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MONO- AND BIS-HYDRAZONES OF D-ERYTHROSE AND 2,3-DIOXO-γ-BUTYROLACTONE*

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ABSTRACT

Aryl- and benzoyl-hydrazones of 2,4-*O*-benzylidene-D-erythrose were prepared and acetylated. D-*glycero*-Tetrulose phenyl- and *p*-substituted-phenyl-osazones were acylated with acetyl chloride and benzoyl chloride to give the *N*-acyl-di-*O*-acyl derivatives, which, on boiling with acetic anhydride, afforded the 1-aryl-3-formylpyrazole *N*-acetylarylhydrazones. The bis(hydrazones) of 2,3-dioxo-γ-butyrolactone are partially hydrolyzed with copper(II) chloride to give the 2-hydrazono-3-oxo-γ-butyrolactones, which, on treatment with alkali, rearrange to give the 1-aryl-3-hydroxymethylpyrazoline-4,5-dione 4-arylhydrazones.

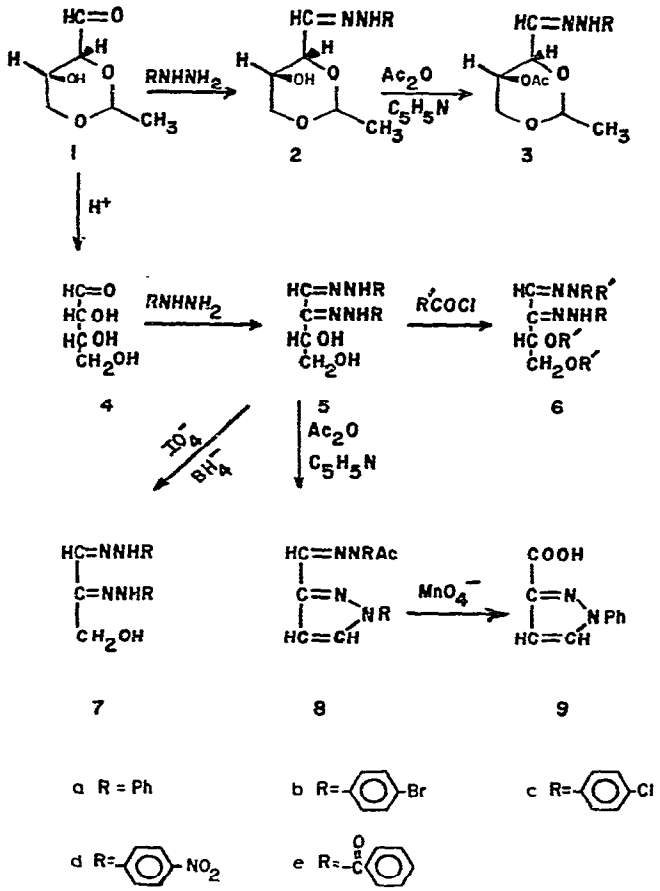
INTRODUCTION

The reactions of the hydrazone derivatives of pentoses, hexoses, and heptoses, as well as those of dehydroascorbic acid, have been extensively studied in our laboratories[1–11]. We now report on the preparation of some hydrazone derivatives of a tetrose, namely D-erythrose, and of the tetrose analog of dehydroascorbic acid.

RESULTS AND DISCUSSION

D-Erythrose was prepared by the standard procedure[12], *via* the periodate oxidation of 4,6-*O*-ethylidene-D-glucose and hydrolysis of the crystalline 2,4-*O*-ethylidene-D-erythrose (**1**). Compound **1** was converted into the crystalline *p*-nitrophenylhydrazone (**2d**) and benzoylhydrazone (**2e**). Hydrazone **2e**, on acetylation with acetic anhydride and pyridine, gave a mono-*O*-acetyl derivative (**3e**). The *p*-bromophenylhydrazone of **1** was amorphous, but the mono-*O*-acetyl derivative (**3b**) was crystalline.

*Dedicated to the memory of Professor Edward J. Bourne.



D-Erythrose (**4**) was converted into the phenyl-, *p*-bromophenyl-, and *p*-chlorophenyl-osazones (**5a–c**). Osazone **5a** showed four absorption maxima at 209, 250, 310, and 400 nm in the ultraviolet and visible region. Its circular dichroism spectrum showed two Cotton effects with opposite signs: a negative Cotton effect at longer wavelength (395 nm) and a positive Cotton effect at shorter wavelength (258 nm), as expected for an osazone having the C-3 hydroxyl group to the right in the Fischer projection formula[13]. Periodate oxidation of osazone **5a** resulted in the consumption of one mole of oxidant, and the separation of mesoxalaldehyde 1,2-bis(phenylhydrazone) which, on reduction with sodium borohydride, afforded glyceraldehyde phenylosazone (**7**). Acylation of osazone **5a** with acetyl chloride or benzoyl chloride afforded the *N*-acyl-di-*O*-acyl derivatives (**6a**; R′ = Ac or Bz). Structure **6** shows the acyl groups attached to the hydrazone residue on C-1, as in the previously studied hexose and pentose derivatives[3].

Three types of anhydrosazones are presently known[1]: (*a*) the 3,6-anhydro-osazones (commonly known as Diels anhydrosazones) that are prepared by the action of methanolic sulphuric acid on the osazones of hexoses and heptoses and cannot be

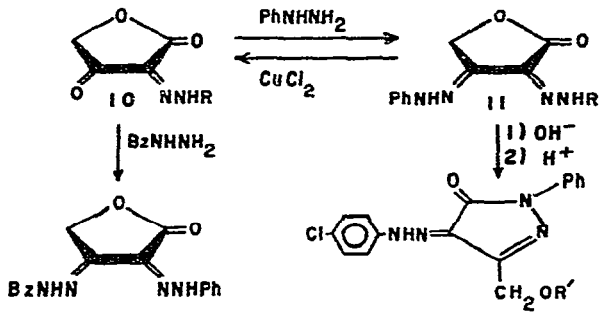
obtained from those of pentoses and tetroses; (*b*) Percival's dianhydro-osazone obtained by the action of acetonic potassium hydroxide on an osazone, and which requires a chain of at least six carbon atoms; and (*c*) the dianhydro-osazones prepared by El Khadem by the action of boiling acetic anhydride on osazones. These compounds were shown to be formylpyrazoles, requiring at least four carbon atoms, and should therefore be obtainable from an erythrose osazone. Upon boiling D-*glycero*-tetrulose phenylosazone (**5a**) or *p*-bromophenylosazone (**5b**) with acetic anhydride, 3-formyl-1-phenylpyrazole *N*-acetylphenylhydrazone (**8a**) and 3-formyl-1-*p*-bromophenylpyrazole *N*-acetyl-*p*-bromophenylhydrazone (**8b**), respectively, were obtained. The i.r. absorption spectra of the pyrozole derivatives showed an amide band at 1660 cm^{-1}. The characteristic OAc band, which appeared in the spectra of anhydro-osazones obtained from pentoses, hexoses, and heptoses, was absent. The u.v. absorption spectra of these anhydro-osazones had λ_{max} at 301–297 and 218–212 nm, similar to the spectra obtained from pentose, hexose, and heptose derivatives. Oxidation of **8a** with potassium permanganate afforded the known 1-phenylpyrazole-3-carboxylic acid (**9**); the corresponding derivatives obtained from pentoses and hexoses give 1-phenylpyrazole-3,5-dicarboxylic acid[4].

The four-carbon analogs of dehydroascorbic acid bis(arylhydrazones) are of interest because the ring-size of dehydro-L-ascorbic acid bis(arylhydrazones) has been a subject of controversy. The bis(hydrazone) 1,4-lactone structure was changed to a 1,5-lactone structure[6,8], and, later, the 1,4-lactone structure was readopted[10,11]. It, therefore, seemed desirable to synthesize a four-carbon analog of dehydroascorbic acid bis(phenylhydrazone) which would be unable to form 1,5-lactone rings, and compare its spectrum with that of dehydroascorbic acid bis(phenylhydrazone). Also, a comparison of the reactions of the hydrazones of the four-carbon analog of dehydroascorbic acid with those of the parent dehydro-L-ascorbic acid bis (phenylhydrazone) seemed worthwhile.

The 2,3-dioxo-γ-butyrolactone 2,3-bis(arylhydrazones) (**11**) needed for this study were prepared by an improved procedure. The modification involved the condensation of the monosodio derivative of diethyl malonate with bromoacetyl bromide instead of chloroacetyl chloride[15], to give, after acidification, 2-ethoxycarbonyl-3-oxo-γ-butyrolactone. This compound, upon saponification and decarboxylation, afforded 3-oxo-γ-butyrolactone, which reacted with the aryldiazonium chloride, giving 2-arylhydrazono-3-oxo-γ-butyrolactone[16] (**10**).

The infrared spectrum of 3-oxo-2-phenylhydrazono-γ-butyrolactone (**10a**) showed two carbonyl absorptions at 1660 and 1760 cm^{-1} due to the 3-keto group and the lactone, respectively. The electronic absorption spectrum showed λ_{max} at 235 and 360 nm. The mass spectrum of **10a** showed the molecular ion peak at *m/e* 204, followed by a fragment at *m/e* 127 corresponding to the loss of a phenyl group.

Condensation of 2-arylhydrazono-3-oxo-γ-butyrolactone (**10**) with aryl- or benzoyl-hydrazones gave the corresponding simple or mixed bis(hydrazones) (**11**). The i.r. absorption spectrum of dehydro-L-ascorbic acid bis(phenylhydrazone) showed a lactone band at 1720 cm^{-1}, whereas that of 2,3-bis(phenylhydrazono)-γ-butyrolactone



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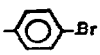
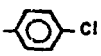
a R= Ph b R=  c R= 

(**11a**) showed the lactone absorption at 1740 cm^{-1}. The reason for the lower frequency of the carbonyl absorption in dehydroascorbic acid bis(phenylhydrazone) is not clear. The ring size of this compound has been established[10,11], and the difference may be due to stronger hydrogen-bonding of the lactone carbonyl with the imino portion of the adjacent hydrazone residue.

When dehydro-L-ascorbic acid bis(phenylhydrazone) was treated with cupric chloride, it did not give the expected phenylosotriazole, as do osazones[1] and other bis(hydrazones) of simple 1,2-dicarbonyl compounds[17,18]. Instead, the red dehydro-L-ascorbic acid bis(phenylhydrazone) gave a yellow, bicyclic product[8–10]. When 2,3-bis(phenylhydrazono)-γ-butyrolactone (**11a**) was boiled with an ethanolic solution of copper(II) chloride, partial hydrolysis occurred and 3-oxo-2-phenylhydrazono-γ-butyrolactone (**10a**) was obtained.

When 2-(*p*-chlorophenylhydrazono)-3-phenylhydrazono-γ-butyrolactone (**11c**) was heated with sodium hydroxide and acidified with acetic acid, it rearranged to 3-hydroxymethyl-1-phenylpyrazoline-4,5-dione 4-*p*-chlorophenylhydrazone (**13**; R′ = H), which gave a monoacetate (**13**; R′ = Ac).

EXPERIMENTAL

General methods.—Solutions were evaporated under reduced pressure at 40–50° unless otherwise stated. Melting points were determined on a Kofler block and are uncorrected. Infrared and ultraviolet spectra were recorded on Unicam SP-200 and Unicam SP-800 instruments, respectively. Microanalyses were determined in the Department of Chemistry and Chemical Engineering, Michigan Technological University, Houghton, Michigan, and in the Department of Chemistry, Faculty of Science, Cairo University, Egypt.

2,4-O-Ethylidene-D-erythrose p-*nitrophenylhydrazone* (**2d**). — 2,4-*O*-Ethylidene-D-erythrose (0.2 g) in water (5 ml) containing acetic acid (0.1 ml) was treated with

p-nitrophenylhydrazine (0.5 g) in ethanol (5 ml), and the mixture was heated on a water bath for 10 min. After cooling, the *p*-nitrophenylhydrazone separated out, and was filtered-off, dried (yield, 0.1 g), and crystallized from diiute ethanol to give **2d** as yellow needles, m.p. 202°. It was soluble in ethanol, methanol, benzene, acetone, and ether, and insoluble in water.

Anal. Calc. for $C_{12}H_{15}N_3O_5$: C, 51.2; H, 5.4; N, 14.9. Found: C, 51.2; H, 5.3; N, 14.5.

2,4-O-Ethylidene-D-erythrose benzoylhydrazone (**2e**). — A solution of 2,4-*O*-ethylidene-D-erythrose (2 g) in water (10 ml) containing acetic acid (1 ml) was treated with benzoylhydrazine (2 g) in water (5 ml), and the mixture was heated on a water bath for 5 min. After cooling, the benzoylhydrazone that separated out was filtered-off, dried (yield, 1.5 g), and crystallized from ethanol to give **2e** as needles, m.p. 220°; λ_{max}^{EtOH} 211 (sh) and 233 nm (log ε 3.94, 4.18). It was soluble in ethanol, methanol, benzene, and ether, and insoluble in water.

Anal. Calc. for $C_{13}H_{16}N_2O_4$: C, 59.1; H, 6.1; N, 10.6. Found: C, 59.4; H, 6.1; N, 10.1.

3-O-Acetyl-2,4-O-ethylidene-D-erythrose benzoylhydrazone (**3e**). — Compound **2e** (0.2 g) in dry pyridine (5 ml) was treated with acetic anhydride (20 ml) overnight at room temperature. The mixture was then poured onto crushed ice, and the acetate was filtered-off (yield, 0.1 g) and crystallized from dilute ethanol to give **3e** as needles, m.p. 142°; ν_{max}^{KBr} 1680 (CON) and 1760 cm^{-1} (OAc); λ_{max}^{EtOH} 223 and 291 nm (log ε 4.23, 4.24), λ_{min} 246 nm (log ε 3.52). It was soluble in ethanol, methanol, benzene, and ether, and insoluble in water.

Anal. Calc. for $C_{15}H_{18}N_2O_5$: C, 59.1; H, 6.1; N, 9.2. Found: C, 59.3; H, 6.2; N, 9.2.

3-O-Acetyl-2,4-O-ethylidene-D-erythrose p-bromophenylhydrazone (**3b**). — 2,4-*O*-Ethylidene-D-erythrose (7 g) in water (125 ml) was treated with *p*-bromophenylhydrazine (7 g) in acetic acid (6 ml), portionwise with continuous stirring and cooling. The product obtained was filtered off, dried (yield, 2 g), dissolved in dry pyridine (10 ml), and treated with acetic anhydride (20 ml) for 24 h at room temperature. The mixture was then poured onto crushed ice, whereby the acetate crystallized; it was filtered-off, washed with water, and dried (yield, 1 g). Recrystallization from ethanol afforded needles, m.p. 148°; λ_{max}^{EtOH} 211, 242, 287, and 310 (sh) nm (log ε 4.07, 3.82, 4.34, and 3.99); λ_{min} 230 and 252 (log 3.75, 3.75).

Anal. Calc. for $C_{14}H_{17}BrN_2O_4$: C, 47.1; H, 4.8; N, 7.8. Found: C, 47.1; H, 4.4; N, 8.0.

D-glycero-*Tetrulose phenylosasone* (**5a**). — A solution of D-erythrose (**4**, 5 g) in water (50 ml) containing acetic acid (2 ml) was treated with phenylhydrazine (15 g), and the mixture was heated on a water bath for 2 h, whereby the osazone separated out on cooling. It was filtered-off, washed with water, dried (yield, 4 g), and crystallized from benzene to give **5a** as needles, m.p. 170° (lit.[19] m.p. 170°); ν_{max}^{KBr} 1600 (C=N) and 3400 cm^{-1} (OH); λ_{max}^{EtOH} 209, 230 (sh), 256, 310, and 400 nm (log ε 4.20,

4.35, 4.06, and 4.33), λ_{min} 218, 280, and 348 nm (log ε 4.12, 3.79, and 3.94). It was soluble in methanol, ethanol, benzene, and ether, and insoluble in water.

Anal. Calc. for $C_{16}H_{18}N_4O_2$: C, 64.4; H, 6.1; N, 18.8. Found: C, 64.5; H, 6.1; N, 19.0.

D-glycero-*Tetrulose phenylosotriazole.* — A suspension of phenylosazone **5a** (3 g) in ethanol (100 ml) was treated with copper(II) chloride (3 g), and the mixture was boiled under reflux for 1 h and then filtered while hot. The filtrate was concentrated under reduced pressure, whereby the triazole separated out. The product was filtered-off, dried (yield; 1 g), and crystallized from ethanol to give the title compound as colorless needles, m.p. 198°.

Anal. Calc. for $C_{10}H_{11}N_3O_2 \cdot 2H_2O$: C, 49.8; H, 6.3; N, 17.4. Found: C, 50.2; H, 5.9; N, 17.5.

N-*Acetyl-di*-O-*acetyl*-D-glycero-*tetrulose phenylosazone* (**6a**; $R = Ac$). — D-*glycero*-Tetrulose phenylosazone **5a**, (0.5 g) in *N,N*-dimethylaniline (5 ml) was treated with acetyl chloride (10 ml), dropwise with shaking and cooling. The mixture was kept at room temperature for 72 h with occasional shaking, and was then poured onto crushed ice with stirring; the product obtained was washed with water several times and then treated with ethanol, whereby the acetyl derivative separated out. It was filtered-off, dried (yield, 0.2 g), and crystallized from ethanol to give the title compound as pale-yellow needles, m.p. 146°; λ_{max}^{EtOH} 220 (sh), 243, 268 (sh), and 390 nm (log ε 3.90, 4.1, 3.7, and 4.02), λ_{min} 314 nm (log ε 3.05).

Anal. Calc. for $C_{22}H_{24}N_4O_5$: C, 62.3; H, 5.7; N, 13.2. Found: C, 62.1; H, 5.5; N, 13.7.

N-*Benzoyl-di*-O-*benzoyl*-D-glycero-*tetrulose phenylosazone* (**6a**; $R' = Bz$). — D-glycero-Tetrulose phenylosazone (**5a**, 0.8 g) in dry pyridine (5 ml) was treated with benzoyl chloride (2 ml), dropwise with shaking, and the mixture was kept overnight at room temperature, with occasional shaking, and then poured onto crushed ice. The solid obtained was filtered-off, washed repeatedly with water, dried (yield; 0.6 g), and crystallized from dilute ethanol to give the title compound as pale-yellow needles, m.p. 165°. It was soluble in ethanol, methanol, benzene, or ether, and insoluble in water.

Anal. Calc. for $C_{37}H_{30}N_4O_5$: C, 72.8; H, 5.0; N, 9.2. Found: C, 73.2; H, 4.6; N, 9.1.

3-Formyl-1-phenylpyrazole N-*acetylphenylhydrazone* (**8a**). — A solution of D-*glycero*-tetrulose phenylosazone (**5a**, 5 g) in acetic anhydride (10 ml) was boiled under reflux for 1.5 h and then poured onto crushed ice. The oily product that separated out solidified after washing with water and standing for 48 h at room temperature. The product was then filtered-off, dried (yield, 0.7 g), and crystallized from dilute ethanol to give **8a** as colorless needles, m.p. 180°; λ_{max}^{KBr} 1660 (N-Ac) cm^{-1}; λ_{max}^{EtOH} 212 and 297 nm (log ε 4.34, 4.61), λ_{min} 251 nm (log ε 4.0).

Anal. Calc. for $C_{18}H_{16}N_4O$: C, 71.0; H, 5.3; N, 18.4. Found: C, 70.7; H, 5.5; N, 17.9.

Compound **8a** (0.2 g) in water (50 ml) was refluxed with excess potassium

permanganate for 3 h. The mixture was filtered while hot, decolorized with SO_2, acidified with conc. hydrochloric acid, and extracted with ether. After evaporation of ether, the residue was crystallized from hot water to give 1-phenylpyrazole-3-carboxylic acid, m.p. 146°, alone or in admixture with an authentic sample.

D-glycero-*Tetrulose* p-*bromophenylosazone* (**5b**). — D-Erythrose (5 g) in water (100 ml) containing acetic acid (2 ml) was treated with *p*-bromophenylhydrazine (18 g) in ethanol (25 ml), as described for **5a**. The product crystallized from dilute ethanol to give **5b** as needles, m.p. 180°; λ_{max}^{EtOH} 210, 230, 264, 318, and 406 nm (log ε 4.18, 4.13, 4.12, and 4.28), λ_{min} 220, 240, 288, and 352 nm (log ε 4.10, 4.10, 3.84, 3.84, and 3.94). It was soluble in ethanol, methanol, or ether, and insoluble in water.

Anal. Calc. for $C_{16}H_{16}Br_2N_4O_2 \cdot H_2O$: C, 40.5; H, 3.8; N, 11.8. Found: C, 40.4; H, 4.1; N, 11.7.

1-p-*Bromophenyl-3-formylpyrazole* N-*acetyl*-p-*bromophenylhydrazone* (**8b**). — A solution of D-*glycero*-tetrulose *p*-bromophenylosazone (**5b**, 2 g) in acetic anhydride (5 ml) was treated as described for **8a**. The product (yield, 0.2 g) crystallized from ethanol to give **8b** as needles, m.p. 235°; λ_{max}^{EtOH} 218 and 301 nm (log ε 4.56, 4.78), λ_{min} 255 nm (log ε 4.20).

Anal. Calc. for $C_{18}H_{14}Br_2N_4O$: C, 46.8; H, 3.1; N, 12.1. Found: C, 46.9; N, 2.9; N, 12.0.

D-glycero-*Tetrulose* p-*chlorophenylosazone* (**5c**). — D-Erythrose (6 g) in water (100 ml) containing acetic acid (2 ml) was heated with *p*-chlorophenylhydrazine (16 g) as described above; the product crystallized from dilute ethanol to give **5c** as needles, m.p. 170°; λ_{max}^{EtHO} 210, 228, 264, 318, and 404 nm (log ε 4.16, 4.10, 4.34, 4.10, and 4.10), λ_{min} 220, 240, 287, and 350 nm (log ε 4.16, 4.03, 3.71, and 3.94).

Anal. Calc. for $C_{16}H_{16}Cl_2N_4O_2$: C, 52.3; H, 4.4; H, 15.3. Found: C, 52.0; H, 4.5; N, 15.2.

N-*Benzoyl-di*-O-*benzoyl*-D-glycero-*tetrulose* p-*chlorophenylosazone* (**6c**; *R'* = *Bz*). — D-*glycero*-Tetrulose *p*-chlorophenylosazone (**5c**, 0.2 g) in dry pyridine (5 ml) was treated with benzoyl chloride (2 ml), as described above, to give **6c** as needles, m.p. 170° (from ethanol).

Anal. Calc. for $C_{37}H_{28}Cl_2N_4O_5 \cdot H_2O$: C, 63.7; H, 4.3; N, 8.0. Found: C, 63.3; H, 4.0; N, 8.0.

3-Oxo-2-phenylhydrazono-γ-butyrolactone (**10a**). — A cooled suspension of the sodio-derivative (45 g) of diethyl malonate in dry ether (500 ml) was stirred with a solution of bromoacetyl bromide (25 g) in dry ether (50 ml), for 30 min. The reaction mixture was then boiled under reflux for 48 h on a water-bath. The solid that separated out was filtered-off, washed with ether, dried, and then dissolved in ice-cold water. The solution was acidified with conc. hydrochloric acid and concentrated under reduced pressure. 2-Ethoxycarbonyl-3-oxo-γ-butyrolactone that separated was filtered-off, dried (yield, 10 g), and crystallized from methanol to give needles, m.p. 125° (lit.[16] m.p. 124–125). A solution of 2-ethoxycarbonyl-3-oxo-γ-butyrolactone (3 g) in 12% aqueous sodium hydroxide (20 ml) was kep tfor 60 h at room temperature. Conc. hydrochloric acid (6 ml) was then added, whereby the temperature of the

reaction mixture rose and carbon dioxide began to be evolved. After 1 h, potassium carbonate (5 g) was added, and the solution was cooled to 0°. Benzenediazonium chloride [obtained from aniline (2 ml), 5M hydrochloric acid (10 ml), and sodium nitrite (2 g) in water (10 ml)] was then added, and the resulting yellow precipitate was filtered-off, washed with water, and dried (yield, 1.5 g). Another crop (0.1 g) was obtained by extraction with chloroform. The combined product was crystallized from chloroform to give **10a** as needles, m.p. 210°; lit.[7] m.p. 210°; ν_{max}^{KBr} 1660 (CO) and 1760 cm^{-1} (CO lactone).

Anal. Calc. for $C_{10}H_8N_2O_3$: C, 58.8; H, 4.0; N, 13.7. Found: C, 58.4; H, 3.8; N, 13.5.

2,3-Bis(phenylhydrazono)-γ-butyrolactone (**11a**). — A solution of **10a** (0.5 g) in ethanol (10 ml) was treated with phenylhydrazine (0.5 ml) and acetic acid (0.1 ml), and the mixture was heated on a water-bath for 1 h. After cooling, the bis(phenylhydrazone) that separated out was filtered-off, washed with a little cold water, dried (yield; 0.1 g), and crystallized from ethanol to give **11a** as red needles, m.p. 240° (lit.[17] m.p. 240°); ν_{max}^{KBr} 1740 cm^{-1} (lactone).

Anal. Calc. for $C_{16}H_{14}N_4O_2$: C, 65.2; H, 4.7; N, 19.1. Found: C, 65.3; H, 4.8; N, 19.0.

2-p-*Chlorophenylhydrazono-3-phenylhydrazono-γ-butyrolactone* (**11c**). — A solution of 2-*p*-chlorophenylhydrazono-3-oxo-γ-butyrolactone[16] (**10c**, 0.2 g) in ethanol (25 ml) was heated with phenylhydrazine (0·1 ml) and acetic acid (0.1 ml) for 0.5 h. After cooling, the product was filtered-off, washed with a little ethanol, dried (yield, 0.1 g), and crystallized from chloroform–ethanol to give **11c** as red needles, m.p. 268–270°.

Anal. Calc. for $C_{16}H_{13}ClN_4O_2$: C, 61.1; H, 4.2; N, 13.3. Found: 61.1; H, 4.1; N, 13.3.

3-Benzoylhydrazono-2-phenylhydrazono-γ-butyrolactone (**12**). — A solution of 3-oxo-2-phenylhydrazono-γ-butyrolactone (**10a**, 0.1 g) in ethanol (20 ml) was treated with benzoylhydrazine (0.1 g) and acetic acid (0.1 ml), and the mixture boiled under reflux on a water-bath for 3 h. After cooling, the product that separated out was filtered-off, washed with a little ethanol, dried (yield, 0.1 g), and crystallized from ethanol to give **12** as needles, m.p. 240°.

Anal. Calc. for $C_{17}H_{14}N_4O_3$: C, 63.4; H, 4.4; N, 17.4. Found: C, 63.4; H, 4.4; N, 17.2.

Action of cupric chloride on 2,3-bis(phenylhydrazono)-γ-butyrolactone (**11a**). — A suspension of **11a** (0.5 g) in ethanolic 5% cupric chloride (20 ml) was refluxed for 10 min. The solution was then concentrated and left to cool. The product that separated out was filtered-off, dried (yield, 0.1 g), and crystallized from ethanol or chloroform to give needles of 3-oxo-2-phenylhydrazono-γ-butyrolactone (**10a**), m.p. 210° alone or in admixture with authentic material.

3-Hydroxymethyl-1-phenylpyrazole-4,5-dione 4-p-chlorophenylhydrazone (**13**; $R' = H$). — A suspension of 2-*p*-chlorophenylhydrazono-3-phenylhydrazono-γ-butyrolactone (**11c**, 0.1 g) in water (20 ml) was heated with 2M sodium hydroxide

(10 ml) for 10 min, whereby the hydrazone dissolved. After cooling, the solution was acidified with acetic acid, and the precipitated material was crystallized from ethanol to give **13** (R′ = H) as needles, m.p. 185°.

Anal. Calc. for $C_{16}H_{13}Cl_6N_4O_2 \cdot H_2O$: C, 56.9; H, 4.2; N, 16.6. Found: C, 56.8; H, 3.7; N, 16.6.

3-Acetoxymethyl-1-phenylpyrazole-4,5-dione 4-p-*chlorophenylhydrazone* (**13**; *R′ = Ac*). — A suspension of **13** (R′ = H) (0.1 g) in dry pyridine (5 ml) was treated with acetic anhydride (5 ml) and left at room temperature overnight with occasional shaking. The mixture was then poured onto crushed ice, and the product that separated out was filtered-off, washed with water, dried (yield, 0.1 g), and crystallized from ethanol to give the title compound as needles, m.p. 182°.

Anal. Calc. for $C_{18}H_{15}ClN_4O_3$: C, 58.0; H, 4.0; N, 15.0. Found: C, 58.1; H, 3.9; N, 15.0.

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