Photochemically Induced Ring Contraction, a Furanoid Ring from a Pyranosidulose

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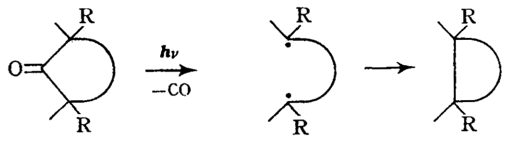
The decarbonylation of ketones upon gas-phase photolysis, which is well documented,[1,2] affords a useful method for bringing about a ring contraction. For example, irradiation of cyclohexanone vapour with u.v. light gives[3] cyclopentane. The scope of this type of reaction is often severely restricted by its failure to occur in solution. This is said[1] to be due to loss in vibrational energy from the electronically excited ketone to the surrounding molecules. There have been reports, however, that cyclic ketones containing aryl substituents at the $\alpha\alpha'$-positions can be induced to undergo photolytic ring contractions in solution.[4] This is because ejection of carbon monoxide in this case forms a diradical in which both radicals are benzylic and therefore stabilized. The overall reaction,[5] where R = Ph, is:



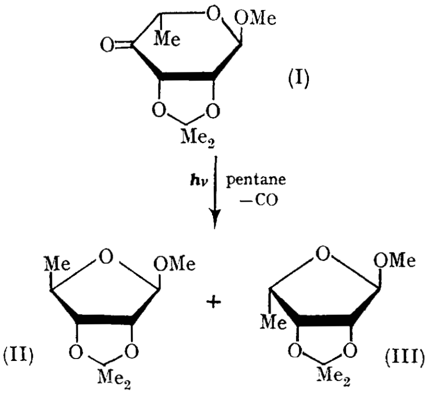
Consequently it was of interest to irradiate ketones with other types of stabilizing substituents at the αα′-positions to discover if similar ring contractions could be brought about in solution. The readily available[6] "oxo-sugars" seemed ideal candidates. These ketones have alkoxy-substituents at the αα′-carbons which would afford considerable stabilization[7] to the diradical intermediate formed where R = OR. Accordingly 2% solution of methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-*lyxo*-hexopyranosid-4-ulose (I) in pentane was agitated by the passage of nitrogen gas, and irradiated with a 450-w medium pressure Hanovia lamp[8] until g.l.c. (187°, 10 ft. × ¼″, SE30 20%), showed that the concentration of pyranosidulose (I) (R_t 6·8 min.) and the one product peak (R_t 3·4 min.), detectable under these conditions, were in the ratio 1 : 9. This change was accompanied by an evolution of carbon monoxide, which was easily detectable in the nitrogen effluent by infrared spectroscopic examination. No reaction occurred under the same conditions in the dark. After cautious solvent removal the residual oil was purified by bulb-to-bulb distillation giving a white mobile oil, in 60% yield (65% based on unrecovered ketone).

The n.m.r. spectrum of the distilled product showed that it was a mixture of two isomers. Re-examination of the oil by g.l.c. (140°, 10′ × ¼″, Carbowax 20M 20%) confirmed this. The slower moving component was the 5-deoxy-riboside (II) (92%) and the faster moving one was the 5-deoxy-lyxoside (III) (8%).

The major product methyl 5-deoxy-2,3-*O*-isopropylidene β-D-*ribo*-furanoside (II) was separated from the lyxoside (III) by g.l.c. and its structure established. The molecular formula was $C_9H_{16}O_4$ (chemical analysis, and mass spectral molecular weight). The i.r. spectrum indicated that carbonyl and hydroxyl groups were absent. Acid hydrolysis afforded a sugar with paper chromatographic mobility identical to that of authentic 5-deoxy-ribose.[9] Treatment of this hydrolysate with 2,4-dinitrophenylhydrazine afforded a yellow hydrazone, m.p. 140—143°. The reported[9] value for the 2,4-dinitrophenylhydrazone of 5-deoxy-ribose is 151—152°.

The n.m.r. spectrum is consistent with this structural assignment and shows the following features: the anomeric proton singlet at τ 5·18, $J < 0{\cdot}5$ Hz,[†] an AB quartet owing to the H-2,H-3 protons at τ 5·58 and 5·46, $J_{2,3}$ 6 Hz (the H-3 component was broadened, $J_{3,4} \sim 1{\cdot}0$ Hz), and H-4 proton quartet, intensities 1 : 3 : 3 : 1, composed of four broadened signals centred at τ 5·74, $J_{4,5}$ 5·0 Hz and the C-5 methyl, to which it was coupled, appeared at τ 8·76 as a doublet; the methoxyl absorption appeared unsplit at τ 6·70 and the geminal methyls of the isopropylidene residue appeared as two singlets at τ 8·59 and 8·75. The small splittings for the H-1,H-2 protons and H-3,H-4 protons are good evidence[10] for the *trans* disposition of these pairs of hydrogens in the furanoid ring.

The structure of photo-product (II) was finally proved by comparing it with methyl 5-deoxy-2,3-*O*-isopropylidene-D-ribofuranoside prepared by the conventional method.[9] The $[\alpha]_D$, i.r., n.m.r. and mass spectrum of both samples were identical. The mass spectrum showed a very weak parent molecular-ion peak at m/e 188; however, an intense $P - 15$ appeared at m/e 173 caused by loss of CH_3 from the isopropylidene residue of the molecular ion.[11]



The minor product methyl 5-deoxy-2,3-*O*-isopropylidene-α-L-lyxofuranoside (III) was enriched in a sample from 8% to 85% by preparative g.l.c. and a structural assignment achieved using this material. Its i.r. spectrum showed no hydroxyl or carbonyl absorption, and the carbon and hydrogen analyses were excellent for either

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[†] All J values reported are measured splittings.

furanosides (II) or (III). Acid hydrolysis of this component afforded a sugar with a paper chromatographic mobility identical to that of authentic 5-deoxy-lyxose‡ distinctly separable from 5-deoxy-ribose. As expected, a trace of the latter compound could be seen on the paper chromatogram of the hydrolysate.

The n.m.r. spectrum showed methoxyl, C-5 methyl and isopropylidene methyls at the same chemical shift as those of the *ribo*-isomer (II). The major differences were the anomeric proton singlet at τ 5·26, the H-2,H-3 protons appearing as an unresolved signal between τ 5·7 and 5·3 and the H-4 proton appearing as a more highly split signal (octet) centred at τ 6·1 $J_{3,4} \simeq 4{\cdot}5$. This coupling is much larger than $J_{3,4}$ for compound (II) and is consistent with H-3 and H-4 being *cis* in compound (II).

The ring closure is highly stereospecific showing a very strong preference for the more sterically favoured situation with the methyl at C-4 and oxygen at C-3 in the *trans* relationship in the furanoid ring. This involved rotation about the original C-5–O_R bond prior to bond formation. A similar preference was found when *cis*-αα′-diphenyl-β-indanone[4a] was irradiated to afford *trans*-diphenylbenzocyclobutene. Cava and Mangold[4b] have also found similar results with dihydrophencyclones. Rickborn and his co-workers[2] on the other hand, have shown that in gas-phase photolysis, pure *cis*- or *trans*-dimethylcyclohexanane ring contracts to an almost equal mixture of *cis*- and *trans*-dimethylcyclopentane. Thus marked stereospecificity is lost when the radicals are not stabilized.

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‡ This compound was prepared from 1,2-*O*-isopropylidene-5-deoxy-α-L-*threo*-pentofuranosidulose (IV) by $LiAlH_4$ reduction and sequential acid hydrolysis. This compound (IV) was generously supplied by Dr. N. R. Williams.

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