

Synthesis, spectral properties, and hydrogen bonding of 4-(*O,O*-dialkyl(diaryl)phosphoryl(thiophosphoryl))hydrazono-2,3-dichloro-2-butenoic acids

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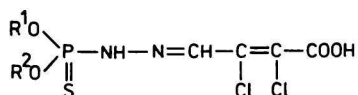
Dedicated to Professor RNDr. V. Sutoris, CSc., in honour of his 60th birthday

The synthesis of twelve novel 4-(*O,O*-dialkyl(diaryl)phosphoryl(thiophosphoryl))hydrazono-2,3-dichloro-2-butenoic acids by the reaction of *O,O*-dialkyl(diaryl)phosphoryl(thiophosphoryl)hydrazines with 3-formyl-2,3-dichloro-2-propenoic acid is described. Infrared, ultraviolet, and ¹H NMR spectra of the prepared compounds forming intramolecular hydrogen bonds of the C=O···H-C=, O-H···Cl, and N-H···Cl types are interpreted.

Описан синтез двенадцати новых 4-(*O,O*-диалкил(диарил)фосфорил(тиофосфорил))гидразоно-2,3-дихлор-2-бутеновых кислот посредством реакции *O,O*-диалкил(диарил)фосфорил(тиофосфорил)гидразинов с 3-формил-2,3-дихлор-2-пропеновой кислотой. Интерпретируются ИК, УФ и ¹H ЯМР спектры полученных соединений, образующих внутримолекулярные водородные связи следующих типов: C=O···H-C=, O-H···Cl и N-H···Cl.

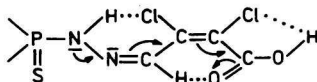
It is known that 3-formyl-2,3-dichloro-2-propenoic acid (mucochloric acid) is a reactive compound, a significant industrial intermediate used in organic synthesis, affording with phenylhydrazine an appropriate hydrazone which by cyclization and following amination afforded 2-phenyl-4-chloro-5-amino-3-oxo-2*H*-pyridazine as an active compound in preparations of Burex and Pyramin, respectively, significant herbicides used by cultivating of the sugar beet [1—6].

By cyclization of some phosphoryl- and thiophosphorylhydrazones of the mucochloric acid phosphoryl- and thiophosphoryl-3-methyl-5-oxopyrazoles, respectively, were formed [7]. The prepared compounds of the formula

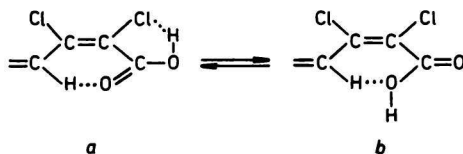


were used as starting compounds in the synthesis of pesticides. The synthesis of novel compounds was carried out in ethanol and hydrocarbon solvents. The yields of the prepared compounds (Table 1) were high (69.3—96.8 %) in all cases according to the both procedures.

In the infrared spectra of compounds prepared (Table 2) the $\nu(\text{N—H})$ medium intense bands are observed at $\tilde{\nu} \approx 3200 \text{ cm}^{-1}$, the wavenumber and the intensity of these bands were not changed even if strong dilution of compounds prepared was used. The low wavenumbers of these bands can be explained by the conjugation effects and by the presence of the $\text{N—H} \cdots \text{Cl}$ intramolecular hydrogen bond as observed in the spectra of similar compounds [8].



The observation of the two $\nu(\text{C=O})$ bands in the region of $\tilde{\nu} = 1660—1800 \text{ cm}^{-1}$ points out the presence of two conformers, while very intense bands at lower wavenumbers belong to the conformer *a* and weak bands at higher wavenumbers to the conformer *b*



The $\nu(\text{P=S})$ [9] bands in the infrared spectra of compounds prepared are observed in the region of $\tilde{\nu} = 642—669 \text{ cm}^{-1}$.

In the ^1H NMR spectra of compounds prepared measured in CDCl_3 (Table 2) two signals of the OH protons are observed in the region of $\delta = 10.00—10.93 \text{ ppm}$ pointing to the conformers *a* and *b*. In the spectra measured in $\text{DMSO}-d_6$ two equally intense singlets are observed at $\delta \approx 10.2 \text{ ppm}$ and $\delta \approx 10.6 \text{ ppm}$ which in the temperature range $25—100 \text{ }^\circ\text{C}$ are shifted to lower δ values ($\delta \approx 9.8 \text{ ppm}$ and $\delta \approx 10.2 \text{ ppm}$), which is evidently connected with disruption of the $\text{S=O} \cdots \text{H—O}$ intermolecular hydrogen bonds. A similar shift to lower δ values is observed in the spectra at the signal of the N—H proton ($\delta \approx 6.6—7.0 \text{ ppm}$).

In the infrared spectra of compounds studied also the $\nu(\text{S—H})$ bands [10] in the region of $\tilde{\nu} = 2550—2626 \text{ cm}^{-1}$ are observed pointing to the presence of the tautomeric form *d*

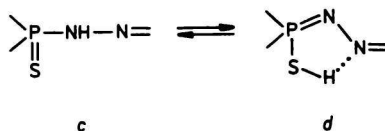
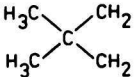


Table 1. Characterization of the synthesized compounds

Compound	R ¹	R ²	Formula	M _r	w _i (calc.)/% w _i (found)/%				Yield/%	M.p./°C
					N	S	P	Cl		
I	C ₂ H ₅	CH ₃	C ₇ H ₁₁ Cl ₂ N ₂ O ₄ PS	321.12	8.72	9.99	9.65	22.08	78.8	103–105
					8.78	10.47	9.56	22.50		
II	C ₂ H ₅	C ₂ H ₅	C ₈ H ₁₃ Cl ₂ N ₂ O ₄ PS	335.15	8.36	9.57	9.24	21.16	79.7	135–138
					8.27	10.30	9.08	21.01		
III	C ₂ H ₅	i-C ₃ H ₇	C ₉ H ₁₅ Cl ₂ N ₂ O ₄ PS	349.16	8.03	9.18	8.87	20.31	88.8	119–121
					8.67	10.42	8.55	20.73		
IV	C ₂ H ₅	i-C ₄ H ₉	C ₁₀ H ₁₇ Cl ₂ N ₂ O ₄ PS	363.14	7.72	8.83	8.53	19.52	84.2	95–98
					8.39	8.99	8.41	18.98		
V	C ₃ H ₇	C ₃ H ₇	C ₁₀ H ₁₇ Cl ₂ N ₂ O ₄ PS	363.14	8.07	9.24	8.92	20.42	69.3	85–88
					7.66	8.86	8.31	20.00		
VI	ClCH ₂ CH ₂	C ₃ H ₇	C ₉ H ₁₄ Cl ₃ N ₂ O ₄ PS	383.62	7.30	8.36	8.07	27.72	85.6	72–75
					6.64	8.44	8.02	27.96		
VII	i-C ₄ H ₉	i-C ₄ H ₉	C ₁₂ H ₂₁ Cl ₂ N ₂ O ₄ PS	391.25	7.16	8.19	7.92	18.12	96.8	116–117
					7.29	8.54	7.82	18.36		
VIII			C ₉ H ₁₃ Cl ₂ N ₂ O ₄ PS	347.28	8.07	9.23	8.92	20.42	94.5	170–172
					7.91	9.72	9.03	19.67		
IX	C ₆ H ₅	C ₆ H ₅	C ₁₆ H ₁₃ Cl ₂ N ₂ O ₄ PS	431.23	6.50	7.44	7.18	16.44	96.1	163–165
					6.72	8.27	7.23	17.04		
X ^a	C ₂ H ₅	C ₂ H ₅	C ₈ H ₁₃ Cl ₂ N ₂ O ₅ P	319.09	8.72	—	9.71	22.22	70.7	160–163
					9.97	—	9.67	22.65		
XI ^a	C ₄ H ₉	C ₄ H ₉	C ₁₂ H ₂₁ Cl ₂ N ₂ O ₅ P	375.19	7.47	—	8.25	18.89	72.0	130–132
					8.41	—	8.30	18.09		
XII ^b	C ₂ H ₅	C ₂ H ₅	C ₁₀ H ₁₈ ClN ₂ O ₄ PS ₂	360.80	7.77	17.77	8.58	9.82	93.1	75–77
					8.45	19.03	7.88	10.40		

a) Compounds contain the P=O group; b) compound contains the SC₂H₅ group in position 3 instead of the Cl atom.

Table 2

Infrared, ultraviolet, and ^1H NMR data of the synthesized compounds

Compound	$\bar{\nu}/\text{cm}^{-1}$						$\lambda_{\text{max}}/\text{nm}$	$\log (\epsilon/(\text{m}^2 \text{mol}^{-1}))$	δ/ppm		
	$\nu(\text{NH})$	$\nu(\text{SH})$	$\nu(\text{C}=\text{O})$	$\nu(\text{P}=\text{S})$	=CH-	OH					
I	3200	2600	1789	1687	643	637	286	3.34	8.60	10.07	10.81
II	3200	2555	1795	1687	666	644	287	3.32	8.62	10.15	10.75
III	3200	2556	1789	1681	657	636	286	3.34	8.64	10.13	10.91
IV	3200	2561	1789	1680	659	643	287	3.19	—	—	—
V	3202	2551	1791	1688	664	641	287	3.28	8.63	10.18	10.62
VI	3164 ^a	—	1780	1673	660	—	300 ^b	2.64	—	—	—
VII	3200	2553	1787	1680	659	651	285	3.37	8.65	10.16	10.87
VIII	3200 ^a	2621	1780	1718	669	646	284	3.37	8.62	10.46	10.93
IX	3200 ^a	2626	1780	1716	664	642	285	3.28	9.00	10.78	11.50
X	3191	—	1751	1666	c	—	280	3.28	8.62	10.00	10.37
XI	3181	—	1753	1664	d	—	278	3.32	8.63	10.05	10.45
XII	3200	2562	1786	1679	651	640	291	3.32	8.51	10.06	10.41

a) Measured in CH_3CN ; b) additional band at $\lambda = 224 \text{ nm}$ $\log (\epsilon/(\text{m}^2 \text{mol}^{-1}))$, $\nu(\text{P}=\text{O})$, $\bar{\nu}/\text{cm}^{-1}$; c) 1261; d) 1257.

while the tautomeric form *d* is stabilized by the S—H···N intramolecular hydrogen bond.

In the ultraviolet spectra of compounds prepared only one very intense band (Table 2) at $\lambda \approx 285$ nm ($\log(\epsilon/(\text{m}^2 \text{mol}^{-1})) \approx 3.30$) is observed, which is in agreement with the presence of the conjugated system with intramolecular hydrogen bonds enabling a stabilization of the *s-cis* conformer *b*.

Experimental

Procedure A

To 3-formyl-2,3-dichloro-2-propenoic acid (0.1 mol) in ethanol (100 cm³) an appropriate phosphoryl- and thiophosphorylhydrazine, respectively, (0.1 mol) was added with stirring at room temperature. The reaction mixture was stirred for further 4—5 h at room temperature. The completion of the reaction was followed by the thin-layer chromatography. After completion of the reaction ethanol was distilled off under reduced pressure and the residue purified by crystallization from cyclohexane or toluene.

Procedure B

To 3-formyl-2,3-dichloro-2-propenoic acid and 3-ethylthio-3-formyl-2-chloro-2-propenoic acid, respectively, (0.1 mol) in benzene, toluene or xylene (100 cm³) an appropriate phosphoryl- and thiophosphorylhydrazine was added with stirring and then the reaction mixture was heated to reflux and forming water was azeotropically distilled off. After completion of the reaction the reaction mixture was cooled and the solvent was distilled off under reduced pressure. The crude product was purified by crystallization from cyclohexane or toluene.

TLC was carried out on aluminium plates Silufol (Lachema, Brno) in the system benzene—acetone (volume ratio = 9 : 1). The detection was carried out with the 0.5 % petroleum ether solution of 2,6-dibromoquinone-4-chloroimide at 120 °C.

Infrared spectra of compounds prepared were recorded with a Specord IR 71 (Zeiss, Jena) instrument in tetrachloromethane ($c \approx 0.001$ — 0.1 mol dm^{-3}). The wavenumber calibration was checked against the spectrum of polystyrene. Ultraviolet spectra were recorded with a Unicam SP 8000 instrument in methanol ($c = 2 \times 10^{-5}$ — $5 \times 10^{-5} \text{ mol dm}^{-3}$, cell width 1 cm). ¹H NMR spectra were recorded with a Tesla BS 487 C (80 MHz) instrument in CDCl₃ and in DMSO-d₆.

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