Nitrogen-containing Carbohydrate Derivatives. Part XVI.† Re-investigation of the 'Mutarotation' of 3,4,5,6-Tetra-*O*-benzoyl-D-glucose Phenylhydrazone

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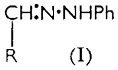
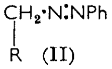
The so-called 'mutarotation' of the title compound, previously assigned to phenylhydrazone–phenylazo-tautomerism, has been shown to be due to formation of a phenylazo-hydroperoxide.

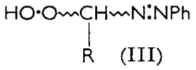
FOLLOWING a suggestion in the literature[1] that the mutarotation of aldose phenylhydrazones might be due to tautomerism to the phenylazo-isomer (rather than an acyclic–cyclic equilibrium[2]), Micheel and Dijong[3] investigated 3,4,5,6-tetra-*O*-benzoyl-D-glucose phenylhydrazone (I). After mutarotation of compound (I), they obtained a yellow product, to which on the basis of ultraviolet spectral data [$\lambda_{max.}$ (dioxan) 410 mμ, $\varepsilon_{max.}$ 132] they assigned the phenylazo-structure (II). However, they were unable to obtain satisfactory elemental analysis results because of the presence of an 'oxygen-rich impurity.'


$\underset{R}{\mathrm{CH{:}N{\cdot}NHPh}}$

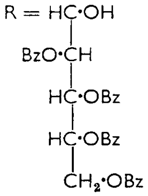
(I)


$\underset{R}{\mathrm{CH_2{\cdot}N{:}NPh}}$

(II)


$\mathrm{HO{\cdot}O{\sim}\underset{R}{CH}{\sim}N{:}NPh}$

(III)


$\mathrm{R = HC{\cdot}OH{-}BzO{\cdot}CH{-}HC{\cdot}OBz{-}HC{\cdot}OBz{-}CH_2{\cdot}OBz}$

Later work on the possibility of phenylazo-phenylhydrazone interconversion,[4-7] showed that the original prediction[1] was most probably incorrect and that by analogy with simple phenylhydrazones[4-6] the most likely explanation of Micheel and Dijong's findings[3] was that a phenylazo-hydroperoxide (III) had been formed. (Phenylazo-hydroperoxides have very similar ultraviolet spectra to the parent phenylazo-derivative.[6b]) We therefore repeated their work.

Exposure of a dioxan solution of the phenylhydrazone (I) to air gave a yellow solution, from which light petroleum precipitated an unstable yellow solid, having properties similar to those recorded by Micheel and Dijong[3] for their product. No colour change took place when a solution of the phenylhydrazone (I) was stirred under nitrogen (cf. refs. 5 and 6*b*). The yellow substance (III) reacted immediately with acidified potassium iodide solution, a characteristic reaction of phenylazo-hydroperoxides.

The n.m.r. spectrum of the product (III) showed two peaks, together integrating for one proton, at τ —0·7, a position characteristic of the hydroperoxy-proton in phenylazo-hydroperoxides;[6b] the presence of two peaks is presumably due to a mixture of 1-epimers.

The apparent[3] tautomerism of the yellow product back to the phenylhydrazone (I) is due to the tendency of the peroxide (III) to spontaneously decompose in solution to nearly colourless products, particularly in the case[3] of material prepared from unrecrystallised phenylhydrazone; the visible spectrum of a mutarotated specimen showed that the peak at 410 mμ had been replaced by broad absorption.

EXPERIMENTAL

3,4,5,6-Tetra-*O*-benzoyl-D-glucose was prepared according to Brigl and his co-workers;[8] it could be conveniently recrystallised from dioxan. The phenylhydrazone was prepared as described by Micheel and Dijong;[3] it was recrystallised from acetone–light petroleum, minimising contact with air, to yield colourless needles, m. p. 133° (decomp., rapid heating) [lit.,[3] 126—128° (decomp.)].

The phenylhydrazone (340 mg.) was dissolved in dioxan (15 ml.) and the solution stirred in air for 30 min. Addition of light petroleum precipitated a yellow solid (250 mg., 72%), which was further purified by successive precipitation from dioxan–light petroleum. After two such precipitations 3,4,5,6-*tetra*-O-*benzoyl*-1-*deoxy*-1-*hydroperoxy*-1-*phenylazo*-D-*glucitol* was obtained as a yellow powder, m. p. 183—185° (decomp., rapid heating), $[\alpha]_D$ $-6{\cdot}3° \longrightarrow$ (4 hr.) $+20{\cdot}1°$ (*c* 0·57 in dioxan) $\lambda_{max.}$ (dioxan) 408 mμ ($\varepsilon_{max.}$ 123) (Found: C, 66·6; H, 5·05; N, 3·4. $C_{40}H_{34}N_2O_{11}$ requires C, 66·85; H, 4·8; N, 3·9%) {lit.,[3] m. p. 179—180° (decomp.), $[\alpha]_D^{24}$ -6 to $-8° \longrightarrow$ (6 days) $+29°$ (*c* 0·8 in dioxan); $\lambda_{max.}$ (dioxan) 410 mμ ($\varepsilon_{max.}$ 132)}. The product (52 mg.) in acetone (2 ml.) gave an immediate iodine colour with a solution of potassium iodide (20 mg.) in acetone (0·5 ml.) and water (0·5 ml.), containing hydrochloric acid (1 drop).

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