Furan derivatives. LXXIII.
Synthesis and properties of *O*-(R-carbamoyl)-5-(X-phenyl)-2-furaldehyde oximes

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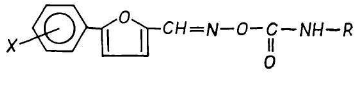
Preparation of new *O*-(R-carbamoyl)-5-(X-phenyl)-2-furaldehyde oximes by reaction of methyl and phenyl isocyanates with 5-(X-phenyl)-2-furaldehyde oximes is described. Infrared and ultraviolet spectra of the prepared compounds are interpreted and the results of tests of their pesticidal activity are given.

Описывается синтез новых *O*-(R-карбамоил)-5-(X-фенил)-2-фуральдегидоксимов реакцией метил- или же фенилизоцианатов с 5-(X-фенил)-2-фуральдегидоксимами. Обсуждаются их ИК и УФ спектры и приводятся результаты испытания их пестицидного воздействия.

Carbamates derived from 2-furaldehyde oxime and 5-nitro-2-furaldehyde oxime possessing significant insecticidal, fungicidal, and herbicidal properties are known from the literature [1, 2]. The aim of this work was to prepare carbamates with the phenyl group in the position 5 of the furan ring substituted by various substituents and to find out their physicochemical properties as well as their possible pesticidal efficiencies.

By a reaction of methyl and phenyl isocyanates with appropriate 5-(X-phenyl)-2-furaldehyde oximes, *O*-(R-carbamoyl)-5-(X-phenyl)-2-furaldehyde oximes of the following general formula were synthesized



where X = H, 4-CH_3O, 4-CH_3, 4-Br, 4-Cl, 4-NO_2, 3-NO_2, 2-NO_2;
R = CH_3, phenyl.

Table 1

Characteristics of *O*-(R-carbamoyl)-5-(X-phenyl)-2-furaldehyde oximes

No.	X	R	Formula	*M*	Calculated/found % C	% H	% N	% Hal	Yield %	M.p. °C
I	4-CH_3O	CH_3	$C_{14}H_{14}N_2O_4$	274.26	61.21	5.13	10.21		85.6	143–145
					61.38	5.03	10.19			
II	4-CH_3	CH_3	$C_{14}H_{14}N_2O_3$	258.24	65.08	5.45	10.84		73.8	162–164
					65.23	5.37	10.73			
III	H	CH_3	$C_{13}H_{12}N_2O_3$	244.22	63.90	4.94	11.06		70.[illegible]	163–165
					64.12	5.02	11.26			
IV	4-Br	CH_3	$C_{13}H_{11}BrN_2O_3$	323.13			8.63	24.72	78.6	139–140
							8.54	24.70		
V	4-Cl	CH_3	$C_{13}H_{11}ClN_2O_3$	278.65			10.05	12.82	71.2	135–137
							10.12	12.94		
VI	4-NO_2	CH_3	$C_{13}H_{11}N_3O_5$	289.22	53.96	3.82	14.54		97	123–125
					53.85	3.95	14.47			
VII	3-NO_2	CH_3	$C_{13}H_{11}N_3O_5$	289.22	53.96	3.82	14.54		95.6	140–142
					54.08	3.78	14.39			
VIII	2-NO_2	CH_3	$C_{13}H_{11}N_3O_5$	289.22	53.96	3.82	14.54		66	102–104
					54.25	3.89	14.64			
IX	4-CH_3O	Phenyl	$C_{19}H_{16}N_2O_4$	336.3	67.83	4.78	8.32		92	121–123
					67.90	5.01	8.40			
X	4-CH_3	Phenyl	$C_{19}H_{16}N_2O_3$	320.31	71.24	5.03	8.74		91	119–120
					71.38	5.00	8.56			
XI	H	Phenyl	$C_{18}H_{14}N_2O_3$	306.29	70.52	4.60	9.14		82	102–103
					70.58	4.78	9.36			
XII	4-Br	Phenyl	$C_{18}H_{13}BrN_2O_3$	385.19			7.27	20.74	87	143–144
							7.32	20.84		
XIII	4-Cl	Phenyl	$C_{18}H_{13}ClN_2O_3$	340.72			8.23	10.42	85	133–135
							8.29	10.50		
XIV	4-NO_2	Phenyl	$C_{18}H_{13}N_3O_5$	351.29	61.51	3.72	11.95		85	146–148
					61.46	3.78	12.03			
XV	3-NO_2	Phenyl	$C_{18}H_{13}N_3O_5$	351.29	61.51	3.72	11.95		91	140–142
					61.65	3.86	12.05			
XVI	2-NO_2	Phenyl	$C_{18}H_{13}N_3O_5$	351.29	61.51	3.72	11.95		84	126–128
					61.58	3.80	12.09			

Table 2

Infrared data ν(CO) of the prepared *O*-(R-carbamoyl)-5-(X-phenyl)-2-furaldehyde oximes

No.	X	CCl_4							$CHCl_3$						
		ν_s			ν_{as}			$\nu_s - \nu_{as}$	ν_s			ν_{as}			$\nu_s - \nu_{as}$
		ν	$\Delta\nu_{1/2}$	ϵ	$\tilde{\nu}$	$\Delta\nu_{1/2}$	ϵ		$\tilde{\nu}$	$\Delta\nu_{1/2}$	ϵ	$\tilde{\nu}$	$\Delta\nu_{1/2}$	ϵ	
I	4-CH_3O	1779	23.7	153	1761	23.7	270	18	1774	23.5	360	1754		120	20
II	4-CH_3	1780.5	17.5	160	1761.5	22.5	285	19	1775.5	23.5	335	1758		115	17.5
III	H	1782	28.5	170	1735.5	30	210	46.5	1777	24	270	1762		120	15
IV	4-Br	1761	17.5	585	—	—	—	—	1742	23.5	395	—	—	—	—
V	4-Cl	1788	14	238	1743	30	109	45	1776	22.5	340	1751	—	85	25
VI	4-NO_2	1763.5	23.5	270	1737.5	23.5	180	26	1781.5	27.3	215	1744.5	31	283	37
VII	3-NO_2	1763	25	155	1737	25	120	26	1780	30	127	1743.5	32.5	210	36.5
VIII	2-NO_2	1765	26.5	175	1739	26.5	120	26	1780.5	23.5	280	1749.5		75	31
IX	4-CH_3O	1778	—	s	sh	—	—	—	1753	28.5	465	—	—	—	—
X	4-CH_3	1767	—	s	sh	—	—	—	1752.5	27.5	366	—	—	—	—
XI	H	1765.5	—	s	sh	—	—	—	1754	27.3	346	—	—	—	—
XII	4-Br	1767	—	s	sh	—	—	—	1756	26	635	—	—	—	—
XIII	4-Cl	1767	—	s	sh	—	—	—	1757	27	640	—	—	—	—
XIV	4-NO_2	1769	—	s	sh	—	—	—	1758	27.5	595	—	—	—	—
XV	3-NO_2	1766	—	s	sh	—	—	—	1751.5	31	400	—	—	—	—
XVI	2-NO_2	1770	—	s	sh	—	—	—	1755	26	565	—	—	—	—

s — saturated solution, sh — shoulder.

The compounds *I—VIII* (Table 1) were prepared by a reaction of appropriate oximes and isocyanates in the presence of triethylamine as catalyst. Formation of side products was not observed in these reactions. However, when the compounds *IX—XVI* (Table 1) were prepared in the presence of the catalyst mentioned, 5-(X--phenyl)-2-furancarbonitriles were obtained as by-products in addition to carbamates. The amount of the new-formed nitrile increased with increasing reaction temperature and with prolongation of the reaction time. In some cases (*e.g.* for X = NO_2) almost a quantitative yield of nitriles was reached. Therefore the compounds *IX—XVI* were prepared without using a catalyst. The synthesized compounds were yellow to orange-brown crystalline substances stable in the solid state and at room temperature. When heated in solutions, their decomposition occurred depending on the solvents used (the original components, nitriles, aniline, and carbamates were isolated). The results of a detailed study of the conditions of decomposition as well as of kinetic measurements will be presented in a subsequent paper.

The study of the i.r. spectra of the investigated compounds [3] proved that the high values of wavenumbers of the bands in the region of 1735—1780 cm^{-1} could not be explained by electric effects of the substituents, but must be treated in terms of vibrational interactions similarly as in the case of acid anhydrides [4].

In the spectra of the compounds *I—VIII* measured in chloroform (Table 2) it was observed that the wavenumber of the ν_s band increased with an increasing electron-withdrawing nature of the substituents (1777—1781 cm^{-1}) while the ν_{as} decreased (1754—1744 cm^{-1}). This phenomenon could be explained by different degree of vibrational interaction, due to the differently influenced C=O and C=N groups, as evident from the ratio of both bands intensities. This assumption was also supported by the increasing differences in wavenumbers ($\Delta\nu = 18 \rightarrow 26$).

In the spectra of compounds *IX—XVI* measured in chloroform only one absorption band was observed. High values of the half-band width as well as of absorptivities pointed to a coincidence of the absorption bands ν_s and ν_{as}.

Because of a small thermal stability of the synthesized compounds, we failed in finding the temperature dependence of the studied ν_s and ν_{as} bands. Both compounds decomposed on heating in chloroform or carbon tetrachloride and their spectra changed in the entire i.r. region.

In accordance with a longer conjugated system, the u.v. spectra of compounds *IX—XVI* showed λ_{max} at higher wave (λ_{max} 327—308 nm, log ε = 4.56—4.26) than those of the compounds *I—VIII* (λ_{max} 314—298 nm, log ε = 4.54—4.30). The position and the nature of the substituent affects the u.v. spectra in the same way as it was observed with other compounds of the arylfuran series [5, 6].

Investigation of insecticidal, acaricidal, fungicidal, and herbicidal activity showed that none of the studied compounds was more efficient than the currently used compounds.

Experimental

The starting 5-(X-phenyl)-2-furaldehyde oximes were prepared according to [7, 8].

The i.r. spectra (800—3650 cm^{-1}) were measured in KBr pellets (2 mg compound/1 g KBr) using a double-beam UR-20 spectrophotometer. The spectra of compounds in the 1900—1500 cm^{-1} region were taken in chloroform and carbon tetrachloride.

The u.v. spectra were taken on a Specord UV-VIS (Zeiss, Jena) recording spectrophotometer in the 200—480 nm region at room temperature using cells of 1 cm thickness; concentration 2.5—5.0 × 10^{-5} M in dioxan of spectral grade.

O-(Methylcarbamoyl)-5-(X-phenyl)-2-furaldehyde oximes (I—VIII)

To 5-(X-phenyl)-2-furaldehyde oxime (0.05 mole) dissolved in benzene (*ca.* 100 ml), methyl isocyanate (0.05 mole) and triethylamine (0.1 ml) were added under stirring. The reaction mixture was stirred for 6 hrs at room temperature. The separated product was filtered off and washed thoroughly with benzene.

O-(Phenylcarbamoyl)-5-(X-phenyl)-2-furaldehyde oximes (IX—XVI)

To 5-(X-phenyl)-2-furaldehyde oxime (0.01 mole) dissolved in benzene (*ca.* 60—100 ml), phenyl isocyanate (0.011 mole) was added and the reaction mixture was maintained at the boiling point of solvent for one hour. After cooling the reaction mixture, the separated product was filtered off and washed thoroughly with benzene.

Testing of pesticidal activity

Pesticidal activity was determined according to [9—11]. For testing the synthesized compounds the following test-organisms were used: Insecticidal activity was followed on *Musca domestica* L., *Calandra granaria* L., systemic insecticidal activity on *Macrosyphoniella sanborni* THEOB., acaricidal activity on *Tetranychus urticae* KOCH, ovicidal activity on the eggs of *Tetranychus urticae* KOCH, and contact insecticidal activity on *Aphis fabae* SCOP.

Fungicidal activity was determined by both *in vitro* and *in vivo* methods. The inherent activity was tested on the spores of the fungi *Sclerotinia fructicola* (WINT.), *Aspergillus niger* TIEGH, *Fusarium nivale* (FR). *Ces.*, *Alternaria sp.*, and *Stemphylium sarcinoformae* (CAV.) *Withshire*, using the method proposed by Sharvell. Antifungal activity on living plants was tested on barley, sort Dunajský trh (*Erysiphe graminis* DC.), on cucumbers, sort Znojemské (*Erysiphe cichoracearum* DC.), and on tomatoes (*Phytophtora infestans de* BY).

The herbicidal activity was determined by the method of preemergence (into the soil) and postemergence (to the leaf) application on *Avena sativa*, *Polygonum persicaria*, *Fagopyrum sagitatum*, and *Sinapis alba*.

References

1. Nakanishi, M., Saheki, T., and Ao, H., *Jap. Patent* 43218 (1971); *Chem. Abstr.* ***76***, 45978 (1972).
2. Kureha Chem. Ind. Co. Ltd., *Jap. Patent* 32719 (1970), *Jap. Patent*, Rep. Vol. R., No. 41 (1970).
3. Piklerová, A. and Jedlovská, E., *Zborník prednášok II. konferencie organických chemikov v Smoleniciach.* (Proceedings of the Conference of Organic Chemists at Smolenice.) May 1973, p. 202.
4. Abramovitch, R. A., *J. Chem. Soc.* ***1957***, 1413.
5. Krutošíková, A., Kováč, J., Frimm, R., Kováč, Š., and Sticzay, T., *Chem. Zvesti* ***25***, 142 (1971).

6. Krutošíková, A., *Thesis*. Slovak Technical University, Bratislava, 1970.
7. Frimm, R., Kováč, Š., and Giller, S. A., *Chem. Zvesti* ***23***, 916 (1969).
8. Oleinik, A. F., Vozyakova, T. I., Modnikova, G. A., and Novickii, K., Yu., *Khim. Geterotsikl. Soedin.* ***1972***, 1448.
9. Demečko, J. and Konečný V., *Agrochémia* ***10***, 5 (1970).
10. Furdík, M., Konečný, V., Šály, A., and Truchlik, Š., *Acta Facult. Rer. Natur. Univ. Comenianae (Chimia)* ***XII,*** 45 (1968).
11. Krutošíková, A., Konečný, V., Kováč, J., and Špirková, K., *Collect. Czech. Chem. Commun.*, in press.

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