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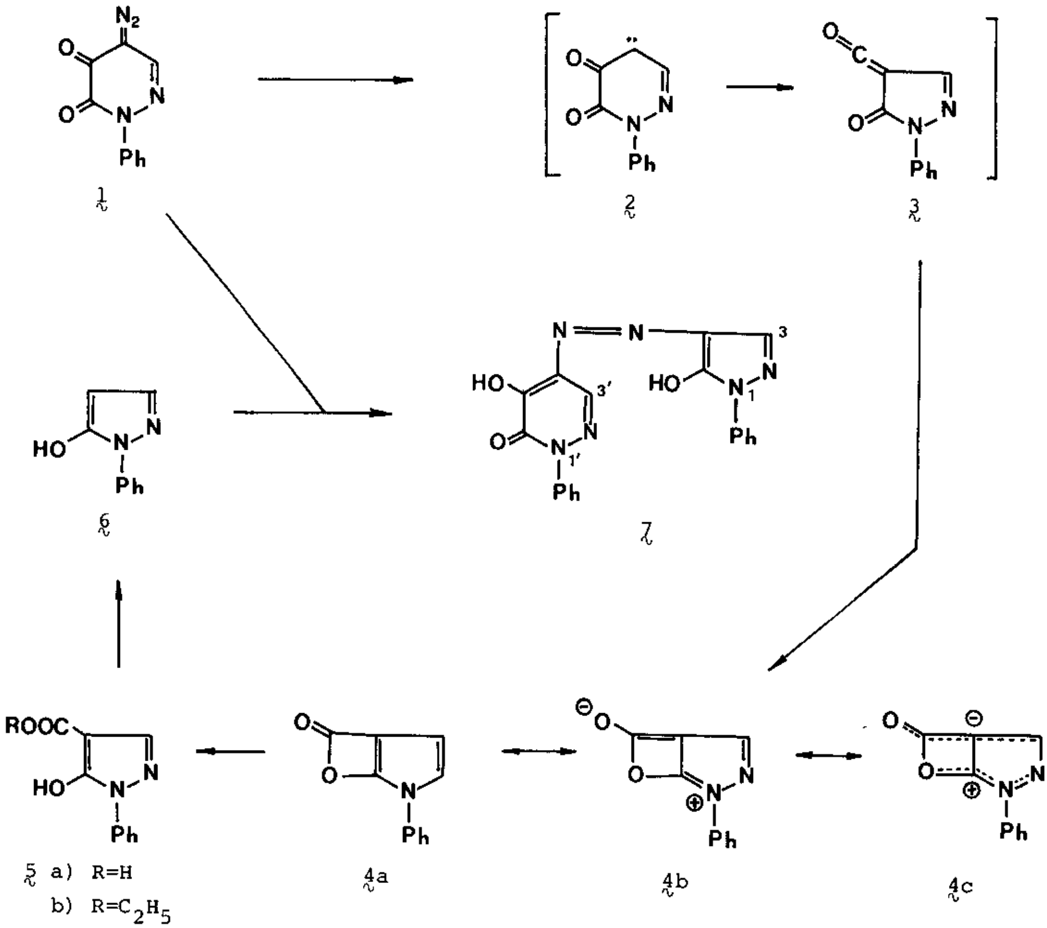
Abstract - Conversion of 4-diazo-1-phenyl-5,6-dioxo-1,4,5,6-tetrahydropyridazine into "pyrazolo-lactone", from which different 5-hydroxy-1-phenyl-pyrazoles can be formed in the solid state, is described.

Several examples of ring contraction of substituted pyridazinones into pyrazole derivatives either under basic or acidic conditions have been reported[2-6]. On the other hand, since the Süss´s first report[7], a number of heterocyclic carboxylic acids and their derivatives has been prepared from heterocyclic α-diazo ketones[8] either by thermal or photochemical Wolff rearrangement[9]. 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 ester[10].

In continuation of our studies in the series of heterocyclic α-diazo ketones[11-14] 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 stricktly anhydrous conditions, it was quantitatively transformed into a new compound with mp. 99-100° ((nmr ($CDCl_3$) $\tau$ = 2,3-2,7(m,$C_6H_5$), 2,5(s,$H_3$), 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 $C_{10}H_6N_2O_2$.



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 ∿2100 $cm^{-1}$ 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-thiobenzpropiolactone[17].

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 **5**a (mp. 92°, nmr ($CDCl_3$) $\tau$ = 2,3-2,7 (m, $C_6H_5$), 2,15 (s, $H_3$), 5,6 (broad s, OH) ; the compound is in every respect identical with the authentic sample prepared by the known method[19]), or ethyl ester (**5**b) (mp. 118°, nmr ($CDCl_3$) $\tau$ = 2,0-2,6 (m, $C_6H_5$), 2,15 (s, $H_3$), 8,55 (t, $CH_2C\underline{H}_3$), 5,55 (q, $C\underline{H}_2CH_3$), $J_{CH_2CH_3}$ = 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 stricktly 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 (**5**a) (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 (**5**a), 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 method[19]). To this the coupling of the starting diazo compound (**1**) took place affording the azo compound (**7**) ((mp. 260-262° analyzing for $C_{19}H_{14}N_6O_3$, ms $M^+$ = 374, nmr (DMSO-$d_6$) $\tau$ = 1,65 (s, $H_3'$), 1,81 (s, $H_3$), 2.1 (m) and 2,5 (m) (1-$C_6H_5$), 2,5 (broad s) 1'-$C_6H_5$)) 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 $8^{O}K$. 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 $77^{O}K$ [18].

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