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First X-Ray Study on Orientation of Addition of Phosphorus Compounds to 3-O-Alkyl-5,6-dideoxy-1,2-O-isopropylidene-6-C-nitro-α-D-xylo-hexo-5-(Z)-enofuranoses

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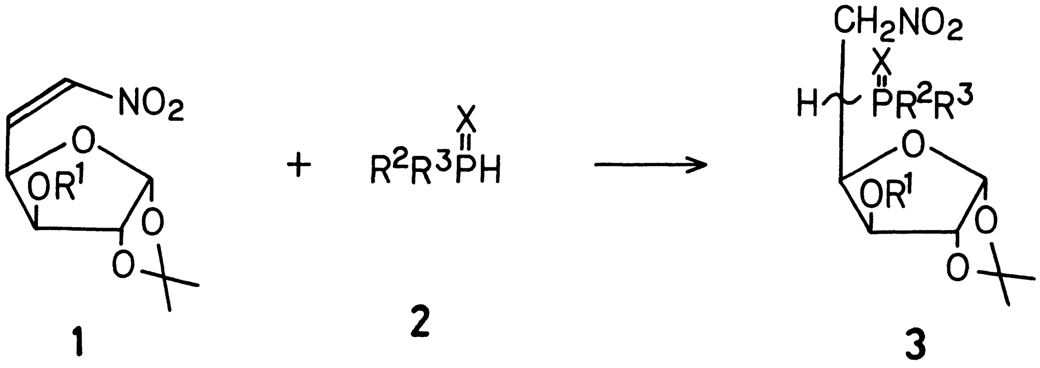
Stereochemical control of the addition of phosphorus compounds to 3-O-alkyl-5,6-dideoxy-1,2-O-isopropylidene-6-C-nitro-α-D-xylo-hexo-5-(Z)-enofuranoses was first investigated by X-ray crystallographic analysis of the adduct.

Addition of phosphorus compounds to 3-O-alkyl-5,6-dideoxy-1,2-O-isopropylidene-6-C-nitro-α-D-xylo-hexo-5-(Z)-enofuranoses in the presence of triethylamine at 90 °C afforded 3-O-alkyl-5,6-dideoxy-1,2-O-isopropylidene-6-C-nitro-5-C-(phosphinyl)-α-D-glucofuranoses and -β-L-idofuranoses.[1-4]



The ratios of D-glucose to L-idose derivatives were varied from 1:2 to 1:11 depending on substituents of phosphorus compounds and C_3 carbon atom of enofuranose 1. These data are summarized in Table 1.

The structure of 3a-ido was determined by X-ray crystallographic analysis. The absolute configuration (°E conformation) is shown in Fig. 1.

The reason why the major product is L-idose derivative is steric hindrance caused by 3-O-alkyl group and phosphorus compounds as shown in Fig. 2 indicated by Carm's rule.[5]

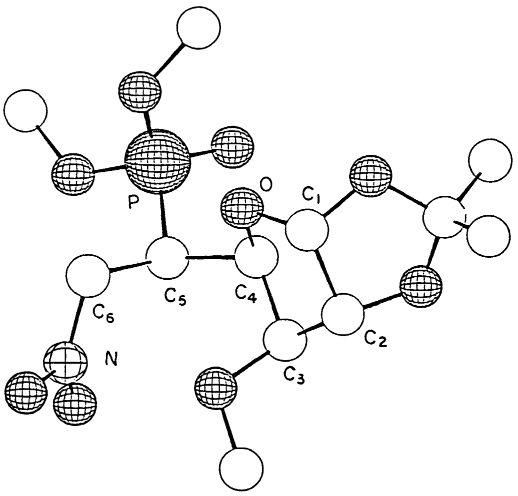


Fig. 1. Computer-generated drawing of 5,6-dideoxy-1,2-O-isopropylidene-3-O-methyl-6-C-nitro-5-C-(dimethoxyphosphinyl)-β-L-idofuranose.

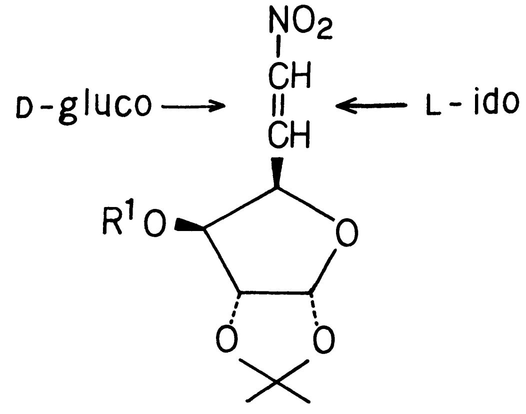


Fig. 2. Direction of attack of phosphorus compounds on 3-O-alkyl-5,6-dideoxy-1,2-O-isopropylidene-6-C-nitro-α-D-xylo-hexo-5-(Z)-enofuranoses.

Table 1. Ratios of D-glucoses to L-idoses produced

Product	R^1	R^2	R^3	X	Ratio of D-glucose to L-idose
3a	Me	MeO	MeO	O	1 : 2
3b	Me	EtO	EtO	O	1 : 2.5
3c	Me	Ph	H	··[a]	1 : 3.8[3]
3d	Ac	Ph	H	··[a]	1 : 3.5[4]
3e	Me	BnO	BnO	O	1 : 7
3f	Me	Ph	Ph	O	1 : 11[2]
3g	Bn	MeO	MeO	O	1 : 3
3h	Bn	Mes	H	··[a]	——[b]

a) ·· Means lone paired electrons.

b) No reaction was observed.

The larger the alkyl groups are the more facile the L-idose derivatives seem to form. The observed ratios of D-glucose to L-idose may reflect the seriousness of the steric hindrance caused by substituents at C_3 and phosphorus atoms. When dimesitylphosphine was used for the addition reaction no reaction was observed. The steric hindrance of the phosphine seems to be large enough to prevent the attack even on the less hindered side.

References

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