D-Ribose Hydrazone

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For comparison of its properties with those of D-ribosylamine,[2] the title compound was synthesized by condensation of D-ribose with hydrazine. Although innumerable *substituted* hydrazones of sugars (and of reducing, substituted sugars) have been described in the literature, this appears to be the first *unsubstituted* hydrazone of a sugar that has been prepared.

In order to minimize possible formation of 1,2-di-D-ribosylhydrazine or of the azine, the following conditions were used: A ten-fold excess of hydrazine was employed, the reaction solution was quite concentrated, and the condensation was conducted at room temperature.

Experimental

D-Ribose Hydrazone.—Anhydrous hydrazine (16 g.) was weighed into a 50-ml. Erlenmeyer flask and 16 ml. of absolute methanol was added; heat was evolved, and so the solution was cooled in ice–salt. Dry, finely powered D-ribose (7.5 g.) was now added and the flask was quickly stoppered. On swirling, part of the D-ribose dissolved and a new kind of colorless crystals rapidly formed. After the mixture had stood at room temperature for 24 hr., with occasional swirling, all of the crystals had dissolved to a clear, colorless solution. This was transferred to an evaporating dish and evaporated in a vacuum desiccator, over phosphorus pentoxide and soda lime, to a thick, viscous, colorless sirup which was dried at 0.1 mm. (Desiguard). The sirup was redissolved by stirring it with 10 ml. of absolute methanol; addition of 10 ml. of absolute ethanol now gave a white, gummy precipitate. The solution was decanted, and the precipitate was stirred with 20 ml. of absolute methanol, affording a suspension of colorless crystals which was filtered with suction (rubber dam); the crystals were washed with 10 ml. of absolute methanol and dried at 0.1 mm.; wt., 5.4 g.; m.p. 127–129°. The infrared absorption spectrum was recorded; it showed a band at 1613 cm.$^{-1}$, possibly indicative of C=N absorption. (The combined mother liquors were evaporated to dryness and the resulting crystalline mass, on stirring with 10 ml. of absolute methanol, gave a crop (1.9 g.) of less pure crystals, m.p. 115–117°.)

Anal. Calcd. for $C_5H_{12}N_2O_4$: C, 36.58; H, 7.37; N, 17.07. Found: C, 36.63; H, 7.64; N, 16.89.

The compound is practically insoluble in all organic solvents tested, except boiling acetic acid. It is sparingly soluble in water (<1 g. per 100 ml.); the saturated, aqueous solution had α^{25}_D −0.13° (l = 2 dm.), and its ultraviolet absorption spectrum was recorded. A band at *ca.* 280 mμ suggested the presence of the open-chain, *aldehydo* form, rather than of a cyclic D-ribosylhydrazine.

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[2] R. S. Tipson, *J. Org. Chem.*, **26**, 2462 (1961).

The Synthesis of *trans*-3-Oxa-4-oxo- and *trans*-4-Oxa-3-oxobicyclo[5.4.0]undecanes

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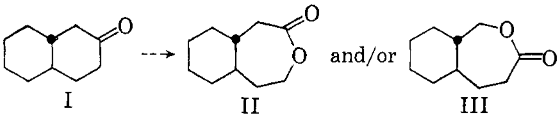
Notable by its absence in the work performed to date on the Baeyer–Villiger reaction[2] is a study of the more subtle differences prevailing in positions other than those alpha to the carbonyl function. In an attempt to study the requirements of the migrating group and yet avoid primary steric effects,[3] we were prompted to consider the Baeyer-Villiger oxidation of *trans*-β-decalone (I). The molecule could further serve as a model for rearrangements in steroids possessing an A/B *trans*-ring fusion.



I II III

Of the various approaches to the problem available to us, we chose first to prepare and characterize authentic samples of the lactones II and III. A knowledge of the physical properties of these substances might subsequently allow a method of composition analysis to be applied directly to the *trans*-β-decalone oxidation mixtures. The purpose of this paper is to report the unequivocal synthesis of *trans*-4-oxa-3-oxobicyclo[5.4.0]undecane (II) and *trans*-3-oxa-4-oxobicyclo[5.4.0]undecane (III).

Reaction of *trans*-β-(2-carboxycyclohexane) propionic acid (IV)[4,5] with diazomethane gave methyl *trans*-β-(2-carbomethoxycyclohexane)propionate (Va) which was selectively saponified with one equivalent of sodium hydroxide in refluxing aqueous methanol to produce *trans*-β-(2-carbomethoxycyclohexane)propionic acid (Vb). Near theoretical quantities of VI were obtained by reduction of Vb with sodium–ethanol–liquid ammonia.[6] Distillation of this hydroxy acid readily furnished *trans*-3-oxa-4-oxobicyclo[5.4.0]undecane (III).

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[2] For a recent review of this reaction see C. H. Hassall, *Org. Reactions*, IX, 73 (1957).

[3] The present status of knowledge on primary steric effects is discussed in R. R. Sauers and J. P. Ahearn, *J. Am. Chem. Soc.*, **83**, 2759 (1961) and references cited therein.

[4] G. A. Page and D. S. Tarbell, *Org. Synthesis*, **34**, 8 (1954).

[5] C. D. Gutsche and H. H. Peter, *J. Am. Chem. Soc.*, **77**, 5971 (1955).

[6] The new selective reduction method described herein is far superior to the Bouveault-Blanc procedure[7,8] presumably because the temperature of the reaction, when performed in this medium, is sufficiently low to allow the reduction to proceed rapidly without the problem of concomitant ester hydrolysis.

[7] P. Chuit and J. Hausser, *Helv. Chim. Acta*, **12**, 463 (1929).

[8] D. C. Sayles and E. F. Degering, *J. Am. Chem. Soc.*, **71**, 3161 (1949).