Photochemical Removal of Methoxy-groups in Pyranosiduloses

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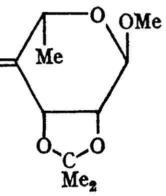
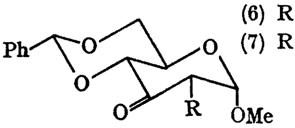
WE recently reported that the u.v. irradiation of solutions of the cyclic ketone (1) caused extrusion of carbon monoxide and ring contraction.[1] Thus, certain alkoxy-substituents αα′ to the carbonyl group are sufficient to make Norrish Type I cleavage the favoured reaction pathway in solution. We have since found other examples of Type I cleavage,[2] and found further, that if one of the adjacent alkoxy-groups was a methoxy-group (or presumably any alkoxy-group with a hydrogen atom in a 1,6-relationship to the carbonyl oxygen atom) then Norrish Type II cleavage[3] became dominant.

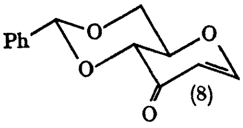
Irradiation of a 5% solution of methyl 3,4-*O*-isopropylidene-β-L-*erythro*-pentosidulose (2) in t-butyl alcohol for 1½ hr. through quartz gave formaldehyde, detected as its 2,4-dinitrophenylhydrazone, and one other major product. Analysis (g.l.c.) showed this product reached an optimum yield of 40% accompanied by 50% unchanged starting material. It was collected and found to be 4,5-*O*-isopropylidene-4(*S*), 5(*S*)-dihydroxy-3-oxotetrahydropyran (3)† m.p. 81—82°, $[\alpha]_D$ + 63°, ν_{max} 1725 (C = O), λ_{max} 300 nm. (ε *ca.* 75), *m/e* 172 (*M*) and 157 (*M* − Me). These constants and its n.m.r. spectrum were identical with those of a sample of (3) prepared[2] by oxidation of 1,5-anhydro-3,4-*O*-isopropylidene-L-arabinitol.[4]



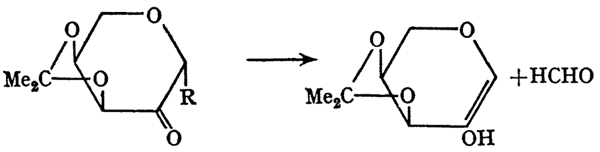
(1)



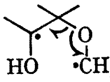
(6) R=OMe (7) R=H



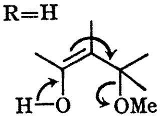
(8)



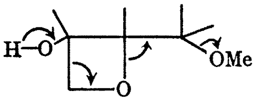
(2) R=OMe; (3) R=H (4)



(5)



(9)



(10)

The formation of compound (3) can be accounted for as shown schematically in structure (5). The oxygen of the excited carbonyl abstracts a γ hydrogen from the methoxy-group. This can then lose formaldehyde [see arrows on (5)] and produce (3) *via* its enolic form (4).[5,6]

Other consequences can ensue from this mode of cleavage. Irradiation of a 0·5% solution of methyl 4,6-*O*-benzylidene-2-*O*-methyl-α-D-*ribo*-hexopyranosid-3-ulose (6)[7] in benzene under similar conditions gave, on t.l.c. (SiO_2), compound (6) and three other components. The band with the same mobility‡ as 2-deoxy-3-ulose (7) was isolated. Examination of the n.m.r. and i.r. spectra of this crude material showed it to be mainly the enone (8) *ca.* 90% containing less than 10% of (7). Recrystallisation gave the pure enone (8), m.p. 127—129 $[\alpha]_D$ + 189° ν_{max} 1700, 1600(C=C–C=O), λ_{max} 262 nm. (8·4 × 10^3) and an n.m.r. spectrum identical with that of a sample prepared by oxidation of 4,6-*O*-benzylidene-D-allal.[8]

The possibility that (8) was formed from (7), a conversion known to occur in the presence of acid,[9] was excluded in the present case. Although the photolysate did not become acidic the behaviour of (7) in a benzene solution was investigated in the presence of formic acid,§ with and without u.v. irradiation, but (8) was not produced. Furthermore, irradiation of this solution in the absence of acid did not produce (8) either. The formation of both (7) and (8) can be explained by Type II cleavage [see (5)]. This would give (7) in its enolic form which could ketonize to (7) in the usual way, or alternatively as shown in (9) to afford (8). A mechanism similar to this has been postulated[10] for the formation of enones by the acid-catalysed elimination of water from β-hydroxy-ketones. Another possibility, which cannot be excluded at present, is that Type II cleavage affords an oxetanol (10) by closure of the diradical depicted in (5).[6,11] This might then break down to afford enone [see arrows on (10)].

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† All new compounds gave satisfactory elemental analyses: $[\alpha]_D$, λ_{max}, and ν_{max} were measured in $CDCl_3$, EtOH, and KBr respectively.

‡ It has been found that (7) and (8) have the same mobility in all t.l.c. systems tried so far.

§ Formic acid might have formed in the photolysate by oxidation of formaldehyde.

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