tetrachloride solution of bromine slowly, and reduced alcoholic silver nitrate rapidly as evidenced by the formation of a silver mirror.

CONTRIBUTION NO. 467 FROM THE CENTRAL RESEARCH DEPARTMENT
EXPERIMENTAL STATION
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1,5-Anhydro-β-D-ribofuranose from Phenyl β-D-Ribofuranoside

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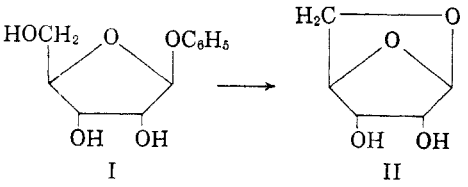
While the action of strong alkali on aryl glycopyranosides represents a familiar procedure for the synthesis of 1,5-anhydroglycopyranoses[2] and other analogous substances containing this ring system, similar treatment of aryl glycofuranosides has not, to our knowledge, been reported to yield 1,5-anhydroglycofuranoses. In a recent paper,[3] indeed, we stated that an attempt to synthesize 1,5-anhydro-β-D-ribofuranose (II, 1,4-anhydro-α-D-ribopyranose) from phenyl β-D-ribofuranoside (I) had



I II

failed to yield a crystalline product. Subsequent work has now shown, however, that I is converted to II (albeit in low yield) through the action of sodium isopropoxide in 2-propanol.

EXPERIMENTAL[4]

Phenyl β-D-ribofuranoside (158 mg.), prepared as described earlier,[3] was dissolved in 10 ml. of 2-propanol and the solution treated with 6 ml. of 2-propanol in which 32.5 mg. of sodium had been dissolved. The reaction mixture was boiled under reflux for 90 hr., cooled, diluted with a few drops of water and neutralized with carbon dioxide. Solvent was removed *in vacuo* and the residue extracted with acetone. Toluene was added to the extract and the solution concentrated *in vacuo* to a sirup which was freed of the remaining phenol by repeated extraction with benzene. Attempts to crystallize the residue failed and it was therefore benzoylated in the usual fashion to yield a sirup which was partially purified by precipitation from benzene with pentane and then from ethanol with water. On standing for several months at −8° in aqueous ethanol a small deposit of crystalline material was obtained. Recrystallized from methanol this product (*ca.* 15 mg., 6%) showed a double melting point: 132–133° and 146–147°. We reported earlier[3] that 1,5-anhydro-2,3-di-*O*-benzoyl-β-D-ribofuranose melts at 132–133°. Reexamination of the authentic material now reveals that it too shows the double melting point just quoted; a mixture of samples of the compound from the two sources shows the same two melting points. Upon appropriate seeding, either the form with the double melting point or one with the higher melting point only could be obtained from solution.

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(3) E. Vis and H. G. Fletcher, Jr., *J. Am. Chem. Soc.*, **79**, **1182** (1957).

(4) Melting points are corrected.

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Reciprocal Resolution of DL-Tryptophan and DL-α-Phenylethylamine

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Our interests in producing large quantities of L-tryptophan from the DL-form by economically feasible methods prompted a study of known methods and a search for new methods of resolution. The availability of *N*-acetyl-DL-tryptophan as an intermediate in commercial synthesis and the ease of racemization of the undesired D-form[1] indicated that this would be the desirable starting compound. Published methods[1–6] for resolving *N*-acetyl-DL-tryptophan suffer from one or more of the usual disadvantages of resolutions; such as, low yields, time consuming and tedious crystallizations, expensive resolving agents, or handling of large volumes. The method of du Vigneaud and Sealock[1] appeared to offer possibilities for attainment of maximum antipodal purity and for large scale use. The main disadvantage was the scarcity of the desired active form of α-phenylethylamine. DL-α-Phenylethylamine is readily available. If one were able to resolve this with the active forms of acetyltryptophan it would be possible to build up large supplies of optically active acid and base by repetition of the reciprocal resolution.

When one mole of *N*-acetyl-DL-tryptophan was combined with 0.5 mole of (−)- α-phenylethylamine and 0.5 mole of potassium hydroxide in ethanol the sparingly soluble diastereoisomeric salt [LA(−)B]

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