

A Photochemical Route to D-Ribulose: a Type I Ring Contraction of a Diulose

By P. M. COLLINS* and P. GUPTA

[Department of Chemistry, Birkbeck College (University of London), Malet Street, London, W.C.1]

Summary D-Fructose is converted to D-ribulose using a photochemical Type I ring contraction as the key step in the sequence: isopropylidenation, oxidation, ring contraction, and hydrolysis.

CONTINUING our investigation^{1,2} into photochemical reactions of 'oxo sugars' we have found the following result which appears to be of synthetic utility. 1,2:4,5-Di-O-isopropylidene- β -D-erythro-2,3-hexodiulose-2,6-pyranose (**1**)³

(10 g.), obtainable by oxidizing 1,2:4,5-di-O-isopropylidene- β -D-fructopyranose with ruthenium tetroxide,⁴ was irradiated with unfiltered light from a 450 w Hanovia lamp (1% in C₆H₆) in two batches for 1½ hr.† Carbon monoxide was evolved, leaving less than 5% of the original diulose (**1**), (g.l.c., R_t 31 min., SE 30, 10 ft. × ¼ in., 130°). Two products, B and A, 1.6:1 were formed, R_t 9 and 10 min., respectively. Removal of the solvent followed by column chromatography (silica gel, C₆H₆:EtOAc, 3:2) gave B as an oil [3.5 g

† A similar result was obtained with light filtered through Pyrex and with several other solvents.

$[\alpha]_D^{21} - 111^\circ$ (Me_2CO), and A as a solid [1.8 g, m.p. 87—89°, $[\alpha]_D^{21} - 5.7^\circ$ (CHCl_3)]. These two products were anomers of 1,2:3,4-di-*O*-isopropylidene-*erythro*-hexulose, (2) and (3) [empirical formula $\text{C}_{11}\text{H}_{18}\text{O}_5$: m/e 215 ($M-15$): i.r., neither carbonyl nor hydroxyl bands: n.m.r. (Table) consistent with those structures]. Furthermore, hydrolysis of either isomer separately (or a mixture of both) afforded a reducing sugar identical to authentic ribulose (paper chromatography). Both hydrolysates afforded an *o*-nitrophenylhydrazone in high yield, m.p. 168° (lit.⁵ 168—169°). Thus D-ribulose was obtainable in 60% yield from (1). Distillation of the crude

isomer (2) and H_Y in isomer (3) approach the sugar ring oxygen much less closely. Therefore the β -isomer (2) should possess the lowest field C-1 proton.

The mechanism for the ring construction probably involves homolytic cleavage between the C-2 and C-3 and C-3 and C-4 bonds, as suggested earlier.¹ It is of interest that ring-closure of the diradical intermediate should give such a large proportion of the isomer formed after prior rotation about the bond between C-2 and the pyranose ring oxygen, since this is not the isomer produced by acid catalysed isopropylideneation of D-ribulose.

The 100 MHz. n.m.r. parameters for the α - and β -anomers of 1,2:3,4-di-*O*-isopropylidene-D-ribulose

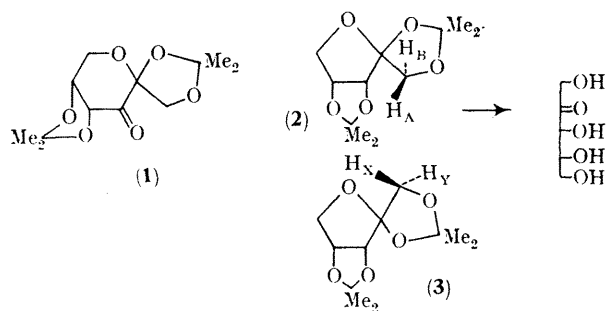
	H-1	H-1'	H-3	H-4	H-5, H-5'	$\text{Me}_2\text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array} \Big\}_2$
Isomer A	5.99d $J_{11'}$ 8.5	6.04 $J_{1'1}$ 8.5	5.45d† J_{34} 6.5	5.25 octet† J_{43} 6.5 J_{45} 4.5 $J_{45'}$ 3.5	6.02 AB, q collapsing to a singlet	8.42s 8.49s 8.57s 8.65s
Isomer B	5.71d $J_{11'}$ 8.5	5.93d $J_{1'1}$ 8.5	5.45d J_{34} 6.0	5.20 octet† J_{43} 6.0 J_{45} 3.0 $J_{45'}$ 1.0	6.15q† 6.10q J_{54} 3.0 $J_{5'4}$ 1.5 $J_{55'}$ 10 $J_{5'5}$ 10	8.45s 8.48s 8.52s 8.62s

* Analysed as an AB quartet; † double resonance studies confirmed the coupling patterns. Chemical shifts on τ scale.

photolysate was also used to isolate the isopropylideneated anomeric mixture.

Only isomer B was previously known.^{5,6} The physical constants reported above for this compound agree with the published values, but these alone do not permit a configurational assignment. Now that isomer A is available this can be done with reasonable confidence: the optical rotation of anomer A is considerably more positive than that of B, indicating that A is the α - (3) and B the β -anomer (2). Further, in the n.m.r. spectra (Table) the two C-1 protons of one isomer and one of these from the other give signals in the region τ 5.93—6.04, while the other appears at lower field (τ 5.71). If the oxygen atoms in the molecule have their electron lone pairs tetrahedrally disposed, it can be seen, from Dreiding models of the two isomers, that H_A in the β -isomer (2) is projected into the space occupied by one of the lone pairs on the C-3 oxygen. This would be expected to deshield this proton. No other C-1 proton is situated in such an electron rich area; the protons H_B in

We thank the S.R.C. for a grant (to P.G.) and Dr. R. J. Ferrier for a sample of D-ribulose.



(Received, September 3rd, 1969; Com. 1342.)

¹ P. M. Collins, *Chem. Comm.*, 1968, 403.

² P. M. Collins and P. Gupta, *Chem. Comm.*, 1969, 90.

³ E. J. MacDonald, *Carbohydrate Res.*, 1967, 5, 105.

⁴ P. J. Beynon, P. M. Collins, P. T. Doganges, and W. G. Overend, *J. Chem. Soc. (C)*, 1966, 1131; P. J. Beynon, P. M. Collins, D. Gardiner, and W. G. Overend, *Carbohydrate Res.*, 1968, 6, 431.

⁵ C. Glalthaar and T. Reichstein, *Helv. Chim. Acta*, 1935, 18, 80.

⁶ R. S. Tipson and R. F. Brady, *Carbohydrate Res.*, 1969, 10, 549.