

Structure of the reaction product of α,β -dichloro- β -formylacrylic acid with phenylhydrazinium chloride

^aV. KONEČNÝ and ^bŠ. KOVÁČ

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

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

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By the reaction of α,β -dichloro- β -formylacrylic (mucochloric) acid with phenylhydrazinium chloride phenylhydrazone of α,β -dichloro- β -formylacrylic acid is formed. Its structure was proved by i.r., u.v., ¹H-n.m.r., ¹³C-n.m.r., and mass spectra.

В результате реакции α,β -дихлор- β -формилакриловой кислоты (мукохлористой) с хлоридом фенолгидразиния образуется фенолгидразон α,β -дихлор- β -формилакриловой кислоты. Его структура была доказана ИК, УФ, ¹H-ЯМР, ¹³C-ЯМР и масс-спектроскопическими методами.

It is known that the most used and active herbicide by cultivation of the sugar beet is 2-phenyl-4-chloro-5-amino-3-oxo-2H-pyridazine (Pyramin, Burex). It was prepared by the reaction of phenylhydrazine with mucochloric acid catalyzed by hydrochloric acid. The product formed in the course of reaction is not isolated but directly cyclized to 2-phenyl-4,5-dichloro-3-oxo-2H-pyridazine (PCC): In this way prepared PCC was aminated by using gaseous ammonia to form 2-phenyl-4-chloro-5-amino-3-oxo-2H-pyridazine (PCA) as a main product and 2-phenyl-4-amino-5-chloro-3-oxo-2H-pyridazine (i-PCA) as a by-product.

Although the product of the reaction of mucochloric acid has been already isolated before, two its structures are reported [1—4] but none of them was proved. This paper deals with the synthesis and the determination of the structure of the above reaction product.

Experimental

Into the solution of mucochloric acid (0.01 mol) in water (330 ml) phenylhydrazinium chloride (0.1 mol) dissolved in water (100 ml) was added under stirring at 20 °C. Stirring

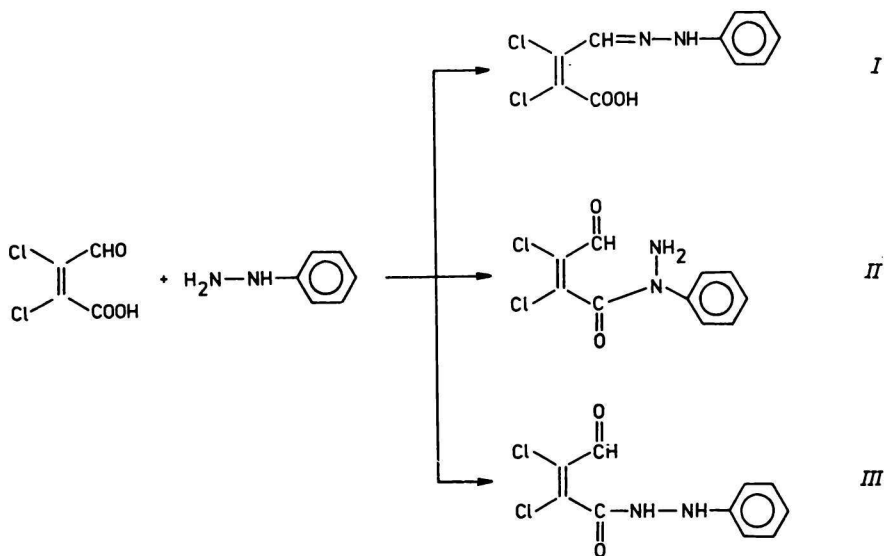
was continued for further 30 min at the same temperature. The excluded yellow compound was filtered off, washed with water and alcohol to neutral reaction and dried at 40 °C. A yellow compound was obtained, m.p. 133—136 °C (in sealed tube) (Ref. [1] reports m.p. 126 °C), in 80 % yield.

For $C_{10}H_7Cl_2N_2O_2$ (258.06) calculated: 46.54 % C, 2.73 % H, 27.47 % Cl, 10.85 % N; found: 46.66 % C, 2.81 % H, 27.40 % Cl, 10.92 % N.

The u.v. spectrum was recorded with a Specord UV VIS (Zeiss, Jena) in methanol ($c = 5 \times 10^{-5}$ mol dm⁻³, cell thickness 1.00 cm), i.r. spectrum with a UR 20 (Zeiss, Jena) in KBr tablets (0.8 mg of compound/300 mg KBr), ¹H-n.m.r. and ¹³C-n.m.r. spectra with an FX-60 Jeol in dimethyl sulfoxide (DMSO_{d-6}) (using tetramethylsilane as an internal reference), mass spectrum (70 eV) with an MS 901 S, the temperature of ionization chamber 90 °C.

Results and discussion

By the reaction of mucochloric acid with phenylhydrazine a formation of the following compounds can be assumed



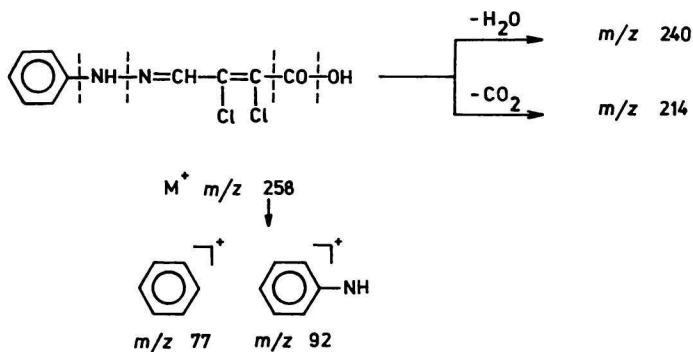
Evidently, only compounds *I* and *II* can afford 2-phenyl-4,5-dichloro-3-oxo-2H-pyridazine by cyclization.

The u.v. spectrum of the obtained reaction product shows five absorption bands, $\lambda_{\text{max}}/\text{nm}$ ($\log \epsilon$): 203 (4.22), 230 (3.98), 250 (4.02), 300 (3.85), and 357 (3.85). The first two bands were assigned to the chromophore system C_6H_5NH and further

bands to the chromophore conjugated system $-\text{N}=\text{CH}-\text{C}=\text{C}-\text{COOH}$, the band at the longest wavelength being the most intense.

The i.r. spectrum showed several bands from which the most significant are: the band at 915 cm^{-1} , $\gamma(\text{COH})$ and the band at 1685 cm^{-1} , $\nu(\text{C}=\text{O})$ indicate the presence of the conjugated carboxyl group. The bands at 1600 cm^{-1} can be assigned to the vibration of the $\text{C}=\text{C}$ and $\text{C}=\text{N}$ bonds and the band at 3275 cm^{-1} to the vibration of the $\text{N}-\text{H}$ bonds participating in intermolecular hydrogen bonding. $^1\text{H-N.m.r.}$ spectrum of compound studied showed four groups of proton signals. A singlet at 4.17 p.p.m. is wide, pointing to the proton attached to the nitrogen atom (NH group); a multiplet at 7.12 p.p.m. belongs to the aromatic protons, singlet at 8.73 p.p.m. can be assigned to the proton of the methine group ($=\text{CH}$) and a singlet at 11.31 p.p.m. to the proton of the carboxyl group (COOH). $^{13}\text{C-N.m.r.}$ spectrum of compound studied showed these signals: a signal at 162.84 p.p.m. can be assigned to the carbon of the carboxyl group, signals at 143.88 p.p.m. to the carbon of the $-\text{C}(\text{Cl})=\text{C}(\text{Cl})\text{COOH}$ group and a signal at 141.93 p.p.m. to the carbon of the $\text{CH}=\text{N}$ group and signals in the region of 137.58—112.98 p.p.m. to the carbons of the benzene ring.

In the mass spectrum of compound studied a molecular peak with m/z 258 and fragment peaks with m/z 240, 149, 92, and 77 can be seen



A peak with m/z 240 is formed by a loss of water $M-18$ and other intense peaks by cleavage of $\text{C}-\text{N}$, $\text{N}-\text{N}$, and $\text{C}-\text{C}$ bonds. From the given spectral data it follows that the reaction product of mucochloric acid with phenylhydrazine has the structure I.

References

1. Dury, K., *Angew. Chem.* 77. 282 (1965).
2. Avota, L. Yu., Ozolin, N. J., and Giller, C. A., *Izv. Akad. Nauk Latv. SSR, Ser. Khim.* 1967. 347.
3. Fischer, A., *Weed Res.* 2. 177 (1962).
4. Giller, C. A., Avota, L. Yu., and Ozolin, N. J., *Izv. Akad. Nauk Latv. SSR, Ser. Khim.* 1968, 348.

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