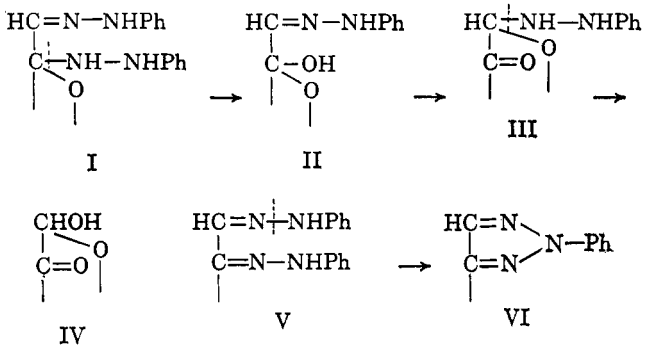
formation of *N*-nitroso compounds on the β-hydrazino nitrogen followed by hydrolytic splitting of the C–N bond. In the case of acetylated osazones which have only hydrazone groups, nitrous acid would be expected to attack the α-nitrogen of the phenylhydrazone residue and cause the hydrolytic scission of the N–N bond and closure of the triazole ring.



The high yields of osotriazole obtained with osazone acetates render this reaction of value for preparative purpose.

Experimental[4]

D-*lyxo*-**Hexose Phenylosotriazole Tetraacetate.**—A suspension of D-*lyxo*-hexose phenylosazone tetraacetate[2] (5.3 g.) in a mixture of ethanol (40 ml.), water (20 ml.), and concentrated hydrochloric acid (2.4 ml.) was treated, with stirring, at 50–55° with a solution of sodium nitrite (1.4 g.) in water (10 ml.) during the course of 30 min. The now clear reddish brown solution was treated with 1.5 g. of sodium acetate trihydrate in water (50 ml.) and extracted with chloroform. The chloroform layer which contained the osotriazole tetraacetate was washed successively with dilute hydrochloric acid, aqueous sodium hydrogen carbonate, and water. The residue obtained after solvent removal from the dried extract crystallized from methanol–ether in needles, m.p. 106° undepressed with authentic D-*lyxo*-hexose phenylosotriazole tetraacetate,[5] yield 3.5 g.

Anal. Calcd. for $C_{20}H_{23}N_3O_8$: C, 55.42; H, 5.35; N, 9.70; CH_3CO, 39.73. Found: C, 55.27; H, 5.00; N, 9.54; CH_3CO, 39.57.

Deacetylation.—The acetate (3 g.) in methanol (50 ml.) was treated with concentrated aqueous ammonia (20 ml.) and the mixture kept overnight at room temperature. On evaporation and distillation of the residue under reduced pressure at 190–200° (0.05 mm.), D-*lyxo*-hexose phenylosotriazole was obtained in needles, m.p. 111–112° undepressed on admixture with an authentic specimen.[5] Both products had identical infrared spectra.

Anal. Calcd. for $C_{12}H_{15}N_3O_4$: C, 54.33; H, 5.70; N, 15.84. Found: C, 54.20; H, 5.94; N, 15.94.

D-*arabino*-**Hexose Phenylosotriazole.**—D-*arabino*-Hexose phenylosazone tetraacetate[6] (5.3 g.) was treated with nitrous acid in exactly the same manner as the D-*lyxo*-hexose derivative and the residue, after evaporation of the chloroform, was subjected directly to deacetylation with ammonia in aqueous methanol. D-*arabino*-Hexose phenylosotriazole was obtained by evaporation and crystallization from water or ethanol in needles, m.p. 196° undepressed on admixture with an authentic specimen,[7] yield 2 g. Both products had identical infrared spectra.

Anal. Found: C, 54.29: H, 5.79; N, 15.96.

L-*xylo*-**Hexose Phenylosotriazole.**—Amorphous L-*xylo*-hexose phenylosazone tetraacetate (about 5 g.), obtained by the action of acetic anhydride and pyridine on the osazone and carefully washed with water, was treated in exactly the same manner as the D-*arabino*-hexose derivative, yielding finally L-*xylo*-hexose phenylosotriazole. This crystallized from water in needles, m.p. 159° undepressed on admixture with an authentic specimen,[5] yield 2 g. Both products gave identical infrared spectra.

Anal. Found: C, 54.82; H, 6.03; N, 16.02.

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(4) Microanalyses were by W. N. Rond, The Ohio State University; infrared spectra were measured with a Perkin-Elmer Infracord spectrophotometer.

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Benzoylation of Sugar Phenylhydrazones

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Acyclic sugar hydrazones when acetylated with pyridine and acetic anhydride yield *O*-acetylated derivatives[2] which can be converted to tetraacetoxy-1-phenylazo-1-hexene.[3] The more drastic reaction with boiling acetic anhydride[4] yields derivatives having acetyl groups attached to the nitrogen as well as to the oxygen which no longer undergoes this conversion. To study the behavior of sugar hydrazones toward benzoylation, the phenyl hydrazones of D-mannose, D-arabinose, and L-rhamnose were treated with benzoyl chloride in pyridine, and the structure of their crystalline benzoates investigated. D-Mannose phenylhydrazone yielded a hexabenzoate (I) which showed in the infrared spectrum a C=N band at 1610, an ester band at 1725, and an amide band at 1660 cm.$^{-1}$, denoting the presence of *O*- and *N*-benzoyl groups in an acyclic hydrazone. This was confirmed by trans-hydrazonation; the hexabenzoate was treated with *p*-nitrophenylhydrazine, which replaced the *N*-benzoyl phenylazo residue yielding a *p*-nitrophenylhydrazone pentabenzoate (II). This showed the C=N band at 1605 and the ester band at 1730 but not the amide absorption at 1660 cm.$^{-1}$, denoting that all five benzoyl groups were linked to oxygen. The presence of five *O*-benzoyl groups on a hexose aryl hydrazone excludes the possibility of cyclic structures, which would have yielded a benzoate having fewer *O*-benzoyl groups. Accordingly the hexabenzoate (I) was formulated as *N*-benzoylpenta-*O*-benzoyl-*aldehydo*-D-mannose phenylhydrazone (I), and the transhydrazonation product as penta-*O*-benzoyl-*aldehydo*-D-mannose *p*-nitrophenylhydrazone (II). Similarly, D-arabinose and L-rhamnose phenylhydrazones yielded pentabenzoates which showed the C=N bands at 1605 and 1610, the ester bands at 1725 and 1730, and the amide bands at 1670 and 1680 cm.$^{-1}$, respectively, denoting that, like the mannose

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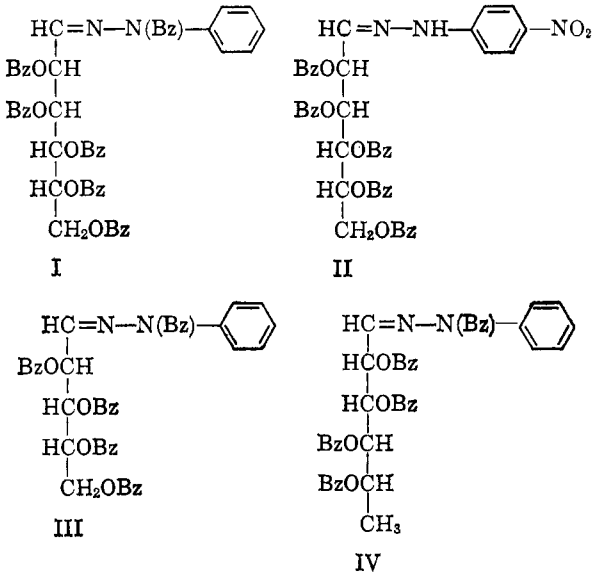
derivative, they were acyclic and possessed both *O*- and *N*-benzoyl groups. They were therefore designated *N*-benzoyltetra-*O*-benzoyl-*aldehydo*-D-arabinose phenylhydrazone (III) and *N*-benzoyltetra-*O*-benzoyl-*aldehydo*-L-rhamnose phenylhydrazone (IV), respectively. It seems that benzoyl chloride in pyridine,



being a more vigorous reagent than acetic anhydride in pyridine, leads in the case of acyclic sugar hydrazones to the acylation of the OH and NH groups and not merely the former ones. The *N*-benzoylated derivatives produced like the *N*-acetylated ones studied earlier[3] do not give azoethylene compounds on boiling with ethanolic pyridine.

Experimental[5]

N-Benzoylpenta-*O*-benzoyl-*aldehydo*-D-mannose Phenylhydrazone (I).—D-Mannose phenylhydrazone[6] (10 g.) was suspended in pyridine (70 ml.) and treated with benzoyl chloride (40 ml.). The reaction mixture warmed up spontaneously, darkened, and after 2 hr. returned to room temperature. It was left overnight, then poured onto crushed ice (1 kg.). The viscous residue that separated was washed repeatedly with water, then with aqueous sodium hydrogen carbonate to remove benzoic acid. After 2 days the *N*-benzoylpenta-*O*-benzoyl-*aldehydo*-D-mannose phenylhydrazone solidified and crystallized from ethanol as needles, yield 30 g. (91%), $[\alpha]^{20}D$ 62.5° (*c*, 1, chloroform), m.p. 169°; λ_{max}^{KBr} 1610 (C=N), 1660 (NBz), 1725 (OBz) cm.$^{-1}$; X-ray powder diffraction pattern[7]: 13.50 s, 12.11 w, 9.80 m, 8.00 vw, 6.86 w, 6.11 w, 5.54 m, 5.12 w, 4.82 s, 4.75 s, 4.08 s, 3.65 m, 3.59 m, 3.43 w, 3.11 m, 2.93 w.

Anal. Calcd. for $C_{54}H_{42}N_2O_{11}$: C, 72.47; H, 4.73; N, 3.13. Found: C, 72.35; H, 4.90; N, 3.18.

Penta-*O*-benzoyl-*aldehydo*-D-mannose *p*-Nitrophenylhydrazone (II).—*N*-Benzoylpenta-*O*-benzoyl-*aldehydo*-D-mannose phenylhydrazone (1 g.) was refluxed for 3 hr. with a solution of *p*-nitrophenylhydrazine (0.4 g.) in ethanol (50 ml.). The mixture was concentrated to 20 ml., whereupon some unchanged hydrazone separated and was filtered. The penta-*O*-benzoyl-*aldehydo*-D-mannose *p*-nitrophenylhydrazone subsequently crystallized from ethanol as yellow needles, yield 0.4 g. (48%), m.p. 105°; λ_{max}^{KBr} 1605 (C=N), 1730 (OBz) cm.$^{-1}$.

Anal. Calcd. for $C_{47}H_{37}N_3O_{12}$: C, 67.54; H, 4.46; N, 5.03. Found: C, 67.56; H, 4.59; N, 5.29.

N-Benzoyltetra-*O*-benzoyl-*aldehydo*-D-arabinose Phenylhydrazone (III).—D-Arabinose phenylhydrazone[8] (10 g.) was treated with pyridine (70 ml.) followed by benzoyl chloride (40 ml.), left to stand overnight at room temperature, then poured onto crushed ice (1 kg.). The viscous residue that separated was washed repeatedly with water, and crystallized by the addition of a few drops of ethanol. The *N*-benzoyltetra-*O*-benzoyl-*aldehydo*-D-arabinose phenylhydrazone was recrystallized from a mixture of ethanol and acetone as needles, yield 30 g. (95%), $[\alpha]^{20}D$ 52.5° (*c* 1, chloroform), m.p. 134°; ν_{max}^{KBr} 1605 (C=N), 1670 (NBz), 1725 (OBz) cm.$^{-1}$; X-ray powder diffraction pattern: 11.79 vs. 9.10 m, 8.67 vw, 7.90 m, 6.92 vw, 6.24 w, 5.80 w, 5.15 s, 5.07 s, 4.79 w, 4.55 vs, 4.13 m, 3.76 m, 3.49 m.

Anal. Calcd. for $C_{46}H_{36}N_2O_9$: C, 72.61; H, 4.77; N, 3.68. Found: C, 72.42; H, 4.64; N, 3.82.

N-Benzoyltetra-*O*-benzoyl-*aldehydo*-L-rhamnose Phenylhydrazone (IV).—L-Rhamnose phenylhydrazone[9] (10 g.) was benzoylated by the procedure used for the arabinose derivative and the product was purified by repeatedly dissolving it in ethanol and precipitating with water. After four such precipitations *N*-benzoyl tetra-*O*-benzoyl-*aldehydo*-L-rhamnose phenylhydrazone was dried in a vacuum desiccator, yield 25 g. (86%), $[\alpha]^{20}D$ 31.6° (*c* 1.3, chloroform), m.p. 95°; λ_{max}^{KBr} 1610 (C=N), 1680 (NBz), 1730 (OBz) cm.$^{-1}$.

Anal. Calcd. for $C_{47}H_{38}N_2O_9$: C, 72.85; H, 4.95; N, 3.62. Found: C, 72.14; H, 5.21; N, 3.36.

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(5) Melting points are corrected; infrared spectra were measured with a Perkin-Elmer Infracord spectrophotometer. Microanalyses were by W. N. Rond, The Ohio State University.

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5-Deoxy-D-glucose (5-Deoxy-D-*xylo*-hexose)[1]

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Deoxy sugars and their derivatives have been evaluated in biological systems as potent glycolytic inhibitors of various tumor tissues,[2-4] as intermediates for the preparation of antimetabolites, and as potential anticancer agents.[5]

This paper describes a convenient method for the preparation of 5-deoxy-D-*xylo*-hexose. The yield from D-glucose is 25%.

3-*O*-Acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose[6] (I), prepared from 3-*O*-acetyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose, is the starting compound. It is tritylated and tosylated in one operation to produce 3-*O*-acetyl-1,2-*O*-isopropylidene-5-*O*-*p*-tolyl-

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