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Note

A sugar phosphorane

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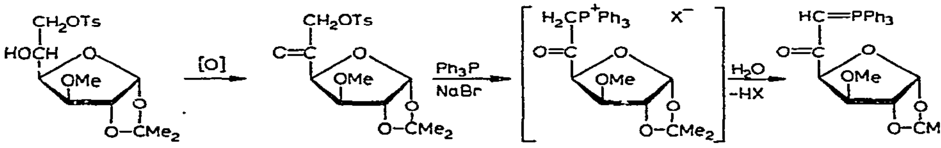
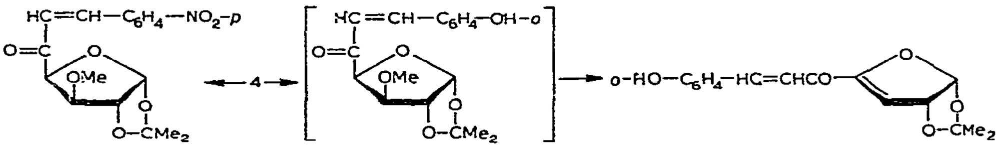
The Wittig reaction is an effective method for the synthesis of carbohydrate derivatives containing new carbon–carbon bonds. In previous reports[1,2], the carbohydrates were used only as the carbonyl components, but we report now the preparation of a carbohydrate phosphorane, using the sequence **1**→**4**.



1 **2** **3** **4**

The ketone **2** did not react directly with triphenylphosphine in a variety of solvents, but reaction occurred readily in acetone in the presence of sodium bromide. Treatment of the resulting solution of the phosphonium salt **3** with water gave the phosphorane **4** which was recovered from the aqueous solution by extraction with chloroform. This behaviour reveals the relatively high acidity of the methylene group of compound **3** and the low reactivity of phosphorane **4**. The constitution of phosphorane **4** follows from its mode of synthesis and from the similarity of its u.v. and i.r. spectra with those of acetylmethylenetriphenylphosphorane.

Compound **4** reacts with such active aldehydes as *p*-nitro- and *o*-hydroxybenzaldehyde, but does not react practically with *p*-dimethylamino-, *p*-hydroxy-, and 2,4-dihydroxy-benzaldehyde.



5 **6** **7**

The product of the reaction of phosphorane **4** with *p*-nitrobenzaldehyde is the expected mixture of *cis, trans* isomers of the unsaturated ketone **5**. The reaction of phosphorane **4** with salicylaldehyde leads to compound **7**, which evidently originates from compound **6** during washing of the reaction mixture with aqueous sodium hydroxide. The absence of the 3-proton singlet for CH_3O at τ 6.60 and the bathochromic shift (*cf.* the data for compound **8**) of the three u.v. bands for compound **7** confirm its constitution.

EXPERIMENTAL

*1,2-*O*-Isopropylidene-3-*O*-methyl-6-*O*-tosyl-α-*D*-glucofuranose* (**1**). — 1,2-*O*-Isopropylidene-3-*O*-methyl-α-D-glucofuranose (47 g) in a mixture of acetone (50 ml) and pyridine (40 ml) was treated with tosyl chloride (46 g) with ice-cooling. The mixture was kept for one day, water was then added with ice-cooling, and, after 1 h, the mixture was poured into water (500 ml) and extracted with chloroform (3 x 100 ml). The chloroform solution was washed with M sodium carbonate and dilute hydrochloric acid, dried, and evaporated to give 62 g (80%) of syrupy **1**, $[\alpha]_D$ −24° (*c* 5.1) ν_{max}^{film} 1354s cm^{-1}.

Anal. Calc. for $C_{17}H_{24}O_8S$: C, 52.58; H, 6.19. Found: C, 52.30; H, 5.80.

*1,2-*O*-Isopropylidene-3-*O*-methyl-6-*O*-tosyl-α-*D-xylo*-hexofuranos-5-ulose* (**2**). — A solution of compound **1** (60 g) in *N,N*-dimethylformamide (100 ml) was added to a solution of phosphorus pentoxide (20 g) in a mixture of methyl sulphoxide (30 ml) and *N,N*-dimethylformamide (300 ml). The mixture was kept for 5 days, and was then poured into saturated, aqueous sodium hydrogen carbonate (1 litre) and extracted with chloroform (3 x 200 ml). The chloroform solution was dried and evaporated to give 47 g (78%) of syrupy **2**, $[\alpha]_D$ −62° (*c* 5.6), ν_{max}^{film} 1748s cm^{-1}; λ_{max} 225 nm (ε 10,000).

Anal. Calc. for $C_{17}H_{22}O_8S$: C, 52.85; H, 5.72. Found: C, 52.30; H, 5.77.

*(1,2-*O*-Isopropylidene-3-*O*-methyl-α-*D*-xylofuranuronylmethylene)triphenylphosphorane* (**4**). — A mixture of compound **2** (31 g), triphenylphosphine (24 g), and sodium bromide (10 g) in dry acetone (200 ml) was refluxed for 3 h. Water (150 ml) was then added, and the mixture was extracted with chloroform (3 x 150 ml). The chloroform solution was washed with M sodium carbonate, dried, and evaporated to give 32 g (83%) of syrupy **4**, $[\alpha]_D$ −46° (*c* 5.3); ν_{max}^{film} 1636 m, 1592 s, 1542 s, 1472 s, 1454 s cm^{-1}; λ_{max} 223 nm (ε 21,400); *cf.* acetylmethylenetriphenylphosphorane, ν_{max}^{Nujol} 1614 w, 1586 m, 1552 s, 1486 s, 1456 s cm^{-1}, λ_{max} 220 nm (ε 31,400).

Anal. Calc. for $C_{28}H_{29}O_5P$: C, 70.59; H, 6.08. Found: C, 70.04; H, 6.20.

*1,2-*O*-Isopropylidene-3-*O*-methyl-4-[3-(*p*-nitrophenyl)acryloyl]-α-*D-xylo*-tetrofuranose* (**5**). — A mixture of compound **4** (1.2 g) and *p*-nitrobenzaldehyde (0.4 g) in xylene (5 ml) was heated for 2 h at 100°. The solution was evaporated under diminished pressure, and the residue was fractionated on aluminium oxide (R_F 0.80 in chloroform) to give **5** as a syrup (0.50 g, 51%), $[\alpha]_D$ −30° (*c* 4.8); ν_{max}^{film} 1706 s, 1610 s, 1522 s, 1346 s cm^{-1}; λ_{max} 218 (ε 4,300), 310 (ε 8,000) nm.

Anal. Calc. for $C_{17}H_{19}NO_7$: C, 58.45; H, 5.45. Found: C, 57.87; H, 5.68.

*3-Deoxy-1,2-*O*-isopropylidene-4-[3-(*o*-hydroxyphenyl)acryloyl]-α-*D-glycero*-tetr-3-enofuranose* (**7**). — A mixture of compound **4** (2.4 g) and salicylaldehyde (0.62 g) in xylene (10 ml) was heated for 3 h at 100°. Benzene (20 ml) was then added, and the solution was extracted with 0.1M sodium hydroxide (4×20 ml). The aqueous layer was acidified with dilute hydrochloric acid and extracted with ether. The dried, ethereal solution was then evaporated to give greenish-yellow crystals of **7** (0.51 g, 30%), m.p. 148° (from carbon tetrachloride), $[\alpha]_D$ +18° (*c* 5.6); ν_{max}^{Nujol} 1656 s, 1604 s, 1578 m cm^{-1}; λ_{max} 256 (ε 6,300), 314 (ε 15,000), 364 (ε 17,000) nm.

Anal. Calc. for $C_{16}H_{16}O_5$: C, 66.66; H, 5.56. Found: C, 66.20; H, 5.60.

*1-(*o*-Hydroxyphenyl)-but-1-en-3-one* (**8**). — The reaction of salicylaldehyde with acetylmethylenetriphenylphosphorane, performed as above, gave **8**, m.p. 138°; ν_{max}^{Nujol} 1675 m, 1640 s, 1604 s cm^{-1}; λ_{max} 236 (ε 8,000), 285 (ε 16,000), 338 (ε 1,000) nm.

Anal. Calc. for $C_{10}H_{10}O_2$: C, 74.07; H, 6.18. Found: C, 73.90; H, 6.20.

U.v. spectra were measured for methanol solutions; specific rotations were measured for ethanol solutions

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