The Isomerization of αβ-Di(arylhydrazono)-γ-butyrolactones.

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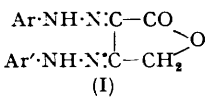
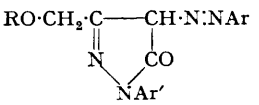
The lactone osazones (I) are converted by hot alkali into 1-aryl-4-arylazo-3-hydroxymethylpyrazol-5-ones (II; R = H). Reduction of the pyrazolone (II; Ar = Ar′ = Ph, R = H) gives 4-amino-3-hydroxymethyl-1-phenylpyrazol-5-one (IV; Y = OH) which is oxidized by ferric chloride to the substituted rubazonic acid (V; Y = OH).

Wolff and Lüttringhaus (*Annalen*, 1900, **312**, 155) reported that a dihydrazone (I; Ar = Ar′ = Ph) with hot alcoholic alkali gave an alkali-soluble yellow compound which was not examined and for which no structure was postulated. Investigation of the pure compound has shown that it is isomeric with the dihydrazone and although soluble in aqueous sodium hydroxide is insoluble in aqueous sodium carbonate, indicating that it has weakly acidic properties. With acetic anhydride it gives a monoacetyl derivative which is soluble without decomposition in aqueous sodium hydroxide, and on reduction it gives aniline and a basic compound isolated as the hydrochloride. This hydrochloride is also obtained, together with *p*-chloroaniline, by reduction of the corresponding isomer (I; Ar = *p*-chlorophenyl, Ar′ = Ph), showing that, in the isomer, it is only the hydrazono-group originally in the α-position of the osazone which undergoes reduction. It is suggested, therefore, that of two possible isomers (II; Ar = Ar′ = Ph, R = H) and (III), Wolff and Lüttringhaus's compound is the former, whilst its acetyl derivative and reduction product have structures (II; Ar = Ar′ = Ph, R = Ac) and (IV; Y = OH) respectively.



(I)



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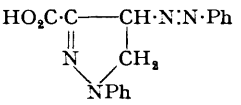
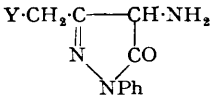
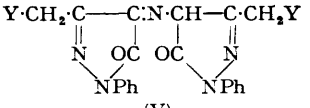


(III)



(IV)



(V)

Confirmation of the structure (IV; Y = OH) and therefore of (II) is given by the similarity of the behaviour of the former compound to 4-amino-3-methyl-1-phenylpyrazol-5-one (IV; Y = H) on oxidation with ferric chloride. The oxidation product (V; Y = OH), like rubazonic acid (V; Y = H), is purple in alkaline solution and with

phenylhydrazine in acetic acid gives the pyrazolone (II; Ar = Ar′ = Ph, R = H) (cf. Knorr, *Annalen*, 1887, **238**, 189).

Experimental

β-Oxo-α-phenylhydrazono-γ-butyrolactone.—The following procedure avoids the tedious isolation of tetronic acid. α-Ethoxycarbonyl-β-oxo-γ-butyrolactone (17·2 g.) (Benary, *Ber.*, 1907, **40**, 1080) was dissolved in 12% aqueous sodium hydroxide (100 ml.) and left for 60 hr. at 18°. Concentrated hydrochloric acid (30 ml.) was added, the temperature rising to 42° and carbon dioxide being evolved. After 1 hr. potassium carbonate (25 g.) was added and the solution cooled to 0°. Benzenediazonium chloride [from aniline (9·0 ml.), 5N-hydrochloric acid (50 ml.), and sodium nitrite (7·5 g.) in water (30 ml.)] was added at 0—2°. After 1 hr. at 0°, the resulting yellow precipitate was filtered off, washed with water, dried *in vacuo*, and recrystallized from chloroform to give β-oxo-α-phenylhydrazono-γ-butyrolactone as yellow leaflets, m. p. 210° (12·8 g., 58%), identical with the compound obtained from tetronic acid (Wolff and Lüttringhaus, *loc. cit.*). Similarly were prepared *β-oxo-α-o-tolylhydrazono-γ-butyrolactone*, yellow needles (from ethanol), m. p. 160° (48%) (Found: C, 60·5; H, 4·7. $C_{11}H_{10}O_3N_2$ requires C, 60·6; H, 4·6%), and α-o-, yellow needles (from ethanol), m. p. 158° (62%) (Found: C, 50·4; H, 3·0; Cl, 14·7. $C_{10}H_7O_3N_2Cl$ requires C, 50·3; H, 2·94; Cl, 14·9%), and α-p-*chlorophenylhydrazono-β-oxo-γ-butyrolactone*, orange needles (from acetic acid), m. p. 228·5° (decomp.) (75%) (Found: C, 50·5; H, 3·0; Cl, 15·0. $C_{10}H_7O_3N_2Cl$ requires C, 50·3; H, 2·95; Cl, 14·9%).

αβ-Di(phenylhydrazono)-γ-butyrolactone was prepared by the method of Wolff and Lüttringhaus (*loc. cit.*) and the following derivatives similarly: αβ-*di*-(o-*tolylhydrazono*)-, red needles (from ethanol), m. p. 166—167° (68%) (Found: C, 66·8; H, 5·7; N, 17·4. $C_{18}H_{18}O_2N_4$ requires C, 67·2; H, 5·6; N, 17·4%), αβ-*di*-(o-*chlorophenylhydrazono*)-, bright orange-red plates (from acetic acid), m. p. 220° (84%) (Found: C, 53·15; H, 3·5; Cl, 19·45. $C_{16}H_{12}O_2N_4Cl_2$ requires C, 52·85; H, 3·3; Cl, 19·55%), and α-p-*chlorophenylhydrazono-β-phenylhydrazono-γ-butyrolactone* (from acetic acid), orange leaflets, m. p. 251° (decomp.) (79%) (Found: Cl, 10·9. $C_{16}H_{13}O_2N_4Cl$ requires Cl, 10·8%).

3-Hydroxymethyl-1-phenyl-4-phenylazopyrazol-5-one.—αβ-Di(phenylhydrazono)-γ-butyrolactone (27·5 g.), ethanol (1 l.), and 40% aqueous sodium hydroxide (25 ml.) were heated at 100° for 5 min., the initially purple solution becoming deep yellow. Water (500 ml.) was added and the ethanol removed by distillation. The solution was cooled, filtered from a tarry impurity, and acidified with concentrated hydrochloric acid (25 ml.) to give a yellow precipitate which was filtered off and recrystallized from ethanol. This afforded *3-hydroxymethyl-1-phenyl-4-phenylazopyrazol-5-one* as orange-yellow needles, m. p. 155° (19·1 g., 70%) (Found: C, 65·2; H, 4·8; N, 19·1. $C_{16}H_{14}O_2N_4$ requires C, 65·3; H, 4·75; N, 19·05%). The following analogues were obtained similarly: 4-p-*chlorophenylazo-3-hydroxymethyl-1-phenylpyrazol-5-one*, orange-red needles (from ethanol), m. p. 186° (54%) (Found: C, 54·4; H, 4·1; Cl, 10·7. $C_{16}H_{13}O_2N_4Cl$ requires C, 54·5; H, 3·95; Cl, 10·8%); *3-hydroxymethyl-1-o-tolyl-4-o-tolylazopyrazol-5-one* (from ethanol), orange-yellow needles, m. p. 149° (4%) (Found: C, 67·0; H, 5·7. $C_{18}H_{18}O_2N_4$ requires C, 67·2; H, 5·6%); and 1-o-*chlorophenyl-4-o-chlorophenylazo-3-hydroxymethylpyrazol-5-one* (from ethanol), yellow leaflets, m. p. 203° (decomp.) (68%) (Found: C, 53·15; H, 3·4. $C_{16}H_{12}O_2N_4Cl_2$ requires C, 52·85; H, 3·3%).

3-Acetoxymethyl-1-phenyl-4-phenylazopyrazol-5-one.—The compound (II; Ar = Ar′ = Ph, R = H) (1·0 g.) and acetic anhydride (5 ml.) were boiled for 5 min., then diluted with water (30 ml.), and the precipitated solid recrystallized from ethanol, to give the *acetoxy-compound* as orange-yellow plates, m. p. 131° (0·65 g., 53%) (Found: C, 64·3; H, 5·0. $C_{18}H_{16}O_3N_4$ requires C, 64·3; H, 4·75%).

Reduction of the Compound (II; Ar = Ar′ = Ph, R = H).—3-Hydroxymethyl-1-phenyl-4-phenylazopyrazol-5-one (2·0 g.), ethanol (20 ml.), 10N-hydrochloric acid (10 ml.), and granulated tin (5 g.) were boiled under reflux; a vigorous reaction occurred and the solution became colourless. The solution was filtered, the filtrate diluted with water, ethanol distilled off, and tin removed from the boiling solution with hydrogen sulphide. Concentration to 20 ml. gave, after 20 hr. at 0°, colourless crystals which recrystallized from 5N-hydrochloric acid to give *4-amino-3-hydroxymethyl-1-phenylpyrazol-5-one hydrochloride* (cf. IV; Y = OH) as needles, m. p. 201—203° (0·92 g., 65%) (Found: C, 49·6; H, 4·9; Cl, 14·8. $C_{10}H_{12}O_2N_3Cl$ requires C, 49·8; H, 5·01; Cl, 14·7%). The combined acid filtrates were basified and steam-distilled to give aniline, which was converted into acetanilide (84%). Reduction of 4-*p*-chlorophenylazo-3-hydroxymethyl-1-phenylpyrazol-5-one under similar conditions gave the identical amine hydrochloride (70%) and *p*-chloroacetanilide (79%).

Oxidation of the Pyrazolone (IV; Y = OH).—The amine hydrochloride (0·5 g.) from the above reduction in water (10 ml.) was warmed for 5 min. on the water-bath with 10% aqueous ferric chloride (10 ml.). The orange crystalline precipitate, after filtration and recrystallization from ethanol, gave *3-hydroxymethyl-4-(3-hydroxymethyl-1-phenylpyrazol-5-on-4-ylidene)amino-1-phenylpyrazol-5-one* (V; Y = OH) as orange needles, m. p. 199° (0·38 g., 92%) (Found: C, 61·5; H, 4·2. $C_{20}H_{17}O_4N_5$ requires C, 61·3; H, 4·35%).

The product (V; Y = OH) (0·5 g.), acetic acid (5 ml.), and phenylhydrazine (1·0 ml.) were boiled under reflux for 5 min. and then diluted with water. Recrystallization of the precipitated solid gave the pyrazolone (II; Ar = Ar′ = Ph, R = H) (0·37 g., 50%).

Conversion of the pyrazolone (II; Ar = *p*-chlorophenyl, Ar′ = Ph, R = H) into the same product (V; Y = OH) was also carried out without the isolation of the material (IV; Y = OH) by the following procedure: Zinc dust (5·0 g.) was added gradually to 4-*p*-chlorophenylazo-3-hydroxymethyl-1-phenylpyrazol-5-one (2·0 g.) in acetic acid (10 ml.) and ethanol (50 ml.) on a steam-bath. When colourless the mixture was filtered and diluted with water (100 ml.), ethanol removed, and the residue made alkaline with sodium hydroxide. After ether-extraction the alkaline solution was acidified with 10N-hydrochloric acid, 10% aqueous ferric chloride (15 ml.) added, and the mixture warmed on the steam-bath for 5 min., to give the rubazonic acid (V; Y = OH) (68%). From the ether-extracts, *p*-chloroaniline was isolated and identified as *p*-chloroacetanilide (91%).

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