Photochemical Decarbonylation of Cyclic Ketones in Solution: Evidence for a Biradical Intermediate in the Pyranosidulose–Furanoside Conversion

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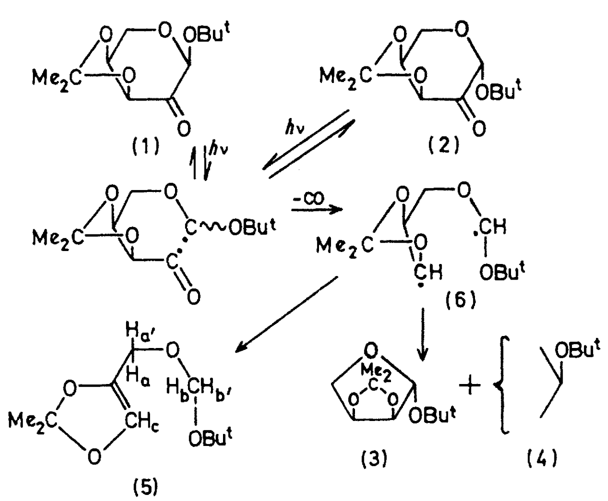
Summary The photolyses of pure pyranosiduloses (1) and (2) afford decarbonylated compounds (3), (4), and (5) in the same ratios, suggesting that they are formed *via* a common stabilised biradical (6).



USING pyranosiduloses as model compounds we recently found[1] that cyclic ketones possessing alkoxy-groups in the αα′-positions to the carbonyl function undergo photochemical decarbonylation upon u.v. irradiation in solution. A stabilised biradical was suggested[2] as a reaction intermediate which ring-closed stereoselectively. A study of the involvement of biradicals in photochemical gas-phase decarbonylations[3,4] and solution-phase ring-opening–hydrogen-transfer reactions[5] of cyclic aliphatic ketones has been the subject of much attention recently, and we now report our evidence which supports such a mechanism for ulose systems.

t-Butyl 3,4-*O*-isopropylidene-α-L-*erythro*-pentopyranosidulose (1) 2·0 g, m.p. 123°; $[\alpha]_D^{20}$ + 4·5° ν_{max} 1750 cm^{-1}; λ_{max} 305 nm (ϵ 16); τ 4·91 (s) 1-H; 5·15 (q) J_{43} 7·5, J_{45} 5·5, $J_{45'}$ 0·5 Hz; 5·40 (d) 3-H, 5·90 (d) 5-H$_2$† (prepared by oxidation[6] of methyl 3,4-*O*-isopropylidene-α-L-arabinoside)

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† All new compounds gave satisfactory elemental analyses. Optical rotations were measured on CHCl$_3$ solutions and n.m.r. spectra on CDCl$_3$ solutions at 60 MHz. Compounds (1—5) all showed signals assignable to the Bu^{t}O and (CH$_3$)$_2$CO$_2$ groups. (s = singlet, d = doublet, q = quartet, and b = broad).

in benzene‡ (150 ml) was irradiated through a Pyrex filter with light from a 450 w medium-pressure mercury arc for 40 min. (an identical result was obtained after 20 min. with unfiltered light).

Analysis of the photolysate (g.l.c. SE 52, 20% on 60—80 mesh Chromosorb W) showed unreacted (1), retention time 16 min. (32%), products (3) 6·5 min. (11%), (5) 6·75 min. (30%), (4) 7·5 min. (8·7%), and (2) 17 min. (17·3%). After g.l.c. separation of these components it was found that (3) $[\alpha]_D - 60°$; τ 4·65 (s) $J_{12} \leq 0·3$ Hz; 5·49 (d) J_{23} 6·0 Hz; 5·16 (m) 3-H; 6·01 4-H; and 6·05 4′-H; *m/e* 217 ($M - 15$); and (4) $[\alpha]_D - 98°$; τ 5·06 (d) J_{12} 3·4 Hz; 5·52 (q) J_{23} 6·5 Hz; 5·28 $J_{34'}$ 4·5, J_{34} 2·0 Hz; 6·0 (q) $J_{44'}$ 10 Hz; 6·38 (q) $J_{4'4}$ 10 Hz; *m/e* 217, were the ring-contracted t-butyl 2,3-*O*-isopropylidene-L-erythro-furanosides with the β- and α-configurations, respectively. These anomeric configurations were determined from the $J_{1,2}$ values[7] and the optical rotations. In accord with the gross structural assignment, acid hydrolysis of either (3) or (4) afforded L-erythrose which was isolated as its 2,5-dichlorophenylhydrazone[8] m.p. 103°; $[\alpha]_D^{20} + 9°$. Compound (5), ν_{max} 1690 cm^{-1} (C=C); τ6·0 (bs) $H_aH_{a'}$; 5·31 (s) $H_bH_{b'}$; 3·99 (bs) H_c, was t-butyl 1-(2,3-*O*-isopropylidene-2, 3-dihydroxypropenyl)formaldehyde acetal. It decolorised a bromine–carbon tetrachloride solution and absorbed 1 mole equivalent of hydrogen in the presence of Adams catalyst to give a product which contained two more hydrogen atoms (mass spec. and ^{1}H n.m.r.) and no double bond. Compound (2), m.p. 76°; $[\alpha]_D^{20} + 159°$; ν_{max} 1760 cm^{-1} (C=O); λ_{max} 308 nm (ϵ 42); τ 4·9 (s) 1-H; 5·28 (d) J_{34} 5·5 Hz; 5·45 (*sextet*) $J_{45'} \simeq J_{45} \simeq 2$ Hz; 5·59 (q) $J_{55'}$ 13·5 Hz; 5·95 (q) 5′-H; *m/e* 229 ($M - 15$), was the β-pyranosidulose anomer.

Irradiation of pure (2) under identical conditions afforded (3), (4), (5), and (1), the first three products being produced in the same ratios as obtained from (1). The proportion of furanosides and olefin formed, based upon the ulose decarbonylated, is similar even in the early stages of the reaction (see Table) irrespective of which ulose is photolysed.

Ulose consumed	Decarbonylated product / Ulose decarbonylated			Isomerised ulose formed
	(4)	(3)	(5)	
21% (1)	0·19	0·22	0·59	13% (2)
15% (2)	0·19	0·22	0·59	8% (1)

Thus prior isomerisation (1) ⇌ (2) can be ruled out as being responsible for the result. This strongly suggests a mechanism involving a common biradical (6) and the one depicted appears to be the most satisfactory.

It is noteworthy that there is a preference for ring closure to occur to give the sterically more favoured furanoside (3) which contrasts with the non-stereoselective ring closure found[3] in gas-phase photolysis of 2,6-dimethylcyclohexanone. The observed selectivity is in keeping with an oxygen-stabilised biradical intermediate.

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‡ Similar, but less clean, results were obtained with Bu^{t}OH and CH_2Cl_2.

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