Photochemical Ring Expansions of Five- and Six-membered Ring Ketones Derived from Pentoses

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Summary U.v. irradiation of the six-membered ring ketone, 1,5-anhydro-3,4-*O*-isopropylidene-L-*erythro*-pentulose (**1**), at −70° in ethanol–diethyl ether (1 : 9) gave two ring-expanded isomeric dioxepans (**4**) in 72% yield; the furanosidulose (**5**) also underwent ring expansion to give two isomeric dioxan derivatives (**6**) when irradiated in methanol at room temperature.

A common photochemical reaction of hexopyranosidulose derivatives in solution at room temperature is decarbonylation accompanied, in many cases, by ring contraction to give furanosides as the major organic products.[1] We report here that although the photochemistry of the 1,5-anhydropentulose derivative (**1**) at room temperature is unexceptional in that it affords carbon monoxide, its reaction at −70° is novel, since decarbonylation is suppressed and ring-expanded products are formed.

U.v. irradiation† at −70° for 1 h of a deoxygenated 2% solution of ketone (**1**)[2] in diethyl ether–ethanol (9 : 1) decomposed 90% of it to form two major products, R_t 8 and 10 min (27 and 38% respectively). These were isolated by preparative g.l.c. and found to be isomeric dioxepans (**4**) from their identical elemental analyses, i.r., and mass spectra [*m/e* 218 (M^+), 203 $(M - \mathrm{Me})^+$, and 173 $(M - \mathrm{OEt})^+$], and their 220 MHz ^{1}H n.m.r. spectra, which both showed signals at similar chemical shifts for $\mathrm{Pr^i}$, EtO, and seven ring protons which were analysed completely by first-order methods.

The results show that the two compounds are stereoisomeric dioxepans probably differing in stereochemistry at

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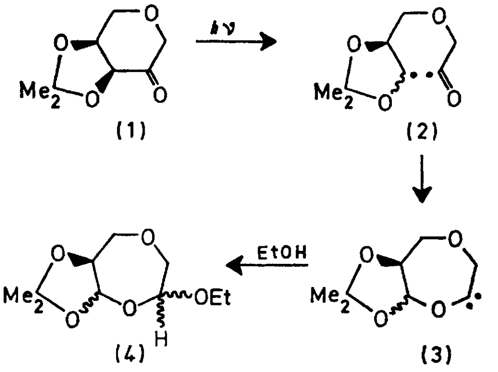
† Irradiations were carried out in cooled quartz tubes situated 2·5 cm from a 450 W medium-pressure mercury arc.

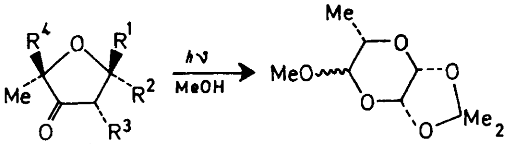
C-2. Both products can be accounted for by a mechanism shown in the Scheme, which has been proposed to explain ring expansions observed with some strained bi-[3] and tricycloalkanones[4] and some cyclobutanones.[5,6] It involves



Scheme

initial α-cleavage of the excited ketone to give the most highly substituted biradical (**2**), followed by rearrangement to the oxacarbene (**3**), which is trapped with ethanol.

Termination of decarbonylation in the low-temperature photoreaction of (**1**) was not unexpected;[7] however, the ring expansion of this unstrained pyranosidulose to seven-membered ring products is unusual and it represents the first example of this type of rearrangement from a six-membered ring ketone.‡ The only related reported case of ring expansion from an unstrained cycloalkanone[5,9] is that of spiro[2,4]heptan-4-one, the expansion of which was thought to be facilitated by stabilisation of the developing carbene centre by the cyclopropyl ring.[5] Significantly the corresponding spiro[2,5]octan-4-one did not undergo ring expansion.[9,10]



(5) $R^1 = R^4 = H$; $R^2, R^3 = -OCMe_2O-$

(7) $R^1 = R^2 = R^4 = Me$; $R^3 = H$

Ring expansion also occurs with a related five-membered ring derivative, 5-deoxy-1,2-*O*-isopropylidene-β-L-*erythro*-pentofurano-3-ulose[11] (**5**), which was found to give two isomeric dioxan derivatives (**6**) when irradiated at *ca.* 20° in methanol. This result contrasts with the reported failure of 2,2,5,5-tetramethyldihydrofuran-3-one (**7**) to undergo ring expansion when similarly treated.[12]

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‡ The mechanism of the photochemical ring expansion of diphenyl-α-silacyclohexanone which Brook and Duff reported[8] is probably different because of the propensity of silicon to bond with oxygen.

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