**1-(3-Deoxy-α-L-*threo*-pentopyranosyl)cytosine (2) (Pentopyranine C).**—Compound **11b** (98 mg) was treated overnight with methanolic ammonia (~10 ml) saturated at 0°. After evaporation of the solvent, the residue was triturated with ether (2 × 10 ml) and chloroform (2 × 10 ml), and the residue was crystallized from ethanol to give compound **2**: 49 mg; mp 144–145°; $[\alpha]^{27}D$ +19° (*c* 1.0, $H_2O$) (lit.[2] mp 143–145°, $[\alpha]^{21}D$ +20°).

**1-(3-Deoxy-α-L-*threo*-pentofuranosyl)cytosine (13).**—Compound **12a** (110 mg) was deacetylated with methanolic ammonia as described for the synthesis of **2** from **11a**. Compound **13** (42 mg) was obtained as needles after recrystallization from methanol: mp 160–163°, $[\alpha]^{27}D$ +19° (*c* 1.0, $H_2O$).

*Anal.* Calcd for $C_9H_{13}N_3O_4$: C, 47.57; H, 5.77; N, 18.49. Found: C, 47.43; H, 5.66; N, 18.20.

**5-*O*-Acetyl-3-deoxy-1,2-di-*O*-isopropylidene-β-L-*threo*-pentose (7).**—Compound **6**[5] (5 g) was acetylated in pyridine (20 ml) with acetic anhydride (5 ml) overnight. The crude acetyl derivative **7** (5 g) was obtained as a syrup which was chromatographically homogeneous and sufficiently pure for the next step.

**Tri-*O*-acetyl-3-deoxy-β-L-*threo*-pentofuranose (9).**—To a cooled and stirred solution of **7** (5 g) in acetic acid (20 ml) and acetic anhydride (10 ml) was added sulfuric acid (1 ml). The mixture was kept overnight at room temperature, then partitioned between dichloromethane (100 ml) and ice–water (100 ml). The organic layer was washed with a saturated solution of sodium bicarbonate (2 × 100 ml), water, dried over sodium sulfate, and evaporated to dryness. The residue was coevaporated several times with toluene to remove traces of acetic acid. This syrup was contaminated with a small amount of the α anomer: nmr ($CDCl_3$, TMS internal standard) β-H-1 δ 6.18 (singlet), α-H-1 6.80 (doublet, $J_{1,2}$ = 3.5 Hz). No anomeric signal corresponding to the pyranose isomers was detected by nmr.

**1-(2,5-Di-*O*-acetyl-3-deoxy-α-L-*threo*-pentofuranosyl)cytosine (12b).**—The anomeric mixture of **9** was condensed with bis(trimethylsilyl)-$N^4$-acetylcytosine[8] (prepared from 5 g of $N^4$-acetylcytosine) in 1,2-dichloroethane (250 ml) in the presence of stannic chloride (8 ml). Compound **12b** (2.2 g) was obtained after two recrystallizations from methanol: mp 179–181°, $[\alpha]^{27}D$ +43° (*c* 1, $CHCl_3$). A mixture melting point of this sample with **12b** prepared as described previously in this paper was undepressed. Ir and nmr spectra of both samples were identical.

**Registry No.**—**2**, 39007-97-1; **7**, 41107-64-6; **8**, 41107-43-1; **9**, 41107-68-0; **10**, 41164-55-0; **11b**, 41164-56-1; **12b**, 41164-57-2; **13**, 41164-58-3.

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## Conversion of 1,2-*O*-Isopropylidene-α-D-xylofuranose into 3-*O*-Benzoyl-5-bromo- and -5-iodo-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose *via* a Cyclic *N,N*-Dimethylbenzamide Acetal Derivative

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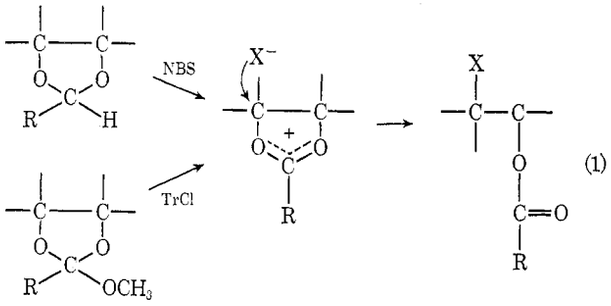
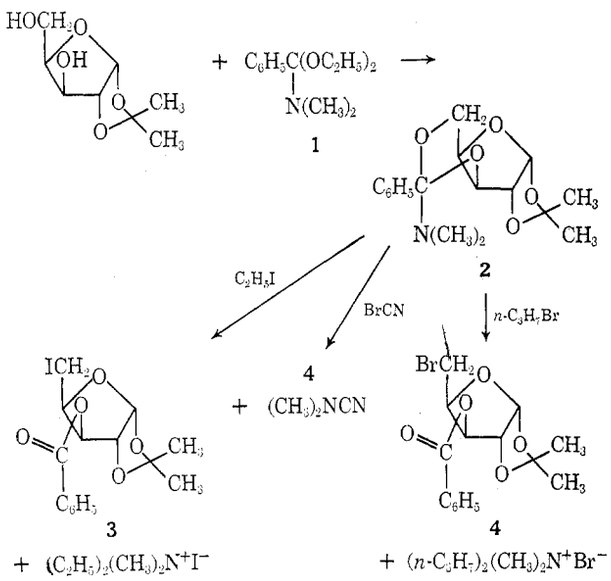
We wish to report a new method for converting glycols into esters of halohydrins under very mild conditions requiring no acid or base catalyst. Previously, cyclic benzylidene acetals of carbohydrates have been opened with *N*-bromosuccinimide to form bromodeoxy benzoate derivatives.[1] For example, methyl 4,6-*O*-benzylidene-α-D-glucopyranoside was converted into methyl 4-*O*-benzoyl-6-bromo-6-deoxy-α-D-glucopyranoside. Recently, it has been reported that acetates of simple aliphatic chlorohydrins are readily prepared by the reaction of cyclic ortho esters with trityl chloride.[2] Both of these reactions are regioselective and stereospecific and it has been proposed that they proceed by a nucleophilic attack by halide ion on an acyloxonium ion intermediate (eq 1).




The dimethyl acetal of *N,N*-dimethylbenzamide is reported to react with methyl β-D-ribofuranoside to give a 2,3-cyclic amide acetal derivative.[3] We have found that 1,2-*O*-isopropylidene-α-D-xylofuranose reacts on standing with a dichloromethane solution of *N,N*-dimethylbenzamide diethyl acetal **1** to give 3,5-*O*-[α-(dimethylamino)benzylidene]-1,2-*O*-isopropylidene-α-D-xylofuranose (**2**). The compound, isolated by distillation, slowly crystallized after standing a few weeks at room temperature and was recrystallized from pentane, mp 74–75.5°. Gas chromatography showed only one peak, but the nmr spectrum indicated the presence of two compounds. Three singlets for the *C*-methyls (δ 1.33, 1.43, and 1.50), two singlets for *N*-methyl (2.07 and 2.27, ratio of 6:1), and two doublets for the C-1 hydrogen (5.97 and 6.07) suggested two isomers differing only in the chirality of the benzyl carbon atom.

When **2** was refluxed with methyl or ethyl iodide a quaternary ammonium iodide salt precipitated. Evaporation of the filtrate gave a colorless syrup (**3**): $C_{15}H_{17}IO_5$. The ir spectrum (liquid film) showed absorption at 1727 $cm^{-1}$, indicative of a benzoate ester. The nmr spectrum was compatible with 3-*O*-benzoyl-5-deoxy-5-iodo-1,2-*O*-isopropylidene-α-D-xylofuranose. A two-proton doublet appeared at δ 3.33 ($J_{4,5}$ = 7 Hz) upfield from a one-proton doublet at 5.58 ($J_{3,4}$ = 3 Hz, $J_{2,3}$ = 0); consequently the iodine substitution was assigned

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to the C-5 methylene while the more electronegative benzoate ester was placed at C-3.

The preparation of 3-*O*-benzoyl-5-bromo-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose (**4**) was carried out by refluxing **2** either in *n*-propyl bromide solution or in a chloroform solution containing cyanogen bromide. In this case the two-proton doublet for the C-5 hydrogens appeared at δ 3.55 ($J_{4,5}$ = 7 Hz) with the C-3 one-proton doublet at 5.58 ($J_{3,4}$ = 3 Hz, $J_{2,3}$ = 0). The reaction with cyanogen bromide appears to be a special case of the von Braun reaction[4] whereby bromide ion attacks the C-5 position either simultaneously or after elimination of dimethylcyanamide.

Cyclic α-(dimethylamino)benzylidene acetals are useful intermediates for functionalizing glycols under very mild conditions. It would appear that the reaction could be carried out with any reagent which would cause elimination of the dimethylamino moiety and supply a suitable nucleophile to open the resulting acyloxonium ion intermediate.

### Experimental Section

Melting points were taken on a Fisher-Johns apparatus. Ir spectra were measured on a Beckman IR-9 spectrometer. Nmr spectra were measured on a Varian Associates A-60 instrument with tetramethylsilane as the internal standard. Optical rotations were measured on a Perkin-Elmer 141 polarimeter. Gas chromatography was performed with an F & M 810 chromatograph equipped with a 4 ft × 0.25 in. glass column containing 100–120 mesh 3% OV-17 Gas-Chrom Q and programmed for 150–300° at 10°/min and 25 ml/min. Tlc was carried out on silica gel Quanta/Gram plates obtained from Quantum Industries. Silica gel for column chromatography was 70–325 mesh from EM Reagents, distributed by Brinkman Instruments.

**3,5-*O*-[α-(Dimethylamino)benzylidene]-1,2-*O*-isopropylidene-α-D-xylofuranose (2).**—A solution of 5.00 g of 1,2-*O*-isopropylidene-α-D-xylofuranose[5] and *N*,*N*-dimethylbenzamide diethyl acetal[6] in 25 ml of $CH_2Cl_2$ was allowed to stand overnight at room temperature. After evaporation of the solvent the residual oil was distilled at reduced pressure to yield 7.12 g (84%) of a thick syrup: bp 143–145° (0.1 mm); $[\alpha]^{25}D$ +25.4° (*c* 1.01, $CHCl_3$); nmr ($CDCl_3$) δ 1.33 (3 H, s, $CHCH_3$), 1.43 and 1.50 (3 H combined, s, s, partially resolved, ratio of ~1:5, respectively, *C*-$CH_3$), 2.08 and 2.27 (6 H combined, s, s, resolved, ratio of 6:1, *N*-$CH_3$), 3.80–4.75 (5 H, m, H-2, -3, -4, and -5), 5.97 and 6.07 (1 H combined, d, d, H-1), 7.4 (5 H, m, $C_6H_5$). The product crystallized after standing for several weeks at room temperature and was recrystallized from pentane: mp 74–75.5°; $[\alpha]^{25}D$ +30.6° (*c* 1.04, $CHCl_3$). The nmr was the same as for the distilled product. Gas chromatography showed only one peak at 8.5-min retention time.

*Anal.* Calcd for $C_{17}H_{23}NO_5$: C, 63.54; H, 7.21; N, 4.36. Found: C, 63.58; H, 7.12; N, 4.42.

**3-*O*-Benzoyl-5-deoxy-5-iodo-1,2-*O*-isopropylidene-α-D-xylofuranose (3).**—A solution of 0.62 g of 3,5-*O*-[α-(dimethylamino)-benzylidene]-1,2-*O*-isopropylidene-α-D-xylofuranose (**2**) in 15 ml ethyl iodide was refluxed for 5 hr. Filtration afforded a white solid which was very water soluble and precipitated AgI on addition of $AgNO_3$ solution. Tlc ($CHCl_3$) of the filtrate showed two spots,[7] $R_f$ 0.8 (major) and 0.1 (minor). Evaporation to a syrup and chromatography on a column of 15 g of silica gel with $CHCl_3$ gave 0.67 g (82%) of a colorless syrup (only $R_f$ 0.8 spot by tlc): $[\alpha]^{25}D$ −50.8° (*c* 1.02, $CHCl_3$); ir (liquid film) 1727 $cm^{-1}$; nmr ($CDCl_3$) δ 1.33 (3 H, s, *C*-$CH_3$), 1.56 (3 H, s, *C*-$CH_3$), 3.33 (2 H, d, $J_{4,5}$ = 7 Hz, $CH_2I$), 4.68 (sextet, $J_{3,4}$ = 3 Hz, $J_{4,5}$ = 7 Hz, H-4), 4.70 (d, overlaid on the H-4 signal, $J_{1,2}$ = 4 Hz, $J_{2,3}$ = 0, H-2; 2 H for H-2 plus H-4), 5.58 (1 H, d, $J_{3,4}$ = 3 Hz, $CHOCOC_6H_5$), 6.03 (1 H, d, $J_{1,2}$ = 4 Hz, H-1), 7.35–8.15 (5 H, m, $CO_2C_6H_5$).

*Anal.* Calcd for $C_{15}H_{17}IO_5$: C, 44.57; H, 4.24; I, 31.39. Found: C, 44.48; H, 4.29; I, 31.60.

**3-*O*-Benzoyl-5-bromo-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose (4). Method A.**—A solution of 0.50 g of **2** and 0.30 g of cyanogen bromide in 15 ml of $CHCl_3$ was refluxed for 17 hr. Tlc ($CHCl_3$) showed a major spot at $R_f$ 0.6 and two minor spots at 0.1 and 0.5.[7] The major spot also moved at $R_f$ 0.3 with toluene. After concentrating the mixture to a syrup it was chromatographed on a column of 10 g of silica gel with toluene. Combining fractions with only the major spot and evaporating gave 0.30 g of a syrup: $[\alpha]^{25}D$ −46.6° (*c* 1.00, $CHCl_3$); ir (liquid film) 1734 $cm^{-1}$; nmr ($CDCl_3$) δ 1.32 (3 H, s, *C*-$CH_3$), 1.55 (3 H, s, *C*-$CH_3$), 3.55 (2 H, d, $J_{4,5}$ = 7 Hz, $CH_2Br$), 4.68 (d, $J_{1,2}$ = 4 Hz, $J_{2,3}$ = 0, H-2; superposed sextet, $J_{3,4}$ = 3 Hz, $J_{4,5}$ = 7 Hz, H-4; total of 2 H), 5.58 (1 H, d, $J_{3,4}$ = 3 Hz, $CHOCOC_6H_5$), 6.03 (1 H, d, $J_{1,2}$ = 4 Hz, H-1), 7.3–8.2 (5 H, m, $C_6H_5$).

*Anal.* Calcd for $C_{15}H_{17}BrO_5$: C, 50.44; H, 4.80; Br, 22.37. Found: C, 50.54; H, 4.83; Br, 22.28.

**Method B.**—A solution of **2** in 5 ml of *n*-propyl bromide was refluxed overnight and filtered from the insoluble dimethyldi-*n*-propylammonium bromide. Gas chromatography showed only one peak with a retention time of 9.8 min, the same as for the product from method A.

**Registry No.**—**1**, 19429-87-9; **2**, 41164-23-2; **3**, 41164-24-3; **4**, 41164-25-4; 1,2-*O*-isopropylidene-α-D-xylofuranose, 20031-21-4.

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(7) Plates were sprayed with a solution prepared from 5 g of ammonium molybdate, 5 ml of concentrated $H_2SO_4$, and 5 ml of 86% $H_3PO_4$ in 100 ml of water and heated at 120°. Gray spots turned blue on standing at room temperature: S. Hanessian and N. R. Plessas, *J. Org. Chem.*, **34**, 2163 (1969).

## γ Substitution of Allyl Ylides in the Wittig Reaction

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There are several reports in the literature describing electrophilic capture of phosphonate- or phosphonamide-stabilized allylic anions by ketones or aldehydes at both the α and γ carbons.[3] Also, allylidenetriphenylphosphorane reacts at the α and γ carbons with ethyl chloroformate, and cinnamyltriphenylphosphonium salt undergoes deuterium exchange in basic solution at both allylic positions.[4] A further example of γ substitution has been reported by Buchi and Wuest in the course of attempted Wittig reaction of allylidenetriphenylphosphorane and an enone,[5] but this appears to be a special case since 1,4 addition to the enone occurs as well. To our knowledge, there is no previously reported instance of γ substitution in a typical Wittig reaction.

We have found that allyltriphenylphosphonium fluoroborate reacts with benzaldehyde and diazabicycloundecene (DBU) in refluxing tetrahydrofuran to form a dienol **1** (26%) in addition to the expected Wittig product 1-phenylbutadiene. The structure of **1** is proved by the nmr spectrum [δ 7.2–7.5 (10 H),

(1) Alfred P. Sloan Fellow, 1971–1973.

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