have added benzoylhydrazine to the aldose–amine mixture, and have obtained a 3-deoxy-aldos-2-ulose bis(benzoylhydrazone) which, upon transhydrazonation with benzaldehyde, gives the 3-deoxy-aldos-2-ulose. In view of the high yields and good crystallizing properties of these new bis(benzoylhydrazones), the present route constitutes an improvement over existing methods[1,2] for the preparation of 3-deoxy-aldos-2-uloses.



The reaction is illustrated by the preparation of 3-deoxy-D-*erythro*-hexos-2-ulose (2) as follows: a solution of D-glucose (2.5 g), benzoylhydrazine (3.2 g), and *p*-toluidine (1 g) in ethanol (50 ml), water (10 ml), and acetic acid (0.5 ml) was boiled

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for 7 h under reflux. The product (1.9 g) crystallized from ethanol, m.p. 191°; $[\alpha]_D^{21}$ + 20.0° (*c* 0.2, pyridine); ν_{max}^{KBr} 1660(CONH) and 3350 cm^{-1} (OH); by mixed m.p. and X-ray powder diffraction pattern, it was identical with 3-deoxy-D-*erythro*-hexos-2-ulose bis-(benzoylhydrazone) (1) obtained from an authentic sample of 3-deoxy-D-*erythro*-hexos-2-ulose[2]. Upon periodate oxidation, compound 1 consumed 2 moles of oxidant per mole, and gave aldehyde 3, m.p. 212°, ν_{max}^{KBr} 1660 (CONH) and 1700 cm^{-1} (CHO). Treatment of the bis(benzoylhydrazone) 1 with benzaldehyde in the same way as described for the preparation of D-*arabino*-hexosulose[3] afforded 0.6 g of 3-deoxy-D-*erythro*-hexos-2-ulose[1,2] (2), identified by conversion into the known[2] bis[(2,4-dinitrophenyl)hydrazone], m.p. and mixed m.p. 265°, and a new bis(phenylhydrazone), m.p. 190°; $[\alpha]_D^{31}$ −73.1° (*c* 0.12, pyridine).

Full details of this synthesis and of the synthesis of other 3-deoxyaldos-2-uloses will be published later.

ACKNOWLEDGMENTS

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REFERENCES

1 H. Kato, *Agr. Biol. Chem.* (Tokyo), 26 (1962) 187; *Nippon Nogei Kagaku Kaishi*, 42 (1968) 9.
2 E. F. L. J. Anet, *J. Amer. Chem. Soc.*, 82 (1960) 1502; *Aust. J. Chem.*, 13 (1960) 396.
3 S. Bayne, *Methods Carbohyd. Chem.*, 2 (1963) 421.

CORRIGENDA

Carbohyd. Res., 12 (1970) page 101, line 1 should read:
pic à *m/e* 88 $MeOCH^{+}$ CHOMe qui a été trouvé pour les méthyl 3,5-di-*O*-acétyl-2-*O*-

page 105, line 4:
(10:1) (2,3 mg), p.f. 90–91°. Le Tableau II indique le temps de rétention de ces anomères

page 105, line 6:
Le temps de rétention de l'anomère α correspond à celui du méthyl 2,5-di-*O*-

page 105, line 9:
pas identique au méthyl 3,5-di-*O*-acétyl-2-*O*-méthyl-rhamnofuranoside.

page 105, line 5 from bottom:
la c.p.g. des produits obtenus après déméthylation sont donnés dans le Tableau I.