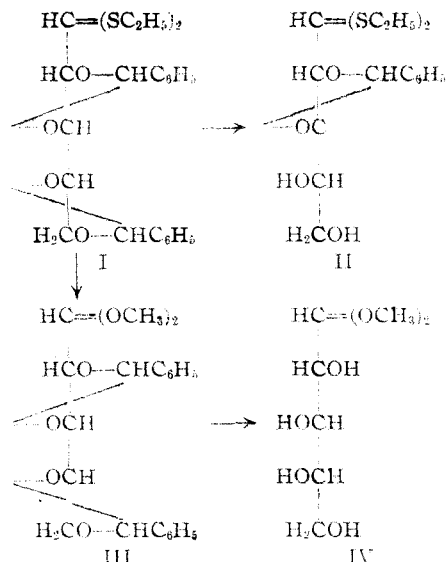


resulted. The physical constants agree well with those of the enantiomorph prepared by another method as reported by Montgomery, *et al.*⁵



Experimental

2,3;4,5-Dibenzylidene-L-arabinose Diethyl Mercaptal (I).—Dry hydrogen chloride was bubbled through a suspension of 25 g. of L-arabinose diethyl mercaptal⁶ in 40 ml. of benzaldehyde cooled to 0°. Solution which occurred after about five minutes was followed by crystallization of I. The crystals were immediately filtered, washed with Skellysolve B and after two recrystallizations from this solvent, 10 g. of long silky needles resulted; m. p. 103–105°, $[\alpha]_{25}^D -12.2^\circ$ (c, 5%; CHCl₃).

Anal. Calcd. for C₂₇H₂₈O₄S₂: C, 63.8; H, 6.5. Found: C, 63.7; H, 6.5.

2,3-Benzylidene-L-arabinose Diethyl Mercaptal (II).—Three grams of I was refluxed with 95 ml. of ethanol, 25 ml. of water and 75 ml. of glacial acetic acid for one hour. The solution was concentrated *in vacuo* to dryness and the residue recrystallized twice from a large volume of water. 1.8 g. of II resulting; m. p. 102–103°, $[\alpha]_{25}^D -25^\circ$ (c, 1.8; CHCl₃).

Anal. Calcd. for C₁₆H₂₄O₄S₂: C, 55.8; H, 7.0. Found: C, 55.9; H, 7.2.

Lead Tetraacetate on I, II and D-Galactose Diethyl Mercaptal Tetraacetate.—0.1 millimole of the test substance was weighed into a 10-ml. volumetric flask and made up to volume with 0.0585 M lead tetraacetate in acetic acid. Two-ml. aliquots were withdrawn for lead tetraacetate determinations.⁷

206 mg. of II was treated with two molar equivalents of 0.0585 M lead tetraacetate. After five minutes the mixture was poured into 100 ml. of water and neutralized with potassium hydroxide. An excess of dimedon reagent was added and after standing several hours, 90 mg. of the formaldehyde condensation product was collected, m. p. 187–189°. A melting point of the mixture with an authentic sample showed no depression. No formaldehyde could be detected when II or D-galactose diethyl mercaptal tetraacetate were treated with two molar equivalents of oxidant.

2,3;4,5-Dibenzylidene-L-arabinose Dimethyl Acetal (III).—To a mixture of 15 g. of II and 20 g. of yellow mer-

curic oxide in 300 ml. of methanol, was added dropwise over a period of one-half hour a solution of 20 g. of mercuric chloride in 200 ml. of methanol. After three hours under reflux, the mercury salts were filtered and 5 ml. of pyridine was added to the filtrate. After twelve hours at 3° a small amount of the pyridine-mercuric chloride complex was removed. The solution was concentrated *in vacuo* till crystals appeared, filtered and the operation repeated until no more crystalline material could be obtained. This material proved to be a mixture of the pyridine-mercuric chloride complex and III. A separation was made by virtue of the latter's solubility in hot Skellysolve B. It was recrystallized from this solvent; weight 6 g., m. p. 67–70°, $[\alpha]_{25}^D +18.4^\circ$ (c, 1; methanol).

Anal. Calcd. for C₂₁H₂₂O₆: C, 67.8; H, 6.5. Found: C, 67.7; H, 6.4.

The pyridine-mercuric chloride complex can be recrystallized from methanol, m. p. 196–197°.

Anal. Calcd. for C₆H₅N·HgCl₂: C, 17.1; H, 1.4. Found: C, 17.0; H, 1.4.

L-Arabinose Dimethyl Acetal (IV).—300 mg. of III in 25 ml. of methanol was hydrogenated at one atmosphere over 20 mg. of platinum oxide. Twelve hours were required for the consumption of the requisite amount of hydrogen. After concentration *in vacuo* of the solution to a few ml., 100 mg. of V was obtained; m. p. 120–121°, $[\alpha]_{25}^D +20.5^\circ$ (c, 0.6; methanol). Montgomery, *et al.*,⁵ report a m. p. of 122° and $[\alpha]_D -18.5^\circ$ (water) for the enantiomorph.

Anal. Calcd. for C₈H₁₆O₄(OCH₃)₂: OCH₃, 33.3. Found: OCH₃, 33.0.

DEPARTMENT OF BIOCHEMISTRY
COLLEGE OF AGRICULTURE
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN

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Periodate Oxidation of D-Glucosazone

BY CHARLES F. HUBBNER¹ AND KARL PAUL LINK

During the course of some studies carried out several years ago involving the application of the periodate oxidation to certain amine and hydrazine derivatives in the carbohydrate class, the oxidation of D-glucosazone was studied. Since that time a paper has appeared on the latter subject.² We wish to record a few supplementary facts. A 60% dioxane–40% water mixture was found superior to ethanol because of its greater solvent power for both the osazone and the oxidant. Sodium periodate was used as the oxidant to allow for a determination of the acid produced during oxidation. Thus with D-glucosazone, two moles of formic acid (as shown by titration), one of formaldehyde (isolated as the formal-dimedon compound) and one of the 1,2-bis-phenylhydrazone of mesoxaldehyde (I) were produced in a rapid reaction with the consumption of three moles of the oxidant. To characterize I, the tris-phenylhydrazone (II) was compared with a sample prepared according to von Pechmann.³

An interesting transformation of II was observed. By recrystallization from acetic acid or ethanol containing mineral acid, after formation

(5) Montgomery, Hann and Hudson, *THIS JOURNAL*, **59**, 1124 (1937).

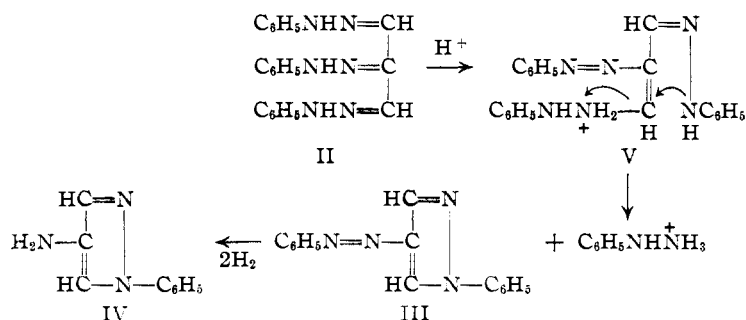
(6) Fischer, *Ber.*, **27**, 673 (1894).

(7) Hockett, Dienes and Ramsden, *THIS JOURNAL*, **65**, 1474 (1943).

(1) Ciba Pharmaceutical Products, Inc., Summit, N. J.

(2) Chargaff and Magasanik, *THIS JOURNAL*, **69**, 1459 (1947).

(3) von Pechmann and Jenisch, *Ber.*, **24**, 3255 (1891).



of a transient red intermediate, a yellow compound $\text{C}_{15}\text{H}_{12}\text{N}_4$ (III) was obtained. III differs from II by the elements of phenylhydrazine. Two molar equivalents of hydrogen were consumed by III to produce aniline and an amine, $\text{C}_6\text{H}_5\text{N}_3$ (IV). Because of the resistance of the second phenylhydrazine group to reduction it is most probably involved in a ring and III is given the structure 1-phenyl-4-benzeneazopyrazole and IV the structure 1-phenyl-4-aminopyrazole. A possible mode of formation of III is shown where the cation (V), one of the resonance forms of this highly colored intermediate loses phenylhydrazine leading to III.

Experimental

Oxidation of D-Glucosazone.—140.5 mg. of D-glucosazone was dissolved in 30 ml. of warm dioxane and rapidly cooled to 25°; 5 ml. of 0.425 M sodium periodate (5.1 molar equivalents) and 15 ml. of water was added. Almost immediately separation of the orange needles of the 1,2-bis-phenylhydrazone of mesoxaldehyde (I) began; 10-ml. aliquots were withdrawn, an excess of potassium nitrate solution added, and the acid present titrated to the methyl red end-point. This sample was then used for a periodate determination by the method of Fleury⁴: at the end of 0.25, 1 and 20 hours, the consumption of 2.84, 3.00 and 4.43 molar equivalents of oxidant and production of 1.9, 2.0 and 1.3 molar equivalents of acid. It appears that by 20 hours slow oxidation of formic acid has begun.

A blank determination showed no periodate consumption by the 60% dioxane and a control oxidation with α -methyl-D-glucopyranoside gave the normal reaction, *i.e.*, the uptake of 2 molar equivalents of oxidant and production of 1 of acid; 12 hours were required for the completion of the reaction.

In a duplicate oxidation after 0.5 hour the orange needles of I were filtered and washed with water, m. p. 196–197°, yield 102 mg. (85%).

Anal. Calcd. for $\text{C}_{15}\text{H}_{14}\text{ON}_4$: C, 67.67; H, 5.26. Found: C, 67.78; H, 5.18.

In a third oxidation by steam distillation of the reaction mixture, 40 mg. of the formal-dimedon compound was obtained, m. p. 187–188°.

1,2,3-Tris-phenylhydrazone of Mesoxaldehyde (II).—One gram of I was heated with an equal weight of freshly distilled phenylhydrazine at 120° for 0.5 hour as directed by von Pechmann, *et al.*,⁵ for the conversion of the 1,3-bis-phenylhydrazone of mesoxaldehyde to II. The yellow crystals appearing on cooling were collected with benzene and recrystallized from benzene and methanol, to yield 0.3 g. of bright yellow needles, m. p. 181–182°; von Pechmann, *et al.*,⁵ reported a melting point of 166°.

Anal. Calcd. for $\text{C}_{31}\text{H}_{26}\text{N}_6$: C, 70.78; H, 5.62; N, 23.60. Found: C, 70.93; H, 5.69; N, 23.59.

To obtain an authentic sample of II by the identical method used by von Pechmann, the 1,3-bis-phenylhydra-

zone of mesoxaldehyde was first prepared.⁴ Our preparation of the latter substance melted at 181–183° rather than the 175–176° reported but agreed with the other recorded physical properties; crystalline, habit, color, etc.³

Anal. Calcd. for $\text{C}_{15}\text{H}_{14}\text{ON}_4$: C, 67.67; H, 5.26. Found: C, 68.00; H, 5.22.

The 1,3-bis-phenylhydrazone of mesoxaldehyde was converted to II, m. p. 181–182°, which was identical to the sample prepared from I.

The possibility of the occurrence of structural and geometric isomers of the 1,3-bis-phenylhydrazone of mesoxaldehyde and of II under slightly different experimental conditions may account for these discrepancies in melting point.

1-Phenyl-4-benzeneazopyrazole (III).—0.5 g. of II was covered with 5 ml. of acetic acid. The yellow crystals immediately became a brilliant red. The mixture was heated to boiling and within a half minute after solution had taken place, the red color had faded to a yellow. Water was added to turbidity and on cooling 0.3 g. of the yellow plates of III were collected, m. p. 124–125°.

Anal. Calcd. for $\text{C}_{15}\text{H}_{12}\text{N}_4$: C, 72.55; H, 4.84; N, 22.61; mol. wt., 248. Found: C, 72.58; H, 4.97; N, 22.62; mol. wt. (Rast in camphor), 246.

The same transformation was brought about by recrystallization of II from ethanolic hydrochloric acid (0.5 N). If the acid solution is kept at room temperature the brilliant red color remains for several hours before the change to yellow becomes complete. von Pechmann³ obtained a substance by the action of acetic anhydride on II melting at 125° to which he assigned the structure "1-phenyl-3-benzolazomethyl-4-benzolazo-5-methylpyrazole" with the formulation $\text{C}_{23}\text{H}_{20}\text{N}_6$. The elemental analyses reported would not distinguish between this formulation and $\text{C}_{15}\text{H}_{12}\text{N}_4$. We have prepared the compound following von Pechmann's directions and it appears to be indistinguishable from III in melting point, behavior in a mixed chromatogram, and in absorption spectra. III in ethanol showed a broad maximum at 335 m μ with log ϵ of 4.4.

1-Phenyl-4-aminopyrazole (IV).—5.3 g. of III in 200 ml. of methanol was hydrogenated at atmospheric pressure over 300 mg. of platinum oxide. By two hours the hydrogen uptake was 2.1 molar equivalents and the reaction complete. The colorless solution was evaporated to give a paste of aniline and the crystals of IV. After two recrystallizations from benzene-petroleum ether, 0.7 g. of the colorless plates of IV was obtained, m. p. 104–105°.

Anal. Calcd. for $\text{C}_9\text{H}_9\text{N}_3$: C, 67.92; H, 5.66. Found: C, 67.93; H, 5.60.

The hydrochloride of IV obtained from ethanol-water melted at 245–250°.

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COLLEGE OF AGRICULTURE
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN

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Condensation of Nitroalkanes with Anils

BY CHARLES D. HURD AND JAMES S. STRONG

It was thought that Schiff bases should condense with nitroparaffins, since they are "ammonaldehydes." Accordingly, benzylideneaniline was treated with both nitromethane and nitroethane. Reaction occurred in accordance with the equation

$$\text{C}_6\text{H}_5\text{CH}=\text{NC}_6\text{H}_5 + \text{RCH}_2\text{NO}_2 \longrightarrow \text{C}_6\text{H}_5\text{CH}-\text{NHC}_6\text{H}_5$$

|
RCHNO₂

It would not have been without precedent if this

(4) Fleury and Lange, *J. Pharm. et Chim.*, **17**, 107 (1933).