Tetrahedron Letters No. 42, pp 4011 - 4014.
©Pergamon Press Ltd. 1978. Printed in Great Britain.

0040-4039/78/1015-4011$02.00/0

PHOTODECARBONYLATION OF KETO-MONOSACCHARIDES

Kurt Heyns, Rainer Neste und Michael Paal
Institut für Organische Chemie und Biochemie der Universität Hamburg
Martin-Luther-King-Platz 6, 2000 Hamburg 13, Germany

The photolysis of carbohydrate uloses has recently been studied by Collins and coworkers [1,2,3].

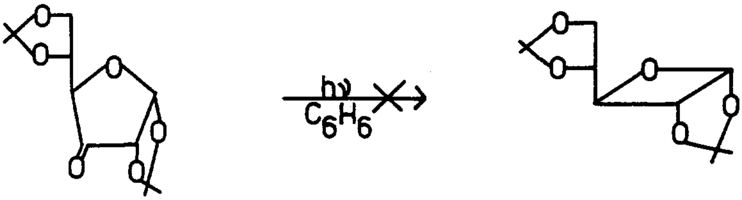
From our own experiments on the photolyses of 1,6-anhydro-hexopyranuloses [4] we know, that these compounds lose carbon monoxide to yield one isomer of the corresponding pentopyranose.

In order to study the influence of ringsize on this reaction, we prepared the following compounds with furanoid, pyranoid and septanoid ringsystems:

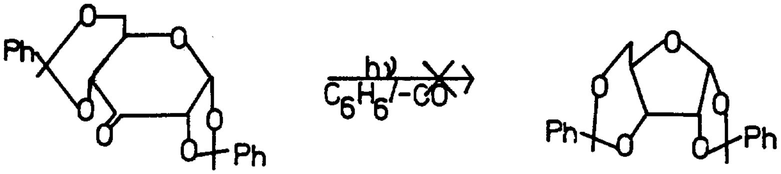
1,2,5,6-Di-O-isopropylidene-α-D-ribo-hexulofuranose-3 1,
1,2,4,6-Di-O-benzylidene-α-D-ribo-hexulopyranose-3 2,
1,2,4,5-Di-O-isopropylidene-α-D-ribo-hexuloseptanose-3 3,
1,2,3,4-Di-O-isopropylidene-α-D-xylo-hexuloseptanose-5 4.

All four uloses have been prepared from the well known corresponding gluco-compounds [5] by oxidation with RuO_2 [6]. As far as we know, compounds 2, 3, and 4 have never been prepared before. Their structures have been elucidated by IR and NMR-spectroscopy (see table). Furthermore, compounds 3 and 4 have been reduced with sodium borohydride yielding a 70/30 mixture consisting of 1,2,4,5-Di-O-isopropylidene-α-D-glucoseptanose and 1,2,4,5-Di-O-isopropylidene-α-D-alloseptanose 5 from 3 and a 50/50 mixture of 1,2,3,4-Di-O-isopropylidene-α-D-glucoseptanose and 1,3,3,4-Di-O-isopropylidene-β-L-idoseptanose 6 from 4. In addition, 5 and 6 have been characterised by NMR-spectroscopy of their acetates 5a and 6a.

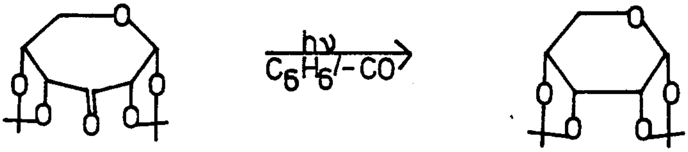
The furanoid and pyranoid compounds 1 and 2 showed no tendency to form ring-contracted products when photolysed in dry benzene in the usual manner.
But from the photolysates of the septanoid compounds 3 and 4 we were able to isolate two sugars that are obviously formed by loss of carbon monoxide from the mother-compound. 3 yields 10 % 1,2,3,4-Di-O-isopropylidene-α-D-ribopentopyranose 7, which has already been described as a by-product from the reaction of ribose



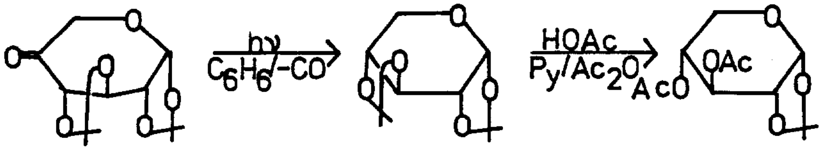
(1)



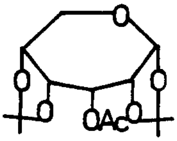
(2)



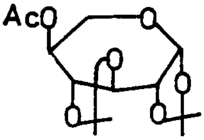
(3) (7)



(4) (8) (8a)



(5a)



(6a)

Chemical shifts (values, TMS inner reference) and coupling constants+) (Hz) at 270 MHz

Cmp. no.	solvent	H1	H2	H3	H4	H5	H6	H6'	PhCH	Ar	OAc	Isopr.
2	$CDCl_3$	5.99	4.66	-	4.44	4.22	4,5	3.89	6.09 5.61	7.33	-	-
3	$CDCl_3$	5.55	4.83	-	4.83	4.45	4.22	3.97	-	-	-	1.64 ; 1.57 1.45 ; 1.39
4	$(CD_3)_2CO$	5.15	4.46	4.21	4.69	-	4.32	4.19	-	-	-	2.50 ; 2.33 2.28
5a	$CDCl_3$	5.35	4.05	5.42	4.15	3.87	3.94	3.36	-	-	2.19	1.69 ; 1.53 1.33
6a	$(CD_3)_2CO$	5.25	4.28	3.99	3.98	4.96	3.28	4.07	-	-	2.09	1.51 ; 1.42 1.38
		H1	H2	H3	H4	H5	H5'					
7	C_6D_6	5.09	3.95	3.78	4.16	4.01	3.87	-	-	-	-	1.62 ; 1.48 1.26 ; 1.07
8	$CDCl_3$	5.43	4.22	3.84	3.67	4.11	3.90	-	-	-	-	1.72 ; 1.47 1.45 ; 1.40
8a	C_6D_6	5.19	3.82	5.52	4.90	3.66	3.78	-	-	-	1.59 1.57	1.53 ; 1.16

	J1,2	J2,3	J3,4	J4,5	J5,6	J5,6'	J6,6'
2	5,2	-	-	10	9,6	5	10,5
3	5,4	-	-	6.4	4,0	4,6	14,2
4	3,6	7.0	10.4	-	-	-	16,0
5a	4,6	2,0	2,8	5.2	10,0	4,8	12,6
6a	3,8	6,8	6.0	9,2	10,4	6,0	12,4

	J1,2	J2,3	J3,4	J4,5	J4,5'	J5,5'	J2,4
7	4,8	4,0	7,4	7,8	8,4	11,2	-
8	4,2	7,2	10,0	10,0	6,2	10,0	-
8a	3,8	3,2	3,7	6,6	4,9	12,0	1,0

+) all coupling constants were determined according to first order analysis with acetone/H_2SO_4 by Hughes and Speakman 7).

Compound 4 gives 1,2,3,4-Di-O-isopropyliden-α-D-xylo-pentopyranose 8 in 10 % yield. This is a new xylose-derivative with a trans-fused isopropylidene-ring. The trans-fused blocking-group is easily split off by the action of 80 % acetic acid. Comparison of the NMR-data of compound 8 with the corresponding diacetate 8a shows a remarkable change of conformation after the trans-fused isopropylidene-ring has been split off.

The results of photolyses of compounds 1 and 2 seem to be reasonable. The proposed biradical intermediate 9) is not able to cyclize because the resulting products will be highly strained.

Although products 7 and 8 are strained too, they are formed because of the greater stability of the six membered ring towards the seven membered ring. The ribo-compound 7 should exist in a conformation minimising the strain put on the pyranose ringsystem by the repelling forces of the hydrogen atoms cis-syn-cis-arrangement 10)

Literature

1) P.M. Collins and P. Gupta, J. Chem. Soc. (C), 1965, (1971)
2) P.M. Collins, P.Gupta and R. Iyer, Chem. Commun. 1261 (1970)
3) P.M. Collins, P. Gupta and R. Iyer, J. Chem. Soc., Perkin I, 1670 (1972)
4) K. Heyns and R. Neste, in preparation
5) A.B. Wood, H.W. Diehl, H.G. Fletcher, J.Am. Chem. Soc. 79, 1986 (1957)
J.D. Stevens, Aust. J. Chem. 28, 525 (1975)
6) B.T. Lawton, W.A. Szarek and J.K.N. Jones, Carbohydr. Res. 10, 456 (1969)
7) N.A. Hughes and P.R. Speakman, Carbohydr. Res. 1, 171 (1965)
8) M. Kisio and A. Hasegawa, Carbohydr. Res. 52, 95 (1976)
9) D.R. Morton and N.J. Turro, Advances Photochem. 9, 197 (1974)
10) J.A. Mills, Adv. Carbohydr. Chem. 10, 33 (1955)

(Received in Germany 7 July 1978; received in UK for publication 22 August 1978)