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Note

Formation of 3′,6′-anhydrosucrose by Mitsunobu dehydration of sucrose

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We have reported[1] that treatment of sucrose with triphenylphosphine and diethyl azodicarboxylate in *N,N*-dimethylformamide gave a 1:1 mixture of the 3′,4′-anhydro derivative **1** and a second derivative, tentatively assigned the 1′,4′-anhydro structure **2**. Compound **2** was considered initially to be 3′,6′-anhydrosucrose (**3**), but the reported[2] physical constants {m.p. 146°, $[\alpha]_D$ +104° (methanol)} were significantly different from those {m.p. 168°, $[\alpha]_D$ +123° (methanol)} that we obtained and hence the closely related structure **2** was suggested.

2,3,4,6,3′,6′-Hexa-*O*-acetyl-1′,4′-anhydrosucrose {m.p. 105–107°, $[\alpha]_D$ +142.5° (chloroform)} has now been prepared[3], and the ^{13}C- and ^{1}H-n.m.r. data are different from those of the hexa-acetate **4** {obtained as an oil, $[\alpha]_D$ +69° (chloroform)} of **3**. The ^{1}H-n.m.r. and i.r. spectral data of an authentic sample[2] of 3′,6′-anhydrosucrose (**3**) show unequivocally that the second compound formed in the Mitsunobu dehydration of sucrose is indeed 3′,6′-anhydrosucrose. We can offer no explanation for the discrepancy in the physical constants, although **3** does crystallise as a hydrate, which might account for the difference in m.p.

The formation of 3′,6′-anhydrosucrose is consistent with our observation[1] that the 3′,4′-epoxide **1** is the only product formed when the reaction is carried out in the presence of acetic acid (2 equiv.). Under these conditions, positions 6 and 6′ are blocked by acetate groups, thus preventing the formation of a 3′,6′-anhydro ring; the Mitsunobu reaction can be used[4,5] to selectively esterify primary hydroxyl groups in sugars.

The formation of 3′,6′-anhydrosucrose is more reasonable on mechanistic grounds than is formation of the 1′,4′-isomer. The transition state for the latter reaction involves nucleophilic attack by HO-4′ on the neopentyl-like position 1′. Attack by the HO-3′ on position 6′ would be expected to be favoured kinetically.

The ^{1}H-n.m.r. spectrum of the hexa-acetate (**4**) of **3** is also more consistent

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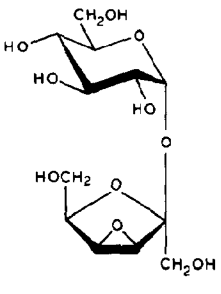
TABLE I

^{1}H-N.M.R. DATA FOR 3′,6′-ANHYDROSUCROSE (**3**) AND ITS HEXA-ACETATE **4**

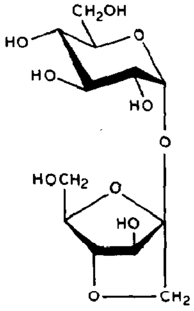
Compound	*Chemical shifts (δ scale)*													
	H-1	*H-2*	*H-3*	*H-4*	*H-5*	*H-6a*	*H-6b*	*H-1′a*	*H-1′b*	*H-3′*	*H-4′*	*H-5′*	*H-6′a*	*H-6′b*
3[a,c]	5.48	3.64	3.78	3.45	3.91	3.85	3.77	4.04	4.04	4.32	4.53	4.47	3.97	3.76
4[b,c]	5.98	5.14	5.67	5.38	4.65	4.26	4.43	4.55	4.06	4.01	4.79	4.06	3.97	3.26
	J *Values (Hz)*													
	1,2	*2,3*	*3,4*	*4,5*	*5,6a*	*5,6b*	*6a,6b*	*1′a,1′b*	*3′,4′*	*4′,5′*	*5′,6′a*	*5′,6′b*	*6′a,6′b*	
3[a]	3.8	9.9	9.3	9.8	2.3	4.8	12.5		2.2	~0	~0	~0	13.0	
4	3.6	10.4	9.3	10.3	2.6	4.4	11.8	11.8	2.2	~0	~0	1.3	8.5	

[a]In D_2O. [b]C_6D_6. [c]At 300 MHz.

with the 3′,6′-anhydro structure than the 1′,4′-structure. Thus, the small (1.3 Hz) coupling constant assigned[1] to an (unusual) long-range coupling between H-1′b and H-5′ is clearly a 6′,5′ coupling constant. The ^{1}H-n.m.r. data and our (new) assignments for **3** and **4** are given in Table I.



1



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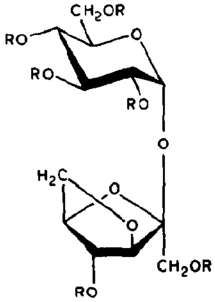

3 R = H

4 R = Ac

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