

Synthesis and spectral properties of diazonium pyridazinones

^aV. KONEČNÝ and ^bŠ. KOVÁČ

^aResearch Institute of Agrochemical Technology,
CS-836 03 Bratislava

^bDepartment of Organic Chemistry, Slovak Technical University,
CS-812 37 Bratislava

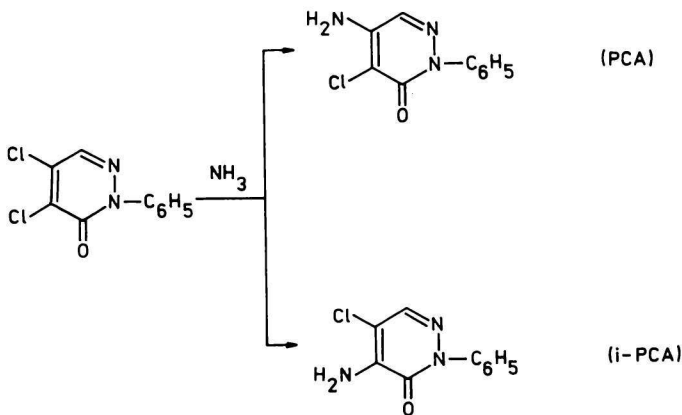
Received 9 June 1981

Accepted for publication 16 December 1982

Synthesis and spectral properties of 4-diazo-3,5-dioxo-2-phenyl-2*H*-pyridazine and 5-diazo-3,4-dioxo-2-phenyl-2*H*-pyridazine are described.

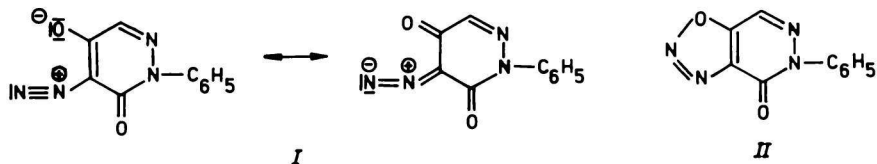
Описаны синтез и спектральные характеристики 4-диазо-3,5-диоксо-2-фенил-2*H*-пиридазина и 5-диазо-3,4-диоксо-2-фенил-2*H*-пиридазина.

By cultivation of the sugar beet the most used herbicide is Pyramin (5-amino-2-phenyl-4-chloro-3-oxo-2*H*-pyridazine, PCA) [1] made by aminating 4,5-dichloro-2-phenyl-3-oxo-2*H*-pyridazine. Besides the main product PCA its isomer 4-amino-5-chloro-2-phenyl-3-oxo-2*H*-pyridazine (i-PCA) in the amount 7—15 % is also formed [2—4] (Scheme 1).



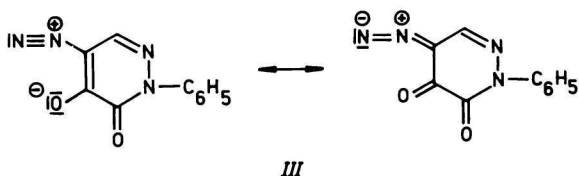
Scheme 1

By the action of nitric acid on the i-PCA two compounds (*I* and *II*) can be assumed to form



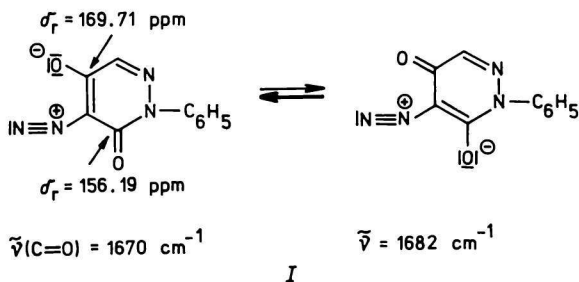
However, by the action of copper(I) chloride on the product of the reaction of i-PCA with sodium nitrite 2-phenyl-5-hydroxy-4-chloro-3-oxo-2*H*-pyridazine [5] is formed, which eliminates compound *II*.

Compound *I* is very stable [6], less reactive and does not afford all reactions of diazonium salts, while compound *III* formed by the action of nitric acid on PCA is unstable, highly reactive and affords a characteristic reaction of diazonium salts [7].



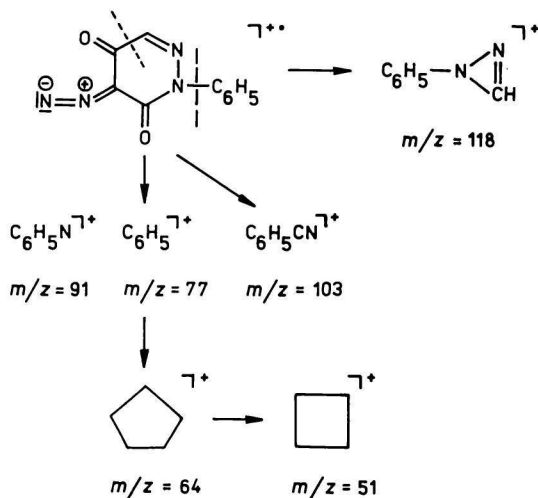
This phenomenon can be explained by the strong electronwithdrawing influence of the carbonyl group in position 3.

The u.v. spectrum of compound *I* shows three absorption bands, λ_{\max}/nm ($\log \{\epsilon\}$): 220 (4.15), 240 (4.05), and 310 (3.75). The i.r. spectrum of compound *I* shows intense bands at $\tilde{\nu} = 1670 \text{ cm}^{-1}$ and 1682 cm^{-1} indicating the presence of two carbonyl groups; the band at lower wavenumber being more intense, which can be explained by the presence of two forms of the compound



and the band at $\tilde{\nu} = 2170 \text{ cm}^{-1}$ indicating the presence of the diazonium group, $\tilde{\nu}(\text{N}^{\oplus} \equiv \text{N})$.

$^1\text{H-N.m.r.}$ spectrum of *I* showed a singlet at $\delta_r = 7.65$ ppm which can be assigned to the proton of the pyridazinone ring and a multiplet at $\delta_r \approx 7.42$ ppm of the protons of the benzene ring. $^{13}\text{C-N.m.r.}$ spectrum of *I* showed the following carbon signals, δ_r/ppm : 169.71, 156.19, 139.82, 138.39, 128.90, 128.25, and 125.00. The presence of two signals at $\delta_r = 169.71$ ppm and 156.19 ppm assigned to the carbonyl and the $=\text{C}-\text{O}^-$ groups, respectively, confirms the structure of *I*. The mass spectrum of *I* showed a molecular peak with $m/z = 214$ and fragment peaks with $m/z = 118, 103, 91, 77, 64,$ and 51 (Scheme 2).



Scheme 2

The u.v. spectrum of *III* showed three absorption bands, $\lambda_{\text{max}}/\text{nm}$: 208, 260, and 365. The i.r. spectrum of *III* showed bands at 1676 cm^{-1} , $\tilde{\nu}(\text{C}=\text{O})$ and 2130 cm^{-1} , $\tilde{\nu}(\text{N}\equiv\text{N})$. $^{13}\text{C-N.m.r.}$ spectrum of *III* showed the following signals, δ_r/ppm : 169.48, 155.20, 141.22, 132.04, 128.53, 127.77, and 125.43. All these spectral data confirm the structure of *III*.

Experimental

The u.v. spectra were recorded with a Specord UV VIS spectrophotometer (Zeiss, Jena) in methanol ($c = 2 \times 10^{-5}$ mol dm $^{-3}$, cell thickness 1.00 cm), the i.r. spectra with a UR 20 instrument (Zeiss, Jena) in chloroform ($c = 6 \times 10^{-2}$ mol dm $^{-3}$, cell thickness 0.089 cm), $^1\text{H-n.m.r.}$ spectra with a Tesla BS 487 C apparatus (80 MHz) in DMSO- d_6 with tetramethylsilane as an internal standard, $^{13}\text{C-n.m.r.}$ spectra with a Jeol FX 100 instrument (25 MHz) in

deuteriochloroform using tetramethylsilane as an internal reference, mass spectra with an AEI MS 902 S instrument at 70 eV, ionization chamber temperature 70 °C.

4-Diazo-3,5-dioxo-2-phenyl-2H-pyridazine (I)

To concentrated hydrochloric acid (750 cm³) a powdered 4-amino-2-phenyl-5-chloro-3-oxo-2H-pyridazine (0.5 mol) and sodium nitrite (1.5 mol) were added with stirring at 20–22 °C over 90 min. Stirring was continued at the same temperature for 2 1/2 h and at 85–90 °C for 1 h. After cooling the crude product was separated by filtration and crystallized from ethanol; m.p. = 114–115 °C.

For C₁₀H₆N₄O₂ (M_r = 214.20) w_i (calculated): 56.07 % C, 2.82 % H, 26.16 % N; w_i (found): 56.16 % C, 2.88 % H, 26.10 % N.

5-Diazo-3,4-dioxo-2-phenyl-2H-pyridazine (III)

To concentrated hydrochloric acid (700 cm³) a powdered 5-amino-2-phenyl-4-chloro-3-oxo-2H-pyridazine (0.5 mol) and sodium nitrite (1.5 mol) were added with stirring at 20–22 °C over 90 min. Stirring was continued at the same temperature for 3 h and at 85–90 °C for 1 h. After cooling to 5 °C the crude product was filtered off, washed with water and dried at 20 °C *in vacuo*; m.p. = 140 °C (decomposition).

For C₁₀H₆N₄O₂ (M_r = 214.20) w_i (calculated): 56.07 % C, 2.82 % H, 26.16 % N; w_i (found): 56.21 % C, 2.94 % H, 26.41 % N.

References

1. Fischer, A., *Weed Res.* 2, 177 (1962).
2. Rapoš, P., Winternitz, P., and Sohler, E., *Czech.* 122103 (1969).
3. Rapoš, P. and Winternitz, P., *Czech.* 120858 (1969).
4. Hensel, H., Baumann, H., and Dury, K., *Ger.* 1135115 (1959); *Chem. Abstr.* 58, 2526a (1963).
5. Sohler, E., Rapoš, P., Macko, J., and Seidler, L., *Czech.* 183942 (1978).
6. Eichenberger, K., Staehelin, A., and Druvey, J., *Helv. Chim. Acta* 37, 837 (1954).
7. Dury, K., *Angew. Chem.* 77, 282 (1965).

Translated by Š. Kováč