

RING CONTRACTION OF 4-DIAZO-1-PHENYL-5,6-DIOXO-1,4,5,6-TETRAHYDROPYRIDAZINE IN THE SOLID STATE VIA "PYRAZOLO-LACTONE"¹.

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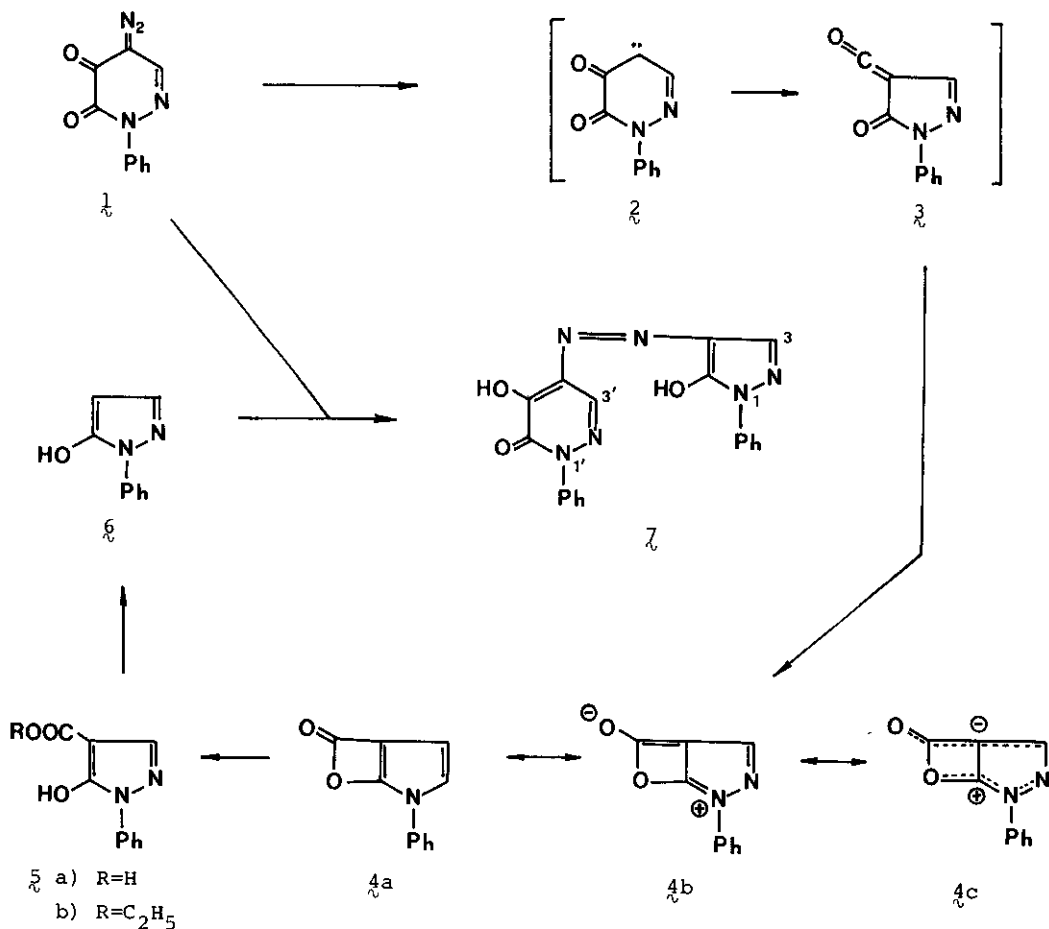
Abstract - Conversion of 4-diazo-1-phenyl-5,6-dioxo-1,4,5,6-tetrahydropyridazine into "pyrazolo-lactone", from which different 5-hydroxy-1-phenyl-pyrazoles can be formed in the solid state, is described.

Several examples of ring contraction of substituted pyridazinones into pyrazole derivatives either under basic or acidic conditions have been reported²⁻⁶. On the other hand, since the Süß's first report⁷, a number of heterocyclic carboxylic acids and their derivatives has been prepared from heterocyclic α -diazo ketones⁸ either by thermal or photochemical Wolff rearrangement⁹. In this manner, 4-diazo-1-phenyl-5,6-dioxo-1,4,5,6-tetrahydropyridazine has been converted thermally into ethyl 5-hydroxy-1-phenyl-pyrazole-4-carboxylate and photochemically into the corresponding methyl ester¹⁰.

In continuation of our studies in the series of heterocyclic α -diazo ketones¹¹⁻¹⁴ we wish to report a transformation of 4-diazo-1-phenyl-5,6-dioxo-1,4,5,6-tetrahydropyridazine in the solid state at room temperature. In this transformation an intermediate was isolated and characterized and further converted into 5-hydroxy-1-phenyl-pyrazole derivatives.

When an analytically pure sample of 4-diazo-1-phenyl-5,6-dioxo-1,4,5,6-tetrahydropyridazine (**1**)¹⁵, precipitated from a chloroform solution by addition of petroleum ether, was left at room temperature in a dark place for approximately 10 days under strictly anhydrous conditions, it was quantitatively transformed into a new compound with mp. 99-100^o ((nmr (CDCl₃) τ = 2,3-2,7 (m, C₆H₅), 2,5 (s, H₃),

which exhibited no diazo, NH or OH band in its ir spectrum. The elemental analysis, the molecular weight, determined by vapor pressure osmometer in CH_2Cl_2 solution (Knauer Dampfdruck Osmometer), and mass spectrum ($M^+ = 186$ and the absence of metastable peaks corresponding to any type of a dimer) together with the nmr spectrum, which shows only one heteroaromatic proton, suggest that the compound is a monomer $\text{C}_{10}\text{H}_6\text{N}_2\text{O}_2$.



Scheme

Among several structures, two of them, either the ketene (3) or the lactone (4), are the most plausible. However, the absence of the ketene absorption band at $\sim 2100\text{ cm}^{-1}$ and the presence of a new carbonyl band at 1760 cm^{-1} in ir

spectrum are in agreement only with the lactone (4), which could be represented by a number of resonance structures, (4a-c). These could explain the relative low carbonyl absorption band in ir spectrum and the relative stability of this compound in comparison to the corresponding benzpropiolactone or 2-thio-benzpropiolactone¹⁷.

The lactone (4) is extremely reactive. When the reactions were followed by nmr technique, it was converted in the presence of equimolar amount of water or ethanol quantitatively into the acid 5a (mp. 92°, nmr (CDCl₃) τ = 2,3-2,7 (m, C₆H₅), 2,15 (s, H₃), 5,6 (broad s, OH); the compound is in every respect identical with the authentic sample prepared by the known method¹⁹), or ethyl ester (5b) (mp. 118°, nmr (CDCl₃) τ = 2,0-2,6 (m, C₆H₅), 2,15 (s, H₃), 8,55 (t, CH₂CH₃), 5,55 (q, CH₂CH₃), J_{CH₂CH₃} = 7,0 Hz); the compound is identical with the authentic sample prepared according to lit.¹⁹), respectively, in less than three minutes at room temperature.

When the strictly anhydrous conditions were not observed during the transformation of the diazo compound (1), into the lactone (4), a number of other products was also isolated. For example, when a sample of the diazo compound (1) was exposed during the 14 days period every day only several seconds to the laboratory atmosphere (60-80 % rel.humidity), in order to take samples for ir spectra, the products (5a) (3%), (6) (2%) and (7) (3%) besides the lactone (4) were formed. (Scheme). The formation of these compounds can be explained in the following way. The lactone (4) was partially converted in the presence of water into the acid (5a), which slowly decarboxylated at room temperature affording the compound (6) (mp. 116°; the compound is in every respect identical with the authentic specimen prepared by the known method¹⁹). To this the coupling of the starting diazo compound (1) took place affording the azo compound (7) ((mp. 260-262° analyzing for C₁₉H₁₄N₆O₃, ms M⁺ = 374, nmr (DMSO-d₆) τ = 1,65 (s, H₃'), 1,81 (s, H₃), 2.1 (m) and 2,5 (m) (1-C₆H₅), 2,5 (broad s) 1-C₆H₅) which was shown to be identical with the compound prepared independently from the compounds (1) and (6) in ethanol solution in 83% yield. On the other hand, when the diazo compound (1) was left open to the laboratory atmosphere besides the compound (6) only compound (7) (5%) was formed after 40 days at room temperature.

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Benzpropiolactone shows a characteristic band at 1904 cm^{-1} and was observed together with the corresponding ketoketene (showing 2139 and 1650 cm^{-1} in ir spectrum) by irradiation of phthaloyl peroxide matrix isolated in argon at 8°K . The corresponding thio analog, 2-thiobenzpropiolactone, also not stable at room temperature, shows a characteristic carbonyl band at 1803 cm^{-1} in ir spectrum at 77°K ¹⁸.
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