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SYNTHESIS, PROPERTIES, AND SPECIAL FEATURES OF THE FRAGMENTATION UNDER ELECTRON IMPACT OF N-SUBSTITUTED NICOTINOYL UREAS

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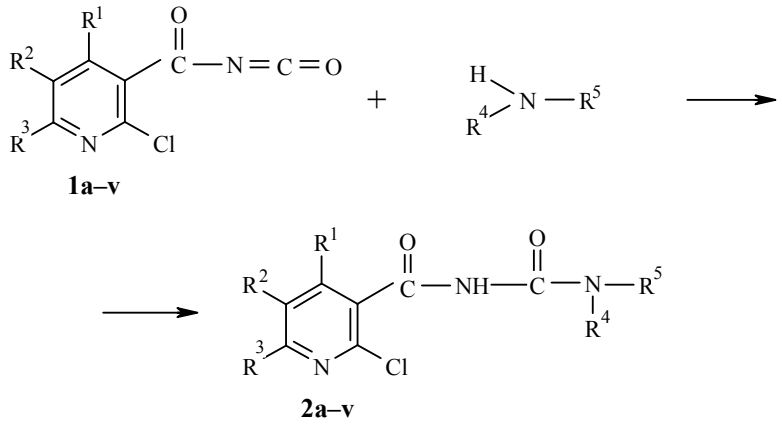
A convenient preparative synthetic route has been developed and N'-substituted nicotinoyl ureas have been obtained for the first time. Possible directions have been studied for their fragmentation under electron impact.

Keywords: substituted nicotinoyl isocyanates, N-substituted amines and nicotinoyl ureas, mass spectra.

We have synthesized highly reactive nicotinoyl isocyanates from amides of substituted nicotinic acids [1]. In view of the high pesticidal activity of certain substituted ureas [2,3] it seemed expedient to study the possibility of obtaining new substituted ureas from nicotinoyl isocyanates and certain aliphatic and aromatic amines and to investigate their structure and biological activity.

Reaction was carried out in absolute benzene with an equimolar ratio of the initial isocyanate and amine according to the following scheme.



1a–v

2a–v

1, **2 a-h**, **o-v** R^1 = Me, **i-n** R^1 = Cl; **a-c** R^2 = Cl, **d-h**, **m**, **n, s-v** R^2 = NO_2, **i-l**, **o-r** R^2 = H;
a-c, s-v R^3 = Me, **d-r** R^3 = Cl; **a-k**, **m-s**, **u**, **v** R^4 = H, **l** R^4 = Et, **t** R^4 = OMe; **a** R^5 = *i*-Pr,
b, **d**, **i**, **m, o** R^5 = *n*-Bu, **c**, **e**, **j**, **n** R^5 = 4-ClC_6H_4, **f** R^5 = 3,4-$Cl_2C_6H_3$, **g** R^5 = 1,2,4-triazol-3-yl, **h** R^5 = 2-$CF_3C_6H_4$,
k R^5 = 3,4-$Cl_2C_6H_3$, **l** R^5 = Et, **p** R^5 = 4-FC_6H_4, **q** R^5 = 4-$ClC_6H_4CH_2$, **r** R^5 = 2,5-$Cl_2C_6H_3$,
s R^5 = Am, **t** R^5 = Me, **u** R^5 = 2-$ClC_6H_4CH_2$, **v** R^5 = 3-$CF_3C_6H_4$

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The high reactivity of the initial isocyanates **1** permits the preparation of substituted nicotinoyl ureas **2a-v** in yields of 56-92% even at room temperature. The structure of the initial amine influences the reaction rate significantly. Strongly basic amines react smoothly with isocyanates at 20°C, but weakly basic (such as 3-amino-1,2,4-triazole) require heating at ~60-80°C for 2-3 h. It is interesting that among the nicotinoyl isocyanates used the greatest reactivity was possessed by compounds containing strong electron-withdrawing substituents (such as the NO_2 group) in the pyridine ring. This is probably linked with strengthening of the polarization of the N=C=O group.

TABLE 1. Characteristics of Compounds **2a-v**

Compound	Empirical formula	Found, % / Calculated, %				mp, °C*	Yield, %
		C	H	N	Cl		
2a	$C_{12}H_{15}Cl_2N_3O_2$	47.20 / 47.37	5.21 / 4.93	13.64 / 13.82	23.23 / 23.36	110-111	74
2b	$C_{13}H_{17}Cl_2N_3O_2$	48.78 / 49.06	5.59 / 5.35	13.11 / 13.21	22.48 / 22.33	114-115	90
2c	$C_{15}H_{12}Cl_3N_3O_2$	48.64 / 48.32	3.42 / 3.22	11.06 / 11.28	28.78 / 28.59	232-233	88
2d	$C_{12}H_{14}Cl_2N_4O_4$	41.48 / 41.26	4.34 / 4.04	16.25 / 16.05	20.47 / 20.34	190–191	81
2e	$C_{14}H_9Cl_3N_4O_4$	41.68 / 41.64	2.08 / 2.23	13.67 / 13.88	26.14 / 26.39	239-241	84
2f	$C_{14}H_8Cl_4N_4O_4$	38.74 / 38.36	1.97 / 1.83	12.56 / 12.79	32.19 / 32.42	234-235	91
2g	$C_{10}H_7Cl_2N_7O_4$	33.25 / 33.33	1.74 / 1.94	27.39 / 27.22	19.34 / 19.72	>400 with dec.	73
2h	$C_{15}H_9Cl_2N_7O_4$	41.45 / 41.19	1.84 / 2.06	12.83 / 12.81	16.02 / 16.25	221-222	77
2i	$C_{11}H_{12}Cl_3N_3O_2$	40.33 / 40.68	3.54 / 3.70	12.73 / 12.94	33.05 / 32.82	94-95	59
2j	$C_{13}H_7Cl_4N_3O_2$	41.02 / 41.16	1.71 / 1.85	10.94 / 11.08	37.60 / 37.47	209-210	56
2k	$C_{13}H_6Cl_5N_3O_2$	37.98 / 37.73	1.69 / 1.45	9.89 / 10.16	42.98 / 42.93	222-223	70
2l	$C_{11}H_{12}Cl_3N_3O_2$	41.04 / 40.68	3.92 / 3.70	12.86 / 12.94	33.07 / 33.82	147-148	67
2m	$C_{11}H_{11}Cl_3N_4O_4$	35.57 / 35.72	2.72 / 2.98	15.32 / 15.16	28.97 / 28.82	74-75	78
2n	$C_{13}H_6Cl_4N_4O_4$	36.98 / 36.79	1.18 / 1.42	12.99 / 13.21	33.26 / 33.49	219-220	86
2o	$C_{12}H_{15}Cl_2N_3O_2$	47.04 / 47.37	4.67 / 4.93	13.63 / 13.82	23.19 / 23.36	98-99	84
2p	$C_{14}H_{10}Cl_2FN_3O_2$	49.34 / 49.12	2.64 / 2.92	12.39 / 12.28	20.64 / 20.76	223-224	75
2q	$C_{15}H_{12}Cl_3N_3O_2$	48.65 / 48.32	3.64 / 3.22	11.13 / 11.28	28.42 / 28.59	175-176	57
2r	$C_{14}H_9Cl_4N_3O_2$	42.53 / 42.75	2.08 / 2.29	10.53 / 10.69	36.01 / 36.13	219-220	63
2s	$C_{14}H_{19}ClN_4O_4$	49.44 / 49.05	5.87 / 5.55	16.24 / 16.35	10.59 / 10.36	135-136	92
2t	$C_{11}H_{13}ClN_4O_5$	41.38 / 41.71	3.92 / 4.11	17.49 / 17.69	10.98 / 11.22	156-157	74
2u	$C_{16}H_{14}Cl_2N_4O_4$	48.68 / 48.36	3.74 / 3.53	14.33 / 14.11	17.72 / 17.88	173-174	82
2v	$C_{16}H_{12}ClF_3N_4O_4$	46.13 / 46.40	2.68 / 2.88	13.26 / 13.45	8.71 / 8.52	213-214	75

* Solvents: ethyl acetate (compounds **2a,b,i,l,o,s**), dioxane (compounds **2c,e-g,k,r**), EtOH (compounds **2d,h,j,n,p,q,t-v**), and cyclohexane (compound **2m**).

The synthesized nicotinoyl ureas **2** were white finely crystalline powders with a wide range of mp (74-239°C). They were readily soluble in alcohol and other polar solvents, insoluble in aliphatic and aromatic hydrocarbons, and in water. Their homogeneity, composition, and structure were confirmed by data of TLC, elemental analysis, IR, and mass spectroscopy (Tables 1 and 2).

TABLE 2. IR and Mass Spectra of Nicotinoyl Ureas **2a-v**

Compound	IR spectrum, ν, cm^{-1}		Mass spectra*, *m/z* (I_{rel}, % maximum, decomposition type)
	C=O	N–H	
1	2	3	4
2a	1709 (br.)	3323, 3220	303 $[M]^+$ (29); 274 $[M - C_2H_5]^+$ (14); 268 $[M - Cl]^+$ (98); 245 $[M - NHC_3H_7]^+$ (24); 218 $[M - C_3H_7NCO]^+$ (22); 202 $[M - NHCONHC_3H_7]^+$ (100); 174 $[202 - CO]^+$ (13)
2b	1705, 1680	3310, 3210	371 $[M]^+$ (13); 282 $[M - Cl]^+$ (82); 274 $[M - C_3H_7]^+$ (17); 245 $[M - NHC_4H_9]^+$ (20); 225 $[282 - C_4H_9]^+$ (18); 218 $[M–C_4H_9NCO]^+$ (22); 202 $[M - NHCONHC_4H_9]^+$ (100)
2c	1705, 1690	3225, 3112	371 $[M]^+$ (13); 336 $[M - Cl]^+$ (34); 218 $[M - 4\text{-}Cl\text{-}C_6H_4\text{-}NCO]^+$ (7); 202 $[M - 4\text{-}NHCONH\text{-}C_6H_4\text{-}Cl]^+$ (25); 153 $[4\text{-}Cl\text{-}C_6H_4\text{-}NCO]^+$ (100); 127 $[4\text{-}Cl\text{-}C_6H_4\text{-}NH_2]^+$ (19)
2d	1702, 1688	3330, 3225	348 $[M]^+$ (37); 319 $[M - C_2H_5]^+$ (3); 313 $[M - Cl]^+$ (14); 305 $[M - C_3H_7]^+$ (13); 233 $[M - NHCONHC_4H_9]^+$ (37); 187 $[233 - NO_2]^+$ (6)
2e	1715, 1705	3250, 3135	402 $[M]^+$ (8); 367 $[M - Cl]^+$ (5); 275 $[M - 4\text{-}Cl\text{-}C_6H_4\text{-}NH_2]^+$ (2); 233 $[M - 4\text{-}Cl\text{-}NHCONH\text{-}C_6H_4\text{-}Cl]^+$ (6); 187 $[233 - NO_2]^+$ (3); 153 $[4\text{-}Cl\text{-}C_6H_4\text{-}NCO]^+$ (100); 127 $[4\text{-}Cl\text{-}C_6H_4\text{-}NH_2]^+$ (29)
2f	1710, 1692	3220, 3120	436 $[M]^+$ (5); 401 $[M–Cl]^+$ (5); 275 $[M - 1,2\text{-}Cl_2\text{-}C_6H_3\text{-}NH_2]^+$ (4); 233 $[M - 1,2\text{-}Cl_2\text{-}C_6H_3\text{-}NHCONH]^+$ (19); 187 $[1,2\text{-}Cl_2\text{-}C_6H_3\text{-}NCO]^+$ (100); 161 $[1,2\text{-}Cl_2\text{-}C_6H_4\text{-}NH_2]^+$ (59)
2g	1745, 1720	3290, 3215, 3140	359 $[M]^+$ (2); 324 $[M - Cl]^+$ (38); 307 $[324 - OH]^+$ (6); 233 $[M - NHCONH\text{-}Het^{*2}]^+$ (100); 110 $[Het - NCO]^+$ (78); 87 $[Het - NH_2]^+$ (75)
2h	1709 (br.)	3250, 3125	436 $[M]^+$ (11); 401 $[M - Cl]^+$ (45); 233 $[M - 2\text{-}CF_3\text{-}C_6H_4\text{-}NHCONH]^+$ (18); 216 $[233 - OH]^+$ (14); 187 $[CF_3C_6H_4NCO]^+$ (100); 203 $[233 - NO]^+$ (18); 160 $[CF_3C_6H_4NH]^+$ (10)
2i	1710, 1695	3360, 3230	323 $[M]^+$ (19); 294 $[M - C_2H_5]^+$ (3); 288 $[M - Cl]^+$ (4); 280 $[M - C_3H_7]^+$ (15); 224 $[M - C_4H_9NCO]^+$ (21); 208 $[M - NHCONH\,C_4H_9]^+$ (100); 99 $[C_4H_9NCO]^+$ (20)
2j	1700 (br.)	3280, 3120	377 $[M]^+$ (20); 250 $[M - 4\text{-}Cl\text{-}C_6H_4\text{-}NH_2]^+$ (2); 224 $[M - 4\text{-}Cl\text{-}C_6H_4\text{-}NCO]^+$ (3); 208 $[M - 4\text{-}Cl\text{-}C_6H_4\text{-}NHCONH]^+$ (31); 180 $[208 - CO]^+$ (4); 153 $[4\text{-}Cl\text{-}C_6H_4\text{-}NCO]^+$ (100); 224 $[Cl\text{-}C_6H_4\text{-}NH_2]^+$ (3)
2k	1707, 1697	3260, 3123	411 $[M]^+$ (6); 250 $[M - 1,2\text{-}Cl_2\text{-}C_6H_3\text{-}4\text{-}NH_2]^+$ (3); 224 $[M - 1,2\text{-}Cl_2\text{-}C_6H_3\text{-}NCO]^+$ (2); 208 $[M - 1,2\text{-}Cl_2\text{-}C_6H_3\text{-}4\text{-}NHCONH]^+$ (24); 180 $[208 - CO]^+$ (3); 187 $[1,2\text{-}Cl_2\text{-}C_6H_3\text{-}NCO]^+$ (100); 161 $[1,2\text{-}Cl_2\text{-}C_6H_3\text{-}NH_2]^+$ (26)
2l	1715, 1665	3260	323 $[M]^+$ (17); 294 $[M - C_2H_5]^+$ (3); 288 $[M - Cl]^+$ (33); 250 $[M - NH(C_2H_5)_2]^+$ (7); 224 $[294 - C_2H_5NCO]^+$ (3); 208 $[M - NHCON(C_2H_5)_2]^+$ (100); 180 $[208 - CO]^+$ (8)
2m	1685 (br.)	3440, 3312	368 $[M]^+$ (22); 333 $[M - Cl]^+$ (16); 325 $[M - C_3H_7]^+$ (46); 269 $[M - C_4H_9NCO]^+$ (47); 253 $[M - NHCONHC_4H_9]^+$ (100); 207 $[253 - NO_2]^+$ (40); 179 $[207 - CO]^+$ (10)
2n	1702 (br.)	3280, 3130	422 $[M]^+$ (5); 387 $[M - Cl]^+$ (5); 295 $[M - 4\text{-}Cl\text{-}C_6H_4\text{-}NH_2]^+$ (3); 253 $[M - 4\text{-}Cl\text{-}C_6H_4\text{-}NHCONH\,]^+$ (10); 207 $[253 - NO_2]^+$ (3); 153 $[4\text{-}Cl\text{-}C_6H_4\text{-}NCO]^+$ (100); 127 $[Cl\text{-}C_6H_4\text{-}NH_2]^+$ (24)
2o	1715, 1685	3337, 3105	303 $[M]^+$ (60); 274 $[M - C_2H_5]$ (4); 268 $[M - Cl]^+$ (23); 260 $[M - C_3H_7]^+$ (21); 230 $[M - C_4H_9NH_2]^+$ (14); 204 $[M - C_4H_9NCO]^+$ (21); 188 $[M - NHCONHC_4H_9]^+$ (100); 99 $[C_4H_9NCO]^+$ (10)

TABLE 2 (continued)

1	2	3	4
2p	1698 (br.)	3275, 3100	341 $[M]^+$ (43); 306 $[M - Cl]^+$ (27); 204 $[M - 4\text{-F-}C_6H_4\text{-NCO}]^+$ (5); 188 $[M - 4\text{-F-}C_6H_4\text{-NHCONH}]^+$ (66); 160 $[188 - CO]^+$ (18); 137 $[4\text{-F-}C_6H_4\text{-NCO}]^+$ (100)
2q	1697 (br.)	3220, 3130	371 $[M]^+$ (11); 336 $[M - Cl]^+$ (6); 204 $[M - 4\text{-Cl-}C_6H_4\text{-}CH_2NCO]^+$ (18); 188 $[M - 4\text{-Cl-}C_6H_4\text{-}CH_2NHCONH]^+$ (29); 141 $[4\text{-Cl-}C_6H_4\text{-}CH_2NH_2]^+$ (100); 161 $[4\text{-Cl-}C_6H_4\text{-}CH_2]^+$ (33)
2r	1712, 1695	3220, 3110	391 $[M]^+$ (14); 356 $[M - Cl]^+$ (44); 204 $[M - Cl_2C_6H_3NCO]^+$ (11); 188 $[M - NHCONHC_6H_3Cl_2]^+$ (69); 187 $[2,5\text{-}Cl_2\text{-}C_6H_3\text{-NCO}]^+$ (100); 161 $[2,5\text{-}Cl_2\text{-}C_6H_3\text{-}NH_2]^+$ (33)
2s	1690 (br.)	3355, 3135	342 $[M]^+$ (60); 307 $[M - Cl]^+$ (25); 299 $[M - C_3H_7]^+$ (28); 285 $[M - C_4H_9]^+$ (83); 256 $[M - NHC_5H_{11}]^+$ (24); 213 $[M - NHCONHC_5H_{11}]^+$ (100); 113 $[C_5H_{11}NCO]^+$ (14)
2t	1720, 1685	3248	316 $[M]^+$ (4); 281 $[M - Cl]^+$ (11); 256 $[M - CH_3NOCH_3]^+$ (5); 213 $[M - NHCONCH_3OCH_3]^+$ (100); 196 $[213 - OH]^+$ (16); 140 $[196 - 2CO]^+$ (14)
2u	1697, 1665	3312, 3222	396 $[M]^+$ (13); 360 $[M - NO_2]^+$ (13); 229 $[M - 4\text{-Cl-}C_6H_4\text{-}CH_2NCO]^+$ (21); 213 $[M - 4\text{-Cl-}C_6H_4\text{-}CH_2NHCONH]^+$ (9); 140 $[4\text{-Cl-}C_6H_4\text{-}CH_2NH]^+$ (100); 125 $[4\text{-Cl-}C_6H_4\text{-}CH_2]^+$ (40)
2v	1718, 1695	3240, 3140	416 $[M]^+$ (18); 381 $[M - Cl]^+$ (98); 213 $[M - NHCONHC_6H_4CF_3]^+$(28); 140 $[213 - OH, -2CO]^+$ (9); 187 $[CF_3C_6H_4NCO]^+$ (100); 161 $[CF_3C_6H_4NH_2]^+$ (30)

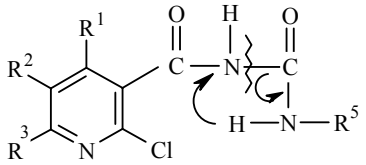
* M and 5-6 most intense ions are given. For chlorine-containing ions *m/z* values of ions containing the ^{35}Cl isotope are given.
*[2] Het = 1,2,4-triazol-3-yl.

As was to be expected, the only features distinguishing the ^1H NMR spectra of nicotinoyl ureas **2** from the spectra of the corresponding initial isocyanates **1** proved to be the appearance of signals for the two protons of the symmetrical NH amide groups in NH–CO–NH, displayed as two characteristic singlets at 8.35-8.58 ppm, and also the proton signals of the amine residues. Otherwise the ^1H NMR spectra of the obtained ureas were similar to those of the initial isocyanates **1**.

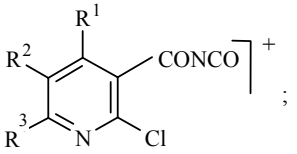
In the IR spectra of compounds **2a-v** the band for the stretching vibrations of the N=C=O group, present in the spectra of the initial isocyanates **1**, disappeared. At the same time a characteristic strong doublet absorption band for $\nu_{C=O}$ is present at 1664-1749 cm^{-1}, which was displaced by ~30 cm^{-1} towards lower frequencies in comparison with that for the isocyanates [1]. For some of them (**2a,h,j,m,n,p,q,s**) the frequencies of the carbonyl group absorption were so close that they appeared as a strong broadened singlet absorption band. This is probably linked with the structural special features of the molecules of these compounds. The stretching vibrations of the N–H single bond in the spectra of ureas **2a-v** appeared as two strongly broadened absorption bands with maxima at 3104-3439 cm^{-1}.

A characteristic special feature of the mass spectra of the nicotinoyl ureas proved to be the low stability of the molecular ions $[M]^+$ at the standard ionization energy (70 eV), due to which the intensities of these peaks were extremely small. However reduction of the ionization energy to 20 eV enabled spectra to be obtained containing M^+ peaks with I_{rel} <60% (Table 2). The molecular ions of N-alkyl-N'-nicotinoyl ureas were the most stable (I_M 17-60%), while in the case of N-(aryl,benzyl)-N'-nicotinoyl ureas I_M did not exceed 2-20%.

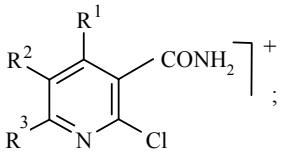
An interesting special feature of the primary fragmentation of the synthesized ureas is the ability to break the least stable C-N single bond of the urea bridge, accompanied by transfer of a hydrogen atom from one nitrogen atom to the other.



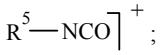
Since such fission is possible on both sides of the central carbon atom then four forms of primary fragment ions are observed in the mass spectra.



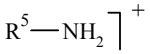
Φ_1



Φ_2

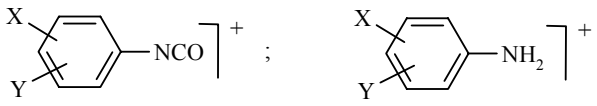


Φ_3



Φ_4

The intensity of the peaks of these splinter ions depends on the character of the substituents at the central bridge of the ureas. In the case of an aryl substituent (as in N-aryl-N'-nicotinoylureas) on dissociation of the indicated bonds under electron impact the positive charge is localized preferentially on the corresponding aryl isocyanate (Φ_3) and arylamine (Φ_4) fragments, and only to an insignificant degree on the nicotinoyl isocyanate (Φ_1) and nicotinoyl amide (Φ_2) fragments. In reality, at the same meanings for the substituents X and Y in the ions

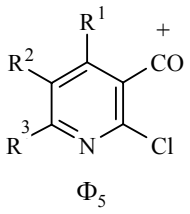


X = F, Cl, CF_3; Y = H, Cl

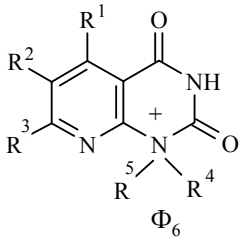
the aryl isocyanate fragments Φ_3 have maximal intensity, and the intensity of the peaks of the arylamine fragments are 19-59%. The intensity of the nicotinoyl isocyanate (Φ_1) and nicotinoyl amide (Φ_2) fragments did not exceed 2-21%.

In the case of alkyl substituents the fragmentation of N-alkyl-N'-nicotinoylureas proceeds by other pathways. It turned out that under electron impact fission of only one of the C–N bonds of the central urea bridge is observed. As a result only two types of fragments of structure Φ_1 and Φ_4 with I_{rel} 3-47 and 4-27% respectively are observed.

Finally, there were characteristic intense (maximal in the case of R^5 = Alk) peaks for ions of the nicotinoyl fragments Φ_5 for the mass spectra of all the compounds investigated, and also peaks for the splinter ions $[M\text{-}Cl]^+$ (98%), which may be explained by the possible stabilization of them due to the formation of a cyclic structure Φ_6.



Φ_5



Φ_6

For the subsequent, deeper stages of fragmentation of compounds **2a-v** a distinctive feature is the elimination of a C=O carbonyl fragment by the nicotinoyl cations Φ_1 and Φ_5, and loss of NO_2 by cations containing it. In further, deeper fragmentation stages elimination of a C≡N group is observed with destruction of the pyridine ring, which is in agreement with already known [4] and established [5] concepts on the fragmentation of pyridine derivatives.

The synthesized nicotinoyl ureas **2a-v** were investigated for certain forms of pesticidal activity. It was established that the majority of compounds **2** containing a nitro group displayed very high fungicidal activity in relation to brown rust of wheat and phytophthora of tomatoes. In the case of compounds **2d,f-h** their protective action on wheat plants in relation to brown rust reached 72-96%, but the most active proved to be substituted nicotinoyl urea **2d**. Furthermore, for some of the synthesized compounds (**2a,e,o**) in the example of sunflower plants a satisfactorily high (up to 33-40%) antidote activity was detected in relation to herbicides of a hormonal type of action, such as 2,4-D and picloram.

Substituted nicotinoyl ureas have been synthesized for the first time from nicotinoyl isocyanate. Some of their properties and the pathways of their fragmentation under electron impact have been studied.

Active fungicides and herbicidal antidotes have been detected in the series of compounds synthesized, which show promise for further biological investigation.

EXPERIMENTAL

The IR spectra were recorded on a Bruker IFS 45 spectrometer with an analyzing Aspekt 1000 PK in KBr disks. The mass spectra were recorded on a LKB 2091 chromato-mass spectrometer with direct insertion of samples into the ion source (ionization energy 20 eV). The ^{1}H NMR spectra were taken on a TESLA 70 (70 MHz) instrument in DMSO-d_6, internal standard was HMDS, δ = 0.05 ppm at 30°C. Elemental analysis of the synthesized compounds was carried out on a Carlo-Erba analyzer model 1106. The progress of reactions and the purity of the products obtained was checked by TLC (Silufol UV 250 in acetone–hexane, 1:1, visualization with iodine vapor). The physicochemical and spectral characteristics of the synthesized compounds are given in Tables 1 and 2.

The initial nicotinoyl isocyanates were synthesized by the procedure of [1]. The benzene used in the synthesis as a solvent was purified from contaminants and made absolute by the known method of [6].

N'-(2,6-Dichloro-4-methylnicotinoyl)-N-(4-fluorophenyl)urea (2p). A solution of 4-fluoroaniline (4.9 mmol) in absolute benzene (10 ml) was added rapidly to a solution of 2,6-dichloro-4-methylnicotinoyl isocyanate (4.9 mmol) in absolute benzene (30 ml) and the mixture was stirred for 1.5-2 h. The solid formed was filtered off, washed with benzene (2 × 25 ml), and dried. The benzene was evaporated from the filtrate, the dry residue added to the main fraction, and the obtained product was purified by crystallization from EtOH. The desired urea **2p** (1.25 g, 75%) was obtained as a white, finely crystalline powder of mp 223-224°C.

Compounds **2a-e,h-j,l-q,s-v** were obtained analogously.

N'-(2,6-Dichloro-4-methyl-5-nitronicotinoyl)-N-(1,2,4-triazol-3-yl)urea (2g). A solution of 2,6-dichloro-4-methyl-5-nitronicotinoyl isocyanate (9.4 mmol) in absolute benzene (30 ml) was added rapidly to a finely powdered suspension of 3-amino-1,2,4-triazole (9.4 mmol) in absolute benzene (20 ml). The mixture

was refluxed for 3 h, cooled, the solid formed was filtered off, washed with benzene (20 ml), and dried. After crystallization from dioxane the desired urea **2g** (2.48 g, 73%) was obtained as a white, finely crystalline powder decomposing at a temperature above 400°C.

Nicotinoyl ureas **2f,k,r** were synthesized analogously.

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