

PREPARATION OF O-(METHYL- AND ARYLCARBAMOYL)-5-NITROPHENYL-2-FURALDEHYDOXIMES*

A. KRUTOŠÍKOVÁ^a, V. KONEČNÝ^b, J. KOVÁČ^a and K. ŠPIRKOVÁ^a

^a Department of Organic Chemistry,

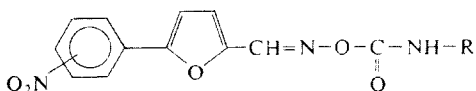
Slovak Technical University, 880 37 Bratislava, and

^b Research Institute for Agrochemical Technology, 810 04 Bratislava

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The preparation of new O-(methylcarbamoyl and arylcarbamoyl)-5-nitrophenyl-2-furaldehydoximes from methyl and arylisocyanates and 5-nitrophenyl-2-furaldehydoximes as reaction components is described.

In continuation of our study of arylfuran derivatives we synthesized *via* the reaction of nitrosubstituted 5-phenyl-2-furaldehydoximes^{1,2} with isocyanates O-(R-carbamoyl)-5-nitrophenyl-2-furaldehydoximes of the general formula



From literature some carbamates are known which are derived from 2-furaldehydoxime or 5-nitro-2-furaldehydoxime and which have insecticidal, fungicidal and herbicidal properties^{3,4}. The aim of our study was the preparation of analogous compounds which would have in the position 5 of the furan nucleus a phenyl residue substituted in various positions with a nitro group, and testing of their pesticidal activity.

During the preparation of compounds *I*, *XXIII* and *XLV* triethylamine was used as catalyst. We observed no formation of by-products. Originally triethylamine was also used for the preparation of O-arylcarbamoyl-5-nitrophenyl-2-furaldehydoximes. We observed that in addition to the corresponding carbamate the nitrile of 5-nitrophenyl-2-furancarboxylic acid is also formed. The amount of the nitrile formed increases with increasing temperature and prolongation of the reaction time. The greatest amount of nitrile was obtained in the preparation of compound *II-XXII*.

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TABLE I
Synthesized O-(R-Carbamoyl)-5-(2-nitrophenyl)-2-furaldehydoximes

No	R	Formula (m.w.)	Calculated/Found		Yield, % m.p., °C
			% N	% Hal	
I	CH ₃ -	C ₁₃ H ₁₁ N ₃ O ₅ (289·2)	14·51	—	66·0
			14·22	—	102—104
II	C ₆ H ₅	C ₁₈ H ₁₃ N ₃ O ₅ (351·3)	11·95	—	65·3
			12·01	—	126—128
III	4-CH ₃ C ₆ H ₄	C ₁₉ H ₁₅ N ₃ O ₅ (365·4)	11·50	—	70·4
			11·69	—	64—66
IV	3-CH ₃ C ₆ H ₄	C ₁₉ H ₁₅ N ₃ O ₅ (365·3)	11·50	—	78·2
			11·78	—	100—102
V	4-CH ₃ OC ₆ H ₄	C ₁₉ H ₁₄ N ₃ O ₆ (381·3)	11·02	—	64·7
			10·90	—	105—107
VI	3-CH ₃ OC ₆ H ₄	C ₁₉ H ₁₄ N ₃ O ₆ (381·3)	11·02	—	68·2
			10·82	—	143—145
VII	2-CH ₃ OC ₆ H ₄	C ₁₉ H ₁₄ N ₃ O ₆ (381·3)	11·02	—	69·7
			11·31	—	127—129
VIII	4-FC ₆ H ₄	C ₁₈ H ₁₂ FN ₃ O ₅ (369·3)	11·40	—	81·2
			11·25	—	119—122
IX	4-ClC ₆ H ₄	C ₁₈ H ₁₂ ClN ₃ O ₅ (385·7)	10·90	9·20	80·4
			10·74	9·20	112—114
X	3-ClC ₆ H ₄	C ₁₈ H ₁₂ ClN ₃ O ₅ (385·7)	10·90	9·20	34·7
			10·72	9·35	136—139
XI	4-BrC ₆ H ₄	C ₁₈ H ₁₂ BrN ₃ O ₅ (430·2)	9·75	18·56	88·3
			9·91	18·50	117—120
XII	4-IC ₆ H ₄	C ₁₈ H ₁₂ IN ₃ O ₅ (477·2)	8·81	—	89·7
			8·58	—	119—121
XIII	4-Cl ₃ CC ₆ H ₄	C ₁₉ H ₁₂ Cl ₃ N ₃ O ₅ (468·6)	8·97	22·68	71·2
			8·59	22·60	147—149
XIV	4-NO ₂ C ₆ H ₄	C ₁₈ H ₁₂ N ₄ O ₇ (396·3)	14·12	—	89·8
			13·92	—	158—161
XV	3-NO ₂ C ₆ H ₄	C ₁₈ H ₁₂ N ₄ O ₇ (396·3)	14·12	—	91·0
			14·34	—	136—138
XVI	3-F ₃ CC ₆ H ₄	C ₁₉ H ₁₂ F ₃ N ₃ O ₅ (419·3)	10·03	—	58·2
			10·33	—	118—121
XVII	4-CH ₃ , 3-ClC ₆ H ₃	C ₁₉ H ₁₄ ClN ₃ O ₅ (399·8)	10·52	8·88	90·0
			10·49	8·90	145—148
XVIII	4-CH ₃ O, 3-ClC ₆ H ₃	C ₁₉ H ₁₄ ClN ₃ O ₆ (415·8)	10·08	8·52	84·0
			10·12	8·40	133—135
XIX	4-Cl, 3-F ₃ CC ₆ H ₃	C ₁₉ H ₁₁ ClF ₃ N ₃ O ₅ (453·7)	9·26	7·79	61·3
			9·42	8·02	107—109
XX	4,3-Cl ₂ C ₆ H ₃	C ₁₈ H ₁₁ Cl ₂ N ₃ O ₅ (420·2)	10·00	16·90	98·0
			10·09	16·88	139—141

TABLE I
(Continued)

No	R	Formula (m.w.)	Calculated/Found		Yield, % m.p., °C
			% N	% Hal	
XXI	4-Cl, 3-NO ₂ C ₆ H ₃	C ₁₈ H ₁₁ ClN ₄ O ₇ (430·7)	13·00	8·24	96·7
			12·72	8·24	125—127
XXII	2,4,5-Cl ₃ C ₆ H ₂	C ₁₈ H ₁₀ Cl ₃ N ₃ O ₅ (454·6)	9·22	23·35	97·0
			9·45	23·30	142—144

TABLE II
Synthesized O-(R-Carbamoyl)-5-(3-nitrophenyl)-2-furaldehydoximes

No	R	Formula (m.w.)	Calculated/Found		Yield, % m.p., °C
			% N	% Hal	
XXIII	CH ₃	C ₁₃ H ₁₁ N ₃ O ₅ (289·2)	14·51	—	95·6
			14·39	—	140—142
XXIV	C ₆ H ₅	C ₁₈ H ₁₃ N ₃ O ₅ (351·3)	11·95	—	87·4
			11·89	—	140—142
XXV	4-CH ₃ C ₆ H ₄	C ₁₉ H ₁₅ N ₃ O ₅ (365·3)	11·50	—	84·7
			11·23	—	139—142
XXVI	3-CH ₃ C ₆ H ₄	C ₁₉ H ₁₅ N ₃ O ₅ (365·3)	11·50	—	81·7
			11·36	—	145—147
XXVII	4-CH ₃ OC ₆ H ₄	C ₁₉ H ₁₄ N ₃ O ₆ (381·3)	11·02	—	80·2
			11·08	—	133—136
XXVIII	3-CH ₃ OC ₆ H ₄	C ₁₉ H ₁₄ N ₃ O ₆ (381·3)	11·02	—	89·7
			11·00	—	130—132
XXIX	2-CH ₃ OC ₆ H ₄	C ₁₉ H ₁₄ N ₃ O ₆ (381·3)	11·02	—	88·2
			11·11	—	154—156
XXX	4-FC ₆ H ₄	C ₁₈ H ₁₂ FN ₃ O ₅ (369·3)	11·40	—	81·2
			11·20	—	119—122
XXXI	4-ClC ₆ H ₄	C ₁₈ H ₁₂ ClN ₃ O ₅ (385·7)	10·90	9·20	84·4
			11·14	9·18	146—148
XXXII	3-ClC ₆ H ₄	C ₁₈ H ₁₂ ClN ₃ O ₅ (385·7)	10·90	9·20	99·0
			11·03	9·21	154—156
XXXIII	4-BrC ₆ H ₄	C ₁₈ H ₁₂ BrN ₃ O ₅ (430·2)	9·75	18·56	90·7
			10·02	18·71	144—146
XXXIV	4-IC ₆ H ₄	C ₁₈ H ₁₂ IN ₃ O ₅ (477·2)	8·81	—	94·3
			8·51	—	148—152
XXXV	4-Cl ₃ CC ₆ H ₄	C ₁₉ H ₁₂ Cl ₃ N ₃ O ₅ (468·6)	8·97	22·68	85·0
			9·28	22·60	147—150

TABLE II
 (Continued)

No	R	Formula (m.w.)	Calculated/Found		Yield, % m.p., °C
			% N	% Hal	
XXXVI	4-NO ₂ C ₆ H ₄	C ₁₈ H ₁₂ N ₄ O ₇ (396·3)	14·12	—	89·3
			13·82	—	149—152
XXXVII	3-NO ₂ C ₆ H ₄	C ₁₈ H ₁₂ N ₄ O ₇ (396·3)	14·12	—	88·6
			14·04	—	160—163
XXXVIII	3-F ₃ CC ₆ H ₄	C ₁₉ H ₁₂ F ₃ N ₃ O ₅ (419·3)	10·03	—	74·3
			10·26	—	148—151
XXXIX	4-CH ₃ , 3 ClC ₆ H ₃	C ₁₉ H ₁₄ ClN ₃ O ₅ (399·8)	10·52	8·88	98·0
			10·56	8·90	106—108
XL	4-CH ₃ O, 3-ClC ₆ H ₃	C ₁₉ H ₁₄ ClN ₃ O ₆ (415·8)	10·08	8·52	95·3
			10·20	8·59	150—152
XLI	4-Cl, 3-F ₃ CC ₆ H ₃	C ₁₉ H ₁₁ ClF ₃ N ₃ O ₅ (453·7)	9·26	7·79	93·0
			9·50	7·99	163—165
XLII	4,3-Cl ₂ C ₆ H ₃	C ₁₈ H ₁₁ Cl ₂ N ₃ O ₅ (420·2)	10·00	16·90	97·3
			10·30	17·10	142—144
XLIII	4-Cl, 3-NO ₂ C ₆ H ₃	C ₁₈ H ₁₁ ClN ₄ O ₇ (430·7)	13·00	8·24	94·7
			13·21	8·20	138—141
XLIV	2,4,5-Cl ₃ C ₆ H ₂	C ₁₈ H ₁₀ Cl ₃ N ₃ O ₅ (454·6)	9·22	23·35	98·2
			8·93	23·22	176—179

 TABLE III
 Synthetized O-(R-Carbamoyl)-5-(4-nitrophenyl)-2-furaldehydoximes

No	R	Formula (m.w.)	Calculated/Found		Yield, % m.p., °C
			% N	% Hal	
XLV	CH ₃	C ₁₃ H ₁₁ N ₃ O ₅ (289·2)	14·51	—	97·0
			14·47	—	123—125
XLVI	C ₆ H ₅	C ₁₈ H ₁₃ N ₃ O ₅ (351·3)	11·95	—	81·3
			11·72	—	146—148
XLVII	4-CH ₃ C ₆ H ₄	C ₁₉ H ₁₅ N ₃ O ₅ (365·3)	11·50	—	92·1
			11·02	—	129—131
XLVIII	3-CH ₃ C ₆ H ₄	C ₁₉ H ₁₅ N ₃ O ₅ (365·3)	11·50	—	88·0
			11·68	—	148—149
XLIX	4-CH ₃ OC ₆ H ₄	C ₁₉ H ₁₅ N ₃ O ₆ (381·3)	11·02	—	91·0
			10·99	—	127—129

TABLE III
(Continued)

No	R	Formula (m.w.)	Calculated/Found		Yield, % m.p., °C
			% N	% Hal	
<i>L</i>	3-CH ₃ OC ₆ H ₄	C ₁₉ H ₁₅ N ₃ O ₆ (381·3)	11·02 10·97	—	81·3 172—174
<i>LI</i>	2-CH ₃ OC ₆ H ₄	C ₁₉ H ₁₅ N ₃ O ₆ (381·3)	11·02 10·97	—	81·2 172—174
<i>LII</i>	4-FC ₆ H ₄	C ₁₈ H ₁₂ FN ₃ O ₅ (369·3)	11·40 11·26	—	79·3 146—148
<i>LIII</i>	4-ClC ₆ H ₄	C ₁₈ H ₁₂ ClN ₃ O ₅ (385·7)	10·90 10·51	9·20 9·32	96·2 186—188
<i>LIV</i>	3-ClC ₆ H ₄	C ₁₈ H ₁₂ ClN ₃ O ₅ (385·7)	10·90 10·65	9·20 9·11	99·0 145—147
<i>LV</i>	4-BrC ₆ H ₄	C ₁₈ H ₁₂ BrN ₃ O ₅ (430·2)	9·75 9·51	18·56 18·51	91·2 139—142
<i>LVI</i>	4-IC ₆ H ₄	C ₁₈ H ₁₂ IN ₃ O ₅ (477·2)	8·81 9·02	—	88·0 161—164
<i>LVII</i>	4-Cl ₃ CC ₆ H ₄	C ₁₉ H ₁₂ Cl ₃ N ₃ O ₅ (468·65)	8·97 8·88	22·68 22·46	93·8 181—183
<i>LVIII</i>	4-NO ₂ C ₆ H ₄	C ₁₈ H ₁₂ N ₄ O ₇ (396·3)	14·12 14·01	—	94·3 163—167
<i>LIX</i>	3-NO ₂ C ₆ H ₄	C ₁₈ H ₁₂ N ₄ O ₇ (396·3)	14·12 14·08	—	90·4 149—151
<i>LX</i>	3-F ₃ CC ₆ H ₄	C ₁₉ H ₁₂ F ₃ N ₂ O ₅ (419·3)	10·03 10·04	—	80·4 155—158
<i>LXI</i>	4-CH ₃ , 3-ClC ₆ H ₃	C ₁₉ H ₁₄ ClN ₃ O ₅ (399·8)	10·52 10·38	8·88 8·93	91·7 171—174
<i>LXII</i>	4-CH ₃ O, 3-ClC ₆ H ₃	C ₁₉ H ₁₄ ClN ₃ O ₆ (415·8)	10·08 10·30	8·52 8·72	84·2 126—129
<i>LXIII</i>	4-Cl, 3-F ₃ CC ₆ H ₃	C ₁₉ H ₁₁ ClF ₃ N ₂ O ₅ (453·7)	9·26 9·40	7·79 8·02	91·0 123—125
<i>LXIV</i>	4,3-Cl ₂ C ₆ H ₃	C ₁₈ H ₁₁ Cl ₂ N ₃ O ₅ (420·2)	10·00 10·16	16·90 17·10	62·5 177—179
<i>LXV</i>	4-Cl, 3-NO ₂ C ₆ H ₃	C ₁₈ H ₁₁ ClN ₄ O ₇ (430·7)	13·03 12·81	8·24 8·20	94·9 160—163
<i>LXVI</i>	2,4,5-Cl ₃ C ₆ H ₂	C ₁₈ H ₁₀ Cl ₃ N ₃ O ₅ (454·6)	9·22 8·91	23·75 23·40	98·0 182—185

For this reason we abandoned the use of the catalyst. In the absence of the catalyst we achieved the same results at room temperature and 8 hours, reaction time as at boiling temperature and 2 hours' refluxing (Table I–III).

In the IR spectra of the synthesized compounds the following values were observed: $\nu(\text{C}=\text{O})$ in the $1780\text{--}1781\text{ cm}^{-1}$ region (R = methyl) and $1752\text{--}1758\text{ cm}^{-1}$ region (R = aryl). The high values of the frequencies of C=O bonds indicate that they are due to the vibrational interactions of C=O and C=N bonds. A similar interaction is already known from literature⁵. From the UV spectra of the substances investigated we determined that λ_{max} at highest wave-lengths is observed in the 298 to 308 nm region, $\log \epsilon = 4.30$ (I–XXII), 313–334 nm, $\log \epsilon = 4.50$ (XXIII–XLIV), 357–365 nm, $\log \epsilon = 4.30$ (XLV–LXVI). The effect of the position of the nitro group on the benzene nucleus attached to the position 5 of the furan nucleus manifested itself in an analogous manner, discussed in our preceding papers⁶.

During the testing of the insecticidal acaricidal, ovidical and herbicidal effect we found that none of the mentioned compounds had an important effect. Compounds XLVI and LIV had a very good fungicidal effect in the tests with *Phytophthora infestans* de BY in comparison with a standard (O-phenylcarbamoyl-5-nitro-2-fural-dehydroxime) ED_{50} in p.p.m.: for compound XLVI 0.56; for LIV 0.74; for the standard 1.12

EXPERIMENTAL

The infrared spectra (800–3650) were measured on a two-beam spectrophotometer UR-20 in chloroform at a 0.02M concentration. The ultraviolet absorption spectra were measured on a recording spectrophotometer Specord UV VIS (Zeiss, Jena) in the 200–480 nm region. The measurements were carried out at room temperature in a cell of 1 cm strength in spectral dioxan at a $4 \cdot 10^{-5}$ mol/l concentration. The starting 5-nitrophenyl-2-furaldehydoximes were prepared according to literature^{1,2}.

O-Methylcarbamoyl-5-nitrophenyl-2-furaldehydoximes

2.9 g (0.05 mol) of methyl isocyanate and 0.1 ml of triphenylamine were added to 11.6 g (0.05 mol) of 5-nitrophenyl-2-furaldehydoxime dissolved in 100 ml of benzene under stirring. The mixture was stirred at 20–25°C for 6 hours. The separated product was filtered off and washed with benzene.

O-Arylcarbamoyl-5-nitrophenyl-2-furaldehydoximes

Aryl isocyanate (0.025 mol) was added under stirring at 15–20°C to a solution of 5.8 g (0.025 mol) of 5-nitrophenyl-2-furaldehydoxime in 100 ml of benzene and the stirring was continued for another 2 hours at reflux temperature. After cooling the separated product was filtered off and washed with benzene.

Testing of Pesticidal Activity

For the determination of pesticidal activity^{7,8} of the products synthesized we used the following test-organisms: Insecticidal activity was tested on *Musca domestica* L., *Calandra granaria* L.; systemic insecticidal activity was tested on *Macrosyphoniella sanborni* THEOB., acaricidal activity on *Tetranychus urticae* KOCH, ovicidal activity on the eggs of the same organism, and contact insecticidal activity on *Aphis fabae* SCOP. For the determination of the fungicidal activity both *in vitro* and *in vivo* tests were employed. The inherent activity proper was followed on the spores of the fungi *Sclerotinia fructicola* (WINT.), *Aspergillus niger* TIEGH, *Fusarium nivale* (FR.) Ces., *Alternaria* sp., *Stemphylium sarcinoformae* (CAV.) WITHSHIRE, using the method according to Sharvell; antifungal activity on living plants was tested on barley, var. Dunajský trh, contaminated by *Erysiphe graminis* DC on cucumbers var. Znojenské contaminated by *Erysiphe cichoracearum* DC, and tomatoes contaminated by *Phytophthora infestans* de BY.

For the determination of the herbicidal activity the method of pre-emergency application (into the soil) and post-emergency application (on the leaf) was used, taking *Avena sativa*, *Polygonum persicaria*, *Fagopyrum sagittatum*, and *Sinapis alba* as test-organisms.

REFERENCES

1. Olejnik A. F., Vozjakova T. I., Modnikova G. A., Novickij K. J.: Chim. Geterocikl. Sojed. 1972, 1448.
2. Frimm R., Kováč Š., Giller S. A.: Chem. zvesti 23, 916 (1969).
3. Nakanishi Mischio, Saheki Tashimi, Ao Hideo: Japan Pat. 43 218 (1971); Chem. Abstr. 76, 45 978 (1972).
4. Kureha Chem. Ind. Co. Ltd.: Japan Pat. 32 719 (1970); Japan Pat. Rep. Vol. R; No 41 (1970).
5. Abramovitch R. A.; J. Chem. Soc. 1957, 1413.
6. Krutošiková A.: Thesis. Slovak Technical University, Bratislava 1970.
7. Demečko J., Konečný V.: Agrochémia 10, 5 (1970).
8. Furdík M., Konečný V., Šaly A., Truchlik Š.: Acta Fac. Rer. Nat. Univ. Comenianae XII, 45 (1968).

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