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PREPARATION OF A SERIES OF PYRIDYL PHENYLUREAS OF POTENTIAL AGRICULTURAL INTEREST

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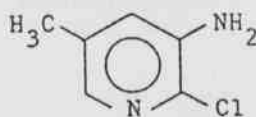
ABSTRACT

Substituted phenylurea derivatives of 3-amino-2-chloro-5-methylpyridine and 5-amino-2-chloro-3-methylpyridine were prepared by treating the amines with appropriately substituted phenyl isocyanates. Structure-confirming spectral data are also presented.

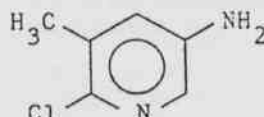
INTRODUCTION

For several years we have synthesized various types of compounds of agricultural interest. Many of these compounds were screened for herbicidal and fungicidal activity by commercial agricultural research laboratories. A few compounds had desirable effects on specific weeds or plant fungi, but none were considered broad enough in spectrum to receive additional attention.

Since several of our halobenzamido derivatives of 3-amino-2-chloro-5-methylpyridine (I) (Setliff and Rankin, 1988) and 5-amino-2-chloro-3-methylpyridine (II) (Setliff and Palmer, 1987) exhibited moderate fungicidal activity toward wheat leaf rust, we have now prepared for screening other derivatives from these amines, namely phenylureas Ia and IIa.

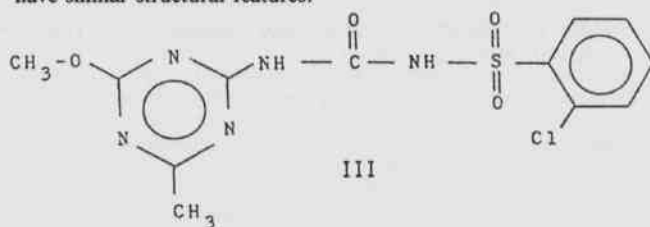


I



II

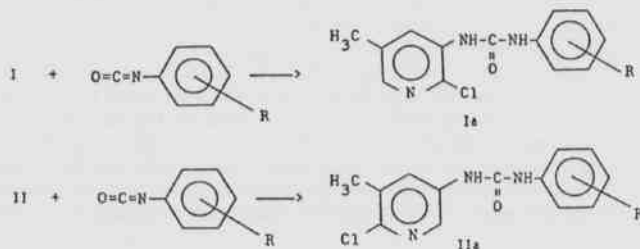
It is noteworthy that chlorosulfuron, (III) one of E.I. duPont's leading herbicides, contains a urea function, in addition to a nitrogen heterocyclic portion, halogens, and a methyl side unit. Our compounds have similar structural features.



III

MATERIALS AND METHODS

The phenylurea derivatives Ia and IIa were prepared by the reaction of amines I and II with the appropriately substituted phenyl isocyanates. Dry chloroform served as the solvent for the reaction.



The substituted phenyl isocyanates were purchased from Aldrich Chemical Company and were technical grade. Amines I and II were prepared in our laboratory as previously described (Setliff, 1970). All phenylureas were recrystallized from aqueous ethanol. Melting points were taken on a Mel-Temp apparatus and are uncorrected. Infrared spectra were taken on a Perkin - Elmer 1430 Spectrophotometer equipped with a Model 7300 Data Station with samples prepared as KBr disks. Proton nuclear magnetic resonance spectra were determined in dimethylsulfoxide - d_6 on a Varian EM 360 or a Varian XL 300 instrument with tetramethylsilane as internal standard. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee or Desert Analytics, Tucson, Arizona.

The preparations of the phenylureas were carried out as follows. Amine I or II (0.5g) was dissolved in dry chloroform (5 ml) in a 25 ml round - bottom flask. The appropriately substituted phenyl isocyanate (1.0 ml) was then added by syringe, and the resulting mixture was stirred under gentle reflux for 15 min. The precipitated solid (Ia or IIa), which rapidly formed, was filtered, washed with cold chloroform, and then recrystallized from aqueous ethanol.

Table 1. Experimental and Infrared Spectral Data for Phenylurea Derivatives Ia from 3-amino-2-chloro-5-methylpyridine (I)

R	Yld (%)	M.P. (°C)	IR, ν , cm^{-1}		Elemental Anal. Cal'd % (Found %)		
			N-H	C=O	C	H	N
H	50	217	3287	1636	59.54(59.70)	4.58(4.68)	16.03(16.01)
<i>o</i> -Cl	47	231	3290	1640	52.52(52.65)	3.70(3.72)	14.14(14.10)
<i>m</i> -Cl	74	221	3285	1637	52.52(52.76)	3.70(3.73)	14.14(14.16)
<i>p</i> -Cl	60	246	3295	1640	52.52(52.78)	3.70(3.65)	14.14(14.13)
<i>p</i> -F	58	234	3284	1635	55.71(55.71)	3.70(3.85)	15.00(14.87)
<i>o</i> -CF ₃	37	208	3298	1645	50.91(50.99)	3.33(3.26)	12.73(12.63)
<i>m</i> -CF ₃	52	227	3346	1713	50.91(50.94)	3.33(3.43)	12.73(12.70)
<i>p</i> -CF ₃	41	230	3349	1659	50.91(51.18)	3.33(3.43)	12.73(12.62)
2,4 - diF	61	238	3288	1640	52.35(52.48)	3.37(3.36)	14.09(14.15)

RESULTS AND DISCUSSION

Nine phenylureas were prepared from both amine I and amine II (Tables 1,2). Yields, although adequate, were generally better with the less sterically hindered amine II. Carbon, hydrogen, and nitrogen elemental analyses fell within acceptable limits of the calculated values. The infrared spectra exhibited the expected N-H and C=O absorption bands. In most cases the phenylureas Ia from amine I (Table 1) show lower frequencies for these absorptions than the phenylureas IIa from amine II (Table 2). This suggests a greater degree of hydrogen bonding in the Ia molecules.

Table 2. Experimental and Infrared Spectral Data for Phenylurea Derivatives IIa from 5-amino-2-chloro-3-methylpyridine (II)

R	Yld (%)	M.P. (°C)	IR, ν , cm^{-1}		Elemental Anal. Cal'd % (Found %)		
			N-H	C=O	C	H	N
H	72	220	3397	1708	59.54(59.20)	4.58(4.58)	16.03(15.92)
<i>o</i> -Cl	73	213	3373	1709	52.52(52.43)	3.70(3.74)	14.14(13.92)
<i>m</i> -Cl	64	226	3385	1710	52.52(52.43)	3.70(3.74)	14.14(14.25)
<i>p</i> -Cl	66	263	3394	1711	52.52(52.51)	3.70(3.76)	14.14(14.10)
<i>p</i> -F	83	243	3393	1711	55.71(55.52)	3.70(3.84)	15.00(14.85)
<i>o</i> -CF ₃	49	235	3292	1643	50.91(50.73)	3.33(3.24)	12.73(12.65)
<i>m</i> -CF ₃	74	211	3393	1711	50.91(50.82)	3.33(3.30)	12.73(12.63)
<i>p</i> -CF ₃	80	253	3390	1712	50.91(50.80)	3.33(3.40)	12.73(12.73)
2,4 - diF	71	308	3403	1709	52.35(52.21)	3.37(3.37)	14.09(14.16)

The proton NMR spectra for both series of compounds showed a sharp three proton singlet at 2.3 ppm for the methyl protons, and a complex array of multiplet signals in the range of 7.0 to 9.5 ppm for the collective aromatic and amido protons.

ACKNOWLEDGMENT

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