NEW SYNTHESIS OF N-ACYLUREA DERIVATIVES

Peter KUTSCHY, Milan DZURILLA, Vlastimír FICERI and Dušan KOŠČÍK

Department of Organic Chemistry,
Faculty of Natural Science, Šafárik University, 041 67 Košice, The Slovak Republic

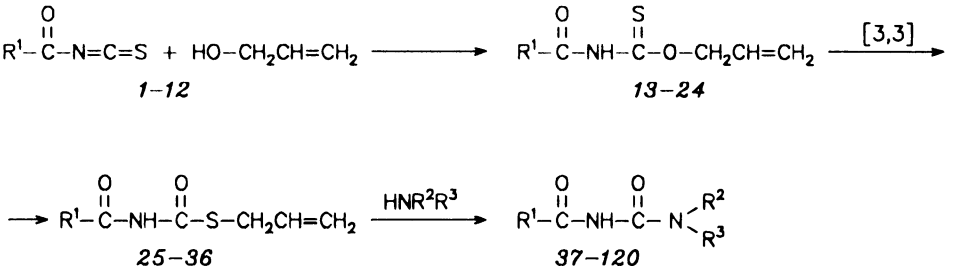
Received January 8, 1992
Accepted March 26, 1992

S-Allyl N-acylmonothiocarbamates react in boiling benzene with primary and secondary amines in the presence of catalytic amounts of triethylamine. In this reaction, the S-allyl group is replaced with the amino group under formation of N-acylurea derivatives in 45 – 90% yields. The wide applicability of the reaction is demonstrated by the synthesis of eighty four N-acyl-N'-substituted and N-acyl-N',N'-disubstituted ureas with various aliphatic, aromatic and heterocyclic substituents.

N-Acylurea derivatives are of interest because of their potential pesticidal activity[1,2]. These compounds are usually synthesized by reaction of acyl isocyanates with amines or of isocyanates with carboxylic acid amides[3]. However, the starting isocyanates, and particularly acyl isocyanates, are unstable and highly toxic and the reactivity of carboxylic acid amides is low.

In the present paper we describe a new simple synthesis of N-acyl derivatives of urea from stable starting compounds and intermediates. Recently, we studied the reaction of allyl alcohol with acyl isothiocyanates leading to O-allyl N-acylmonothiocarbamates which in boiling benzene undergo a [3,3]-sigmatropic rearrangement to give the corresponding S-allyl N-acylmonothiocarbamates[4]. During investigation of the S-allyl esters ***25*** – ***36***, which are stable at room temperature, we have found that in boiling benzene and in the presence of catalytic amounts of triethylamine they react readily with primary and secondary amines to give N-acyl-N'-substituted urea derivatives (***37*** – ***120***, Scheme 1, Table I). The nucleophilic replacement of the S-allyl residue by the amine takes place even in the absence of triethylamine but the reaction is slower, particularly with less basic amines. This reaction was hitherto unknown, probably because the preparation of the S-allyl or the analogous S-alkyl esters was not well elaborated and the known methods were uncomfortable[4]. As seen from Table I, the scope of application is wide and the products are obtained in good yields (the yields stated relate to the last reaction step). Isolation of intermediates ***13*** – ***24*** makes the synthesis longer and more laborious and lowers the yields. We have found that the S-allyl esters can be prepared by a one-pot synthesis starting from the corresponding acyl chloride. After reaction of the acyl chloride with potassium thiocyanate in acetonitrile at room tempe-

rature, the obtained acyl isothiocyanate is rapidly and in a good yield converted into the S-allyl ester by heating with allyl alcohol. This shortens the synthesis from several days to several hours. This approach is suitable particularly in the case of benzoyl derivatives, e.g. S-allyl N-(2,6-difluorobenzoyl)monothiocarbamate (*29*). When the reaction is performed in benzene, after addition of the corresponding amine and catalytic amount of triethylamine the desired urea may be obtained even without isolation of the S-allyl ester but the yields are lower. In this way we prepared products *49* – *52*. The utility of S-allyl N-acylmonothiocarbamates in the synthesis of acylureas is also demonstrated by the preparation of compound *105* from D,L-serine methyl ester hydrochloride using a benzene–water two-phase system. The prepared ureas *37* – *120* are sparingly soluble compounds and therefore only some of them could be studied by



In formulae: ***1, 13, 25;*** $R^1 = 2\text{-Cl-C}_6\text{H}_4\text{-CH}_2$

2, 14, 26; $R^1 = C_6H_5$

3, 15, 27; $R^1 = 2\text{-Cl-C}_6\text{H}_4$

4, 16, 28; $R^1 = 2\text{-Cl-5-NO}_2\text{-C}_6\text{H}_3$

5, 17, 29; $R^1 = 2\text{-F-6-F-C}_6\text{H}_3$

6, 18, 30; $R^1 = C_6H_5CH{=}CH$

7, 19, 31; $R^1 = 2\text{-Cl-C}_6\text{H}_4\text{CH=CH}$

8, 20, 32; $R^1 = 4\text{-Cl-C}_6\text{H}_4\text{CH=CH}$

9, 21, 33; $R^1 = 4\text{-Br-C}_6\text{H}_4\text{CH=CH}$

10, 22, 34; R^1 = 2-Naphthyl

11, 23, 35; R^1 = 5-Chloro-2-thienyl(5-Cl-C_4H_2S)

12, 24, 36; R^1 = 3-Chloro-2-benzo[*b*]thienyl(3-Cl-C_8H_4S)

For compounds ***37–120*** the substituents R^1, R^2, R^3 are defined in Table I.

SCHEME 1

NMR spectroscopy (Table I). Their infrared spectra exhibit absorption bands due to $\nu(CO-NH-CO)_s$ and $\nu(CO-NH-CO)_{as}$ vibrations that are characteristic for ureas[5]; these bands sometimes merge into one broad band. The structure of the N-acylureas is also proved by agreement of their physicochemical properties with those of some already known substances such as e.g. N-benzoyl-N'-phenylurea[6] (*40*), the known insecticide diflubenzuron[7] (*54*) or N-(3-phenylpropenoyl)-N'-phenylurea[8] (*58*).

EXPERIMENTAL

The infrared absorption spectra were recorded on an IR-75 (Zeiss, Jena) spectrometer in chloroform (compounds *1*, *4*, *7*, *8*, *11*, *13*, *17*, *19* – *21*, *23*, *25*, *29*, *31* – *33*, *37* – *39*, 75, *104*) or in KBr pellets (compounds *35*, *40* – *74*, *76* – *103*, *105* – *120*); the wavenumbers are given in cm^{-1}. ^1H and ^{13}C NMR spectra were measured on Tesla BS 487A (80 MHz for ^1H) and Tesla BS 567 (25.15 MHz for ^{13}C) spectrometers in deuterochloroform (compounds *1*, *7*, *8*, *11*, *13*, *19*, *20*, *21*, *23*, *25*, *29*, *31*, *33*, *103*) or in hexadeuterodimethyl sulfoxide (compounds *32*, *35*, *37* – *40*, *42*, *54*, *64*, *75*, *93*, *104*, *105*, *108*) with tetramethylsilane as internal standard. Chemical shifts are given in ppm (δ-scale). 2,6-Difluorobenzoyl isothiocyanate[7] (*5*), 3-(4-bromophenyl)propenoyl isothiocyanate[9] (*9*), S-allyl esters[4] of N-benzoyl- (*26*), N-(2-chlorobenzoyl)- (*27*), N-(3-phenylpropenoyl)- (*30*), N-(2-naphthoyl)- (*34*) and N-(3-chloro-2-benzo[*b*]thienocarbonyl)monothiocarbamic acid (*36*) were prepared according to the literature. The reactions were followed by thin-layer chromatography on Silufol plates (Kavalier, Czechoslovakia).

2-Chlorophenylacetyl Isothiocyanate (*1*)

Lead thiocyanate (4.04 g, 15.5 mmol) was added to a solution of 2-chlorophenylacetyl chloride (2.3 g, 12.5 mmol) in anhydrous benzene (20 ml) and the mixture was refluxed for 2 h under stirring. After filtration with charcoal, the benzene was evaporated and the residue distilled under reduced pressure, b.p. 118 – 120 °C/133 Pa; yield 1.88 g (87%). For C_9H_6ClNOS (211.7) calculated: 51.06% C, 2.85% H, 6.62% N; found: 51.23% C, 2.78% H, 6.79% N. IR spectrum: 1 955 (N=C=S), 1 660 (C=O). ^1H NMR spectrum: 3.95 s, 2 H (CH_2); 7.25 m, 4 H (C_6H_4).

2-Chloro-5-nitrobenzoyl Isothiocyanate (*4*)

The title compound was obtained from 2-chloro-5-nitrobenzoyl chloride (3.12 g, 12.5 mmol) using the same procedure as described in the preceding experiment; yield 2.60 g (80%), m.p. 78 °C (hexane). For $C_8H_3ClN_2O_3S$ (242.7) calculated: 39.58% C, 1.24% H, 11.55% N; found: 39.60% C, 1.22% H, 11.51% N. IR spectrum: 1 920 (N=C=S), 1 700 (C=O).

General Procedure for Preparation of Acyl Isothiocyanates *7*, *8*, and *11*

The corresponding acyl chloride (41 mmol) in anhydrous acetone (20 ml) was added at room temperature to a stirred solution of potassium thiocyanate (4.03 g, 61 mmol) in anhydrous acetone (60 ml). After stirring for 5 min, benzene (about 100 ml) was added until the milky turbidity disappeared and the reaction mixture was filtered. The solvent was evaporated and the residue was crystallized from hexane.

3-(2-Chlorophenyl)propenoyl isothiocyanate (**7**); yield 80%, m.p. 60 – 62 °C. For $C_{10}H_6ClNOS$ (223.7) calculated: 53.69% C, 2.70% H, 6.26% N; found: 53.48% C, 2.81% H, 6.09% N. IR spectrum: 1 917 (N=C=S), 1 675 (C=O), 1 618 (C=C). ^1H NMR spectrum: 6.52 d, 1 H and 8.16 d, 1 H, J(A,B) = 16 Hz (CH=CH); 7.39 m, (C_6H_4).

TABLE I
N-Acyl-N′-monosubstituted and N′,N′-disubstituted urea derivatives R^1–CO–NH–CO–NR^2R^3 *37 – 120*

Compound	R^1	R^2/R^3	Formula (M. w.)	M. p., °C (Solvent)	Yield %	Calculated/Found %C	%H	%N	IR, ν(cm^{-1}) (CO–NH–CO)
37[b]	2-$ClC_6H_4CH_2$	H 4-ClC_6H_4	$C_{15}H_{12}Cl_2N_2O_2$ (322.9)	183 – 185 (E)	72	55.80 55.63	3.75 3.92	8.68 8.41	1 710 1 680
38[b]	2-$ClC_6H_4CH_2$	H 2-CH_3-4-ClC_6H_3	$C_{16}H_{14}Cl_2N_2O_2$ (337.1)	204 – 206 (E)	93	57.01 57.29	4.19 3.98	8.31 8.55	1 720 1 680
39[b]	2-$ClC_6H_4CH_2$	H 4-BrC_6H_4	$C_{15}H_{12}BrClN_2O_2$ (367.4)	168 – 170 (E)	79	49.04 49.31	3.29 3.06	7.63 7.88	1 710 1 685
40[b]	C_6H_5	H C_6H_5	$C_{14}H_{12}N_2O_2$ (240.3)	210[c] (B)	88	69.99 69.80	5.03 5.21	11.61 11.52	1 720 1 680
41	C_6H_5	H 2-CH_3-4-ClC_6H_3	$C_{15}H_{13}ClN_2O_2$ (288.7)	246 – 247 (B)	92	62.40 62.51	4.54 4.39	9.70 9.90	1 695 1 655
42[b]	2-ClC_6H_4	H CH≡CCH_2	$C_{11}H_9ClN_2O_2$ (236.7)	141 – 143 (B–H)	76	55.83 55.91	3.83 3.72	11.84 11.66	1 670
43	2-ClC_6H_4	H 2-$CH_3C_6H_4$	$C_{15}H_{13}ClN_2O_2$ (288.7)	180 – 182 (B+H)	83	62.40 62.55	4.54 4.31	9.70 9.90	1 700
44	2-ClC_6H_4	H 2-$CH_3OC_6H_4$	$C_{15}H_{13}ClN_2O_3$ (304.7)	146 – 147 (B+H)	85	59.12 59.28	4.30 4.16	9.19 9.25	1 690
45	2-ClC_6H_4	H 4-$C_6H_5C_6H_4$	$C_{20}H_{15}ClN_2O_2$ (350.8)	204 – 206 (T)	88	68.48 68.56	4.31 4.19	7.99 8.07	1 695 1 670
46	2-ClC_6H_4	H 4-ClC_6H_4	$C_{14}H_{10}Cl_2N_2O_2$ (309.2)	202 – 203 (B)	66	54.38 54.56	3.26 3.02	9.06 8.87	1 700 1 690
47	2-ClC_6H_4	H 2-CH_3-4-ClC_6H_3	$C_{15}H_{12}Cl_2N_2O_2$ (323.2)	203 – 204 (B)	82	55.74 55.98	3.74 3.61	8.67 8.90	1 700 1 690
48	2-ClC_6H_4	H 4-BrC_6H_4	$C_{14}H_{10}BrClN_2O_2$ (353.6)	216 – 217 (E)	68	47.55 47.39	2.85 2.98	7.92 8.12	1 700 1 680

TABLE I
(*Continued*)

Compound	R^1	R^2/R^3	Formula (M. w.)	M. p., °C (Solvent)	Yield %	Calculated/Found %C	%H	%N	IR, ν(cm^{-1}) (CO–NH–CO)
49	2-Cl-5-$NO_2C_6H_4$	H 4-$NO_2C_6H_4$	$C_{14}H_9ClN_2O_6$ (364.7)	171 – 173 (E)	65	46.11 46.32	2.49 2.54	15.36 15.10	1 720 1 670
50	2-Cl-5-$NO_2C_6H_4$	H 2-BrC_6H_4	$C_{14}H_9BrClN_3O_4$ (399.6)	154 – 155 (E)	61	42.08 41.79	2.27 2.43	10.52 10.71	1 720 1 660
51	2-Cl-5-$NO_2C_6H_4$	H C_6H_5	$C_{20}H_{14}ClN_3O_4$ (395.8)	147 (M–W)	59	60.69 60.54	3.57 3.71	10.62 10.48	1 725 1 640
52	2-Cl-5-$NO_2C_6H_4$	$(CH_2)_2O(CH_2)_2$	$C_{12}H_{12}ClN_3O_5$ (313.7)	159 (M–W)	62	45.95 45.72	3.86 3.99	13.40 13.21	1 725 1 640
53	2-F-6-F-C_6H_3	H 3-$CH_3OC_6H_4$	$C_{15}H_{12}F_2N_2O_3$ (306.3)	179 – 180 (B)	81	58.22 59.00	3.95 3.73	9.15 9.28	1 680
54[b]	2-F-6-F-C_6H_3	H 4-ClC_6H_4	$C_{14}H_9ClF_2N_2O_2$ (310.7)	230 – 232[d]	70	54.12 54.02	2.92 2.77	9.02 10.13	1 695 1 670
55	C_6H_5CH=CH	H $C_6H_5CH_2$	$C_{17}H_{12}N_2O_2$ (280.3	214 – 216 (M)	91	72.85 72.66	5.75 5.92	10.00 9.83	1 692 1 670
56	C_6H_5CH=CH	H CH≡CCH_2	$C_{13}H_{12}N_2O_2$ (228.2)	228 – 230 (M)	70	68.40 68.23	5.30 5.48	12.27 12.36	1 692 1 670
57	C_6H_5CH=CH	H C_6H_5	$C_{16}H_{14}N_2O_2$ (266.3)	217 – 218[e] (E)	85	72.16 72.33	5.30 5.21	10.52 10.64	1 705 1 675
58	C_6H_5CH=CH	H 2-$CH_3C_6H_4$	$C_{17}H_{16}N_2O_2$ (280.3)	218 – 220 (A)	81	72.84 7205	5.75 5.89	9.99 10.12	1 695 1 670
59	C_6H_5CH=CH	H 4-ClC_6H_4	$C_{16}H_{13}ClN_2O_2$ (300.7)	238 – 239 (E)	92	63.90 63.79	4.35 4.31	9.31 8.89	1 698 1 667
60	C_6H_5CH=CH	H 2-CH_3-4-ClC_6H_3	$C_{17}H_{15}ClN_2O_2$ (314.8)	236 – 237 (E)	80	64.86 64.57	4.80 4.63	8.88 8.68	1 700 1 662
61	C_6H_5CH=CH	H 4-BrC_6H_4	$C_{16}H_{13}BrN_2O_2$ (345.2)	254 – 255 (E)	88	55.67 55.95	3.79 3.70	8.11 7.94	1 680 1 665

TABLE I
(*Continued*)

Compound	R^1	R^2/R^3	Formula (M. w.)	M. p., °C (Solvent)	Yield %	Calculated/Found %C	%H	%N	IR, ν(cm^{-1}) (CO–NH–CO)
62	$C_6H_5CH=CH$	H 3-$CH_3OC_6H_4$	$C_{17}H_{16}N_2O_3$ (296.3)	199 – 201 (A)	83	68.91 68.80	5.44 5.51	9.45 9.32	1 700 1 675
63	$C_6H_5CH=CH$	H 4-$CH_3COC_6H_4$	$C_{18}H_{16}N_2O_3$ (307.3)	239 – 241 (E)	84	70.35 70.19	5.24 5.36	9.11 9.27	1 670 1 655
64[b]	$C_6H_5CH=CH$	CH_3 C_6H_5	$C_{17}H_{16}N_2O_2$ (280.3)	110 – 110 (E)	79	72.84 72.70	5.75 5.93	9.99 9.76	1 675 1 660
65	$C_6H_5CH=CH$	$(CH_2)_2O(CH_2)_2$	$C_{14}H_{16}N_2O_3$ (260.3)	167.5 – 168.5 (B+H)	73	64.60 64.78	6.20 6.03	10.76 10.55	1 691 1 665
66	2-$ClC_6H_4CH=CH$	H $HC\equiv CCH_2$	$C_{13}H_{11}ClN_2O_2$ (262.7)	191 – 193 (B+H)	58	59.44 55.28	5.30 5.45	10.66 10.59	1 690 1 670
67	2-$ClC_6H_4CH=CH$	H C_6H_5	$C_{16}H_{13}ClN_2O_2$ (300.7)	236 – 238 (E)	69	63.90 64.09	4.35 4.52	9.31 9.12	1 685
68	2-$ClC_6H_4CH=CH$	H 2-$CH_3C_6H_4$	$C_{17}H_{15}ClN_2O_2$ (314.8)	256 – 258 (E)	70	64.87 64.91	4.80 4.72	8.90 8.67	1 695 1 670
69	2-$ClC_6H_4CH=CH$	H 4-$C_6H_5C_6H_4$	$C_{22}H_{17}ClN_2O_2$ (376.8)	243 – 244 (E)	81	70.12 70.25	4.55 4.32	7.44 7.29	1 695 1 685
70	2-$ClC_6H_4CH=CH$	H 4-ClC_6H_4	$C_{16}H_{12}Cl_2N_2O_2$ (335.2)	251 – 252 (E)	76	57.33 57.20	3.61 3.82	8.36 8.21	1 689 1 675
71	2-$ClC_6H_4CH=CH$	H 2-CH_3-4-ClC_6H_3	$C_{17}H_{14}Cl_2N_2O_2$ (349.2)	245 – 247 (E)	81	58.47 58.52	4.04 4.19	8.02 8.30	1 705 1 680
72	2-$ClC_6H_4CH=CH$	H 4-BrC_6H_4	$C_{16}H_{12}BrClN_2O_2$ (379.6)	241 – 242 (A)	90	50.62 50.45	3.18 3.28	7.38 7.09	1 695 1 680
73	2-$ClC_6H_4CH=CH$	H 3-$CH_3OC_6H_4$	$C_{17}H_{15}ClN_2O_3$ (330.8)	234 – 236 (E)	85	61.73 61.52	4.57 4.71	8.47 8.33	1 710 1 680
74	2-$ClC_6H_4CH=CH$	H 4-$CH_3COC_6H_4$	$C_{18}H_{15}ClN_2O_3$ (342.8)	257 – 259 (E)	60	63.07 63.22	4.41 4.58	8.17 8.23	1 710 1 670

Collect. Czech. Chem. Commun. (Vol. 58) (1993)

TABLE I
(*Continued*)

Compound	R^1	R^2/R^3	Formula (M. w.)	M. p., °C (Solvent)	Yield %	Calculated/Found %C	%H	%N	IR, ν(cm^{-1}) (CO–NH–CO)
75[b]	2-ClC$_6$H$_4$CH=CH	(CH$_2$)$_2$O(CH$_2$)$_2$	$C_{14}H_{15}ClN_2O_3$ (294.7)	147.5 – 148.5 (E)	95	57.05 57.18	5.13 5.22	9.51 9.64	1 690
76	4-ClC$_6$H$_4$CH=CH	H HC≡CCH$_2$	$C_{13}H_{11}ClN_2O_3$ (262.7)	265 – 266 (M)	82	59.44 59.29	5.03 5.00	10.66 10.80	1 695 1 670
77	4-ClC$_6$H$_4$CH=CH	H C$_6$H$_5$	$C_{16}H_{13}ClN_2O_2$ (300.7)	253 – 255 (E)	88	63.90 63.81	4.35 4.48	9.31 9.50	1 710 1 675
78	4-ClC$_6$H$_4$CH=CH	H 4-CH$_3$C$_6$H$_4$	$C_{17}H_{15}ClN_2O_2$ (314.8)	271 - 273 (E)	80	64.87 64.69	4.80 4.91	8.90 8.77	1 695 1 670
79	4-ClC$_6$H$_4$CH=CH	H 2-CH$_3$C$_6$H$_4$	$C_{17}H_{15}ClN_2O_2$ (314.8)	249 – 250 (E)	87	64.87 64.70	4.80 4.99	8.90 8.72	1 700 1 665
80	4-ClC$_6$H$_4$CH=CH	H 4-ClC$_6$H$_4$	$C_{16}H_{12}Cl_2N_2O_2$ (335.2)	262 – 263 (A)	92	57.33 57.21	3.61 3.85	8.36 8.09	1 700 1 670
81	4-ClC$_6$H$_4$CH=CH	H 2-CH$_3$-4-ClC$_6$H$_3$	$C_{17}H_{14}Cl_2N_2O_2$ (349.2)	252 – 253 (E)	80	58.47 58.42	4.04 4.12	8.02 8.16	1 705 1 670
82	4-ClC$_6$H$_4$CH=CH	H 4-BrC$_6$H$_4$	$C_{16}H_{12}BrClN_2O_2$ (379.6)	241 – 242 (A)	84	50.62 50.76	3.18 3.23	7.38 7.48	1 700 1 660
83	4-ClC$_6$H$_4$CH=CH	H 3-NO$_2$C$_6$H$_4$	$C_{16}H_{12}ClN_3O_4$ (345.7)	251 – 253 (E)	96	55.58 55.40	3.50 3.62	12.15 12.01	1 695 1 670
84	4-ClC$_6$H$_4$CH=CH	H 3-CH$_3$OC$_6$H$_4$	$C_{17}H_{15}ClN_2O_3$ (330.8)	250 – 251 (E)	82	61.73 61.50	4.57 4.44	8.47 8.62	1 705 1 680
85	4-ClC$_6$H$_4$CH=CH	H 4-CH$_3$COC$_6$H$_4$	$C_{18}H_{15}ClN_2O_3$ (342.8)	261 – 263 (E)	83	63.07 63.22	4.41 4.25	8.17 8.31	1 695 1 670
86	4-ClC$_6$H$_4$CH=CH	H 2-NH$_2$C$_6$H$_4$	$C_{16}H_{14}Cl_3N_2O_2$ (316.0)	253 – 255 (E)	81	53.23 53.51	3.91 3.76	11.69 11.53	1 695 1 660
87	4-BrC$_6$H$_4$CH=CH	H C$_6$H$_5$	$C_{16}H_{13}BrN_2O_2$ (345.2)	241 – 242 (E)	87	55.67 55.82	3.80 3.64	8.12 8.15	1 695 1 670

TABLE I
(*Continued*)

Compound	R^1	R^2/R^3	Formula (M. w.)	M. p., °C (Solvent)	Yield %	Calculated/Found %C	%H	%N	IR, ν(cm^{-1}) (CO–NH–CO)
88	4-BrC_6H_4CH=CH	H 4-ClC_6H_4	$C_{16}H_{12}BrClN_2O_2$ (379.6)	244 – 246 (E)	92	50.62 50.81	3.19 3.27	7.38 7.42	1 695 1 675
89	4-BrC_6H_4CH=CH	H 2-CH_3-4-ClC_6H_3	$C_{17}H_{14}BrClN_2O_2$ (393.7)	209 – 211 (A)	86	51.87 51.95	3.59 3.64	7.12 7.12	1 705 1 670
90	4-BrC_6H_4CH=CH	H 4-BrC_6H_4	$C_{16}H_{12}Br_2N_2O_2$ (424.1)	259 – 260 (E)	90	45.32 45.53	2.85 2.98	6.61 6.79	1 700 1 670
91	2-naftyl	H C_6H_5	$C_{18}H_{14}N_2O_2$ (290.3)	209 – 212 (E)	86	74.47 74.28	4.86 5.03	9.65 9.90	1 695 1 665
92	2-naftyl	H 2-CH_3-4-ClC_6H_3	$C_{19}H_{15}ClN_2O_2$ (338.8)	241 – 242 (E)	82	67.56 67.51	4.46 4.37	8.27 8.43	1 700 1 654
93[b]	5-ClC_4H_2S	H $CH_3CH_2CH_2$	$C_9H_{11}ClN_2O_2S$ (246.7)	168 – 170 (E)	67	43.82 43.70	4.50 4.63	11.36 11.19	1 675 1 655
94	5-ClC_4H_2S	H $(CH_3)_2CH$	$C_9H_{11}ClN_2O_2S$ (246.7)	174 – 175 (E)	70	43.82 43.71	4.50 4.66	11.36 11.52	1 680 1 655
95	5-ClC_4H_2S	H HC≡CCH_2	$C_9H_7ClN_2O_2S$ (242.7)	220 – 222 (M)	70	44.54 44.38	2.91 2.79	11.54 11.67	1 660 1 635
96	5-ClC_4H_2S	H C_6H_5	$C_{12}H_9ClN_2O_2S$ (280.7)	252 – 254 (E)	80	51.34 51.46	3.23 3.09	9.98 10.13	1 690 1 650
97	5-ClC_4H_2S	H 4-$CH_3C_6H_4$	$C_{13}H_{11}ClN_2O_2S$ (294.7)	257 – 259 (E)	85	52.97 53.09	3.76 3.68	9.50 9.67	1 690 1 655
98	5-ClC_4H_2S	H 4-$CH_3C_6H_4$	$C_{13}H_{11}ClN_2O_2S$ (294.7)	238 – 240 (E)	92	52.97 52.75	3.76 3.91	9.50 9.63	1 690 1 650
99	5-ClC_4H_2S	H 4-$CH_3C_6H_4$	$C_{12}H_8Cl_2N_2O_2S$ (312.2)	240 – 241 (B)	90	45.73 45.91	2.56 2.63	8.89 8.70	1 690 1 645
100	5-ClC_4H_2S	H 4-$CH_3C_6H_4$	$C_{13}H_{10}Cl_2N_2O_2S$ (329.2)	247 – 248 (E)	80	47.41 47.59	3.06 3.18	8.51 8.26	1 690 1 650

TABLE I
(*Continued*)

Compound	R^1	R^2/R^3	Formula (M. w.)	M. p., °C (Solvent)	Yield %	Calculated/Found %C	%H	%N	IR, ν(cm^{-1}) (CO–NH–CO)
101	5-ClC_4H_2S	H 4-BrC_6H_4	$C_{12}H_8BrClN_2O_2S$ (359.6)	253 – 255 (A)	82	40.08 39.86	2.24 2.38	7.71 7.60	1 690 1 650
102	5-ClC_4H_2S	H 4-$CH_3OC_6H_4$	$C_{13}H_{11}ClN_2O_3S$ (310.7)	222 – 224 (E)	84	50.25 50.43	3.57 3.69	9.02 9.18	1 675 1 650
103	5-ClC_4H_2S	H 3-$CH_3OC_6H_4$	$C_{13}H_{11}ClN_2O_3S$ (310.7)	200 – 202 (E)	93	50.25 50.36	3.57 3.47	9.02 9.18	1 690 1 655
104[b]	5-ClC_4H_2S	$-(CH_2)_4-$	$C_{10}H_{11}ClN_2O_2S$ (258.7)	144 – 146 (E+W)	86	46.42 46.61	4.29 4.11	10.83 10.79	1 645
105[b,g]	3-ClC_8H_4S[h]	H $CH(CH_2OH)COOCH_3$	$C_{14}H_{13}ClN_2O_5S$ (356.8)	181 – 182 (M)	45	47.13 47.20	3.67 3.53	7.85 7.72	1 680 1 650
106	3-ClC_8H_4S	H $C_6H_5CH_2$	$C_{17}H_{13}ClN_2O_2S$ (344.8)	172 – 174 (E)	86	59.22 59.08	3.80 3.67	8.12 8.26	1 690 1 640
107[b,g]	3-ClC_8H_4S	H $HC{\equiv}CCH_2$	$C_{13}H_9ClN_2O_2S$ (292.7)	177 – 178 (M)	80	53.34 53.12	3.10 3.28	9.57 9.44	1 690 1 645
108	3-ClC_8H_4S	H C_6H_5	$C_{16}H_{11}ClN_2O_2S$ (330.8	186 – 188 (B)	73	58.10 57.93	3.35 3.51	8.47 8.32	1 690 1 660
109	3-ClC_8H_4S	H 4-$CH_3C_6H_4$	$C_{17}H_{13}ClN_2O_2S$ (344.8)	202 – 204 (A)	79	59.22 59.29	3.80 3.95	8.12 8.31	1 695 1 660
110	3-ClC_8H_4S	H 2-$CH_3C_6H_4$	$C_{17}H_{13}ClN_2O_2S$ (344.8)	183 – 185 (E)	83	59.22 59.41	3.80 3.58	8.12 8.29	1 685 1 655
111	3-ClC_8H_4S	H 4-$C_6H_4C_6H_4$	$C_{22}H_{15}ClN_2O_2S$ (406.9)	205 – 207 (A)	69	64.94 64.77	3.72 3.58	6.89 6.68	1 680 1 660
112	3-ClC_8H_4S	H 4-ClC_6H_4	$C_{16}H_{10}Cl_2N_2O_2S$ (365.2)	204 – 206 (E)	85	52.62 52.86	2.76 2.49	7.67 7.43	1 675 1 650
113	3-ClC_8H_4S	H 2-CH_3-4 ClC_6H_3	$C_{17}H_{22}Cl_2N_2O_2S$ (344.8)	218 – 220 (E)	83	53.84 53.63	3.19 3.32	7.39 7.54	1 690 1 650

TABLE I
(*Continued*)

Compound	R^1	R^2/R^3	Formula (M. w.)	M. p., °C (Solvent)	Yield %	Calculated/Found %C	%H	%N	IR, ν(cm^{-1}) (CO–NH–CO)
114	3-ClC$_8$H$_4$S	H 4-BrC$_6$H$_4$	$C_{16}H_{10}BrClN_2O_2S$ (409.7)	224 – 226 (E)	76	49.91 49.75	2.46 2.62	6.84 6.99	1 710 1 648
115	3-ClC$_8$H$_4$S	H 2-NH$_2$C$_6$H$_4$	$C_{16}H_{12}ClN_3O_2S$ (345.8)	185 – 187 (B)	80	55.57 55.43	3.50 3.71	12.15 12.01	1 690 1 630
116	3-ClC$_8$H$_4$S	H 3-NO$_2$C$_6$H$_4$	$C_{16}H_{10}ClN_3O_4S$ (375.8)	236 – 238 (E)	91	51.14 51.27	2.68 2.62	11.18 10.91	1 710 1 650
117	3-ClC$_8$H$_4$S	H 2-OHC$_6$H$_4$	$C_{16}H_{11}ClN_2O_3S$ (346.8)	217 – 220 (E)	85	55.42 55.61	3.20 3.07	8.08 8.24	1 680 1 650
118	3-ClC$_8$H$_4$S	H 4-CH$_3$OC$_6$H$_4$	$C_{17}H_{13}ClN_2O_3S$ (360.8)	177 – 179 (E)	57	56.60 56.77	3.63 3.48	7.76 7.39	1 680 1 645
119	3-ClC$_8$H$_4$S	H 4-CH$_3$COC$_6$H$_4$	$C_{18}H_{13}ClN_2O_3S$ (372.8)	220 – 222 (E)	82	57.99 58.12	3.52 3.39	7.51 7.44	1 710 1 665
120	3-ClC$_8$H$_4$S	(CH$_2$)$_2$O(CH$_2$)$_2$	$C_{14}H_{13}ClN_2O_3S$ (324.8)	128 – 130 (B+H)	69	51.77 51.63	4.04 4.18	8.63 8.51	1 670

[a] E ethanol, B benzene, H hexane, T tetrachloromethane, M methanol, W water, A acetone. [b] ^{1}H NMR spectra of compounds: ***37***: 3.87 s, 2 H (CH_2); 7.30 m, 8 H (2 × C_6H_4); 10.56 s, 1 H (NH); ***38***: 4.15 s, 2 H (CH_2); 7.55 m, 7 H (C_6H_4 and C_6H_3); 10.60 s, 1 H and 11.28 s, 1 H (2 × NH); ***39***: 3.87 s, 2 H (CH_2); 7.35 m, 8 H (2 × C_6H_4); 10.55 s, 1 H (NH); ***40***: 7.55 m, 10 H (2 × C_6H_5); 10.72 s, 1 H (2 × NH); ***42***: 2.78 t, 1 H, *J*(B,C) = 1.5 Hz (≡CH); 4.52 q, 2 H, *J*(A,B) = 5 Hz, *J*(B,C) = 1.5 Hz (CH_2); 7.85 m, 4 H (C_6H_4); 9.10 t, 1 H, *J*(A,B) = 5 Hz (NH); 10.83 s, 1 H (NH); ***54***: 7.37 m, 7 H (C_6H_3 and C_6H_4); 10.45 s, 1 H and 11.68 s, 1 H (2 × NH); ***64***: 3.31 s, 3 H (CH_3N); 6.45 d, 1 H, *J*(A,B) = 16 Hz and 7.40 m, 11 H (CH=CH and 2 × C_6H_5); ***75***: 3.77 m, 8 H [$(CH_2)_4$]; 6.84 d, 1 H and 8.06 d, 1 H, *J*(A,B) = 16 Hz (CH=CH); 7.82 m, 4 H (C_6H_4); 10.36 s, 1 H (NH); ***93***: 1.18 t, 3 H (CH_3); 1.70 m, 2 H (CH_2); 7.40 d, 1 H and 8.38 d, 1 H, *J*(A,B) = 4 Hz (=CH–CH=); 8.75 t, 1 H (NH); 11.00 s, 1 H (NH); ***104***: 1.93 m, 4 H and 3.58 m, 4 H [$(CH_2)_4$]; 6.98 d, 1 H and 7.80 d, 1 H, *J*(A,B) = 4 Hz (=CH–CH=); 10.20 s, 1 H (NH); ***105***: 4.15 s, 3 H (CH_3O); 4.33 m, 2 H (CH_2); 4.95 m, 1 H (CH); 7.85 – 8.35 m, 4 H (3-chloro-2-benzo[*b*]thienyl); 9.40 d, 1 H (NH); 9.80 s, 1 H (NH); ***107***: 2.70 t, 1 H, *J*(B,C) = 1.5 Hz (≡CH); 4.25 q, 2 H, *J*(A,B) = 5 Hz, *J*(B,C) = 1.5 Hz (CH_2); 7.75 – 8.45 m, 4 H (3-chloro-2-benzo[*b*]thienyl); 8.78 t, 1 H, *J*(A,B) = 5 Hz (NH); 11.00 s, 1 H (NH); [c] ref.[6] gives m.p. 208 – 210 °C; [d] ref.[7] gives m.p. 238 °C; [e] ref.[8] gives m.p. 211 – 212 °C; [f] 5-chloro-2-thienyl. [g] ^{13}C NMR spectra of compounds: ***105***: 51.71 q (CH_3O); 54.85 d (CH); 121.28; 121.52; 123.08; 125.80; 127.75; 129.48; 135.41 and 136.97 (3-chloro-2-benzo[*b*]thienyl); 151.71 s; 161.60 s and 170.26 s (CO–NH–CO) and (COO); ***107***: 28.76 t (CH_2); 72.80 d (≡CH); 80.45 d (≡C–); 121.25; 122.52; 123.08; 125.80; 127.71; 129.47; 135.3 and 136.57 (3-chloro-2-benzo[*b*]thienyl); 151.67 s and 161.45 s (CO–NH–CO); [h] 3-chloro-2-benzo[*b*]thienyl.

3-(4-Chlorophenyl)propenoyl isothiocyanate (**8**): yield 82%, m.p. 106 – 108 °C. For $C_{10}H_6ClNOS$ (223.7) calculated: 53.69% C, 2.70% H, 6.26% N; found: 53.50% C, 2.83% H, 6.47% N. IR spectrum: 1 960 (N=C=S), 1 680 (C=O), 1 620 (C=C). ^{1}H NMR spectrum: 6.25 d, 1 H and 7.75 d, 1 H, J(A,B) = 16 Hz (CH=CH); 7.50 m, 4 H (C_6H_4).

5-Chloro-2-thienocarbonyl isothiocyanate (**11**): yield 88%, m.p. 62 – 64 °C. For $C_6H_2ClNOS_2$ (203.7) calculated: 35.38% C, 0.99% H, 6.87% N; found: 35.51% C, 1.12% H, 6.68% N. IR spectrum: 1 970 (N=C=S), 1 680 (C=O). ^{1}H NMR spectrum: 7.48 d, 1 H and 8.00 d, 1 H, J(A,B) = 8 Hz (=CH–CH=).

General Procedure for Preparation of O-Allyl N-Acylmonothiocyanates *13*, *17*, *19* – *21* and *23*

Allyl alcohol (1.82 g, 2.5 ml, 18 mmol) was added to a solution of the appropriate acyl isothiocyanate (15 mmol) in benzene (20 ml). After standing at room temperature for 4 days, the reaction mixture was mixed with hexane (200 ml) and allowed to stand at 0 °C for 24 h. The precipitate was collected and then crystallized from a suitable solvent.

O-Allyl N-(2-chlorophenylacetyl)monothiocarbamate (**13**): yield 44%, m.p. 71 – 73 °C (benzene–hexane). For $C_{12}H_{12}NO_2S$ (269.8) calculated: 53.42% C, 4.48% H, 5.19% N; found: 53.58% C, 4.31% H, 5.04% N. IR spectrum: 3 390 (N–H), 2 980 (C–H), 1 730 (C=O). ^{1}H NMR spectrum: 3.95 s, 2 H (CH_2); 4.98 m, 2 H (CH_2O); 5.35 m, 2 H (=CH_2); 5.85 m, 1 H (–CH=); 7.25 m, 4 H (C_6H_4); 8.93 s, 1 H (NH).

O-Allyl N-(2,6-difluorobenzoyl)monothiocarbamate (**17**). The title compound was obtained only as a semisolid crude product which, however, was sufficiently pure for the next preparation. ^{1}H NMR spectrum: 5.02 m, 2 H (CH_2O); 5.37 m, 2 H (=CH_2); 5.38 m, 1 H (=CH); 7.15 m, 3 H (C_6H_3); 9.20 s, 1 H (NH).

O-Allyl [N-3-(2-chlorophenyl)propenoyl]monothiocarbamate (**19**): yield 92%, m.p. 94 – 95 °C (methanol–water). For $C_{13}H_{12}ClNO_2S$ (281.8) calculated: 55.42% C, 4.29% H, 4.97% N; found: 55.63% C, 4.39% H, 5.05% N. IR spectrum: 3 385 (N–H); 1 720 (C=O), 1 612 and 1 612 (C=C), 1 459 (NHCS). ^{1}H NMR spectrum: 5.08 m, 2 H (CH_2O); 5.44 m, 2 H (=CH_2); 7.08 d, 1 H and 8.01 d, 1 H, J(A,B) = 16 Hz (CH=CH); 7.50 m, 4 H (C_6H_4); 9.43 s, 1 H (NH).

O-Allyl N-[3-(4-chlorophenyl)propenoyl]monothiocarbamate (**20**): yield 88%, m.p. 94 – 95 °C (methanol–water). For $C_{13}H_{12}ClNO_2S$ (281.8) calculated: 55.42% C, 4.29% H, 4.97% N; found: 55.32% C, 4.36% H, 4.88% N. IR spectrum: 3 380 (N–H), 1 720 (C=O), 1 670 and 1 615 (C=C). ^{1}H NMR spectrum: 5.08 m, 2 H (CH_2O); 5.48 m, 2 H (=CH_2); 6.00 m, 1 H (=CH); 7.00 d, 1 H and 7.75 d, 1 H, J(A,B) = 16 Hz (CH=CH); 7.40 m, 4 H (C_6H_4); 9.28 s, 1 H (NH).

O-Allyl N-[3-(4-bromophenyl)propenoyl]monothiocarbamate (**21**): yield 81%, m.p. 105.5 – 106.5 °C (acetone–water). For $C_{13}H_{12}BrNO_2S$ (326.2) calculated: 47.87% C, 3.71% H, 4.29% N; found: 47.95% C, 3.70% H, 4.38% N. IR spectrum: 3 390 (N–H), 1 715 (C=O), 1 675 and 1 618 (C=C), 1 460 (NHCS). ^{1}H NMR spectrum: 5.12 m, 2 H (CH_2O); 5.50 m, 2 H (=CH_2); 6.00 m, 1 H (=CH); 6.94 d, 1 H and 7.65 d, 1 H, J(A,B) = 16 Hz (CH=CH); 7.47 m, 4 H (C_6H_4); 11.58 s, 1 H (NH).

O-Allyl N-(5-chloro-2-thienocarbonyl)monothiocarbamate (**23**): yield 56%, m.p. 106 – 108 °C (benzene–water). For $C_9H_8ClNO_2S_2$ (261.8) calculated: 41.29% C, 3.08% H, 5.35% N; found: 41.13% C, 3.22% H, 5.77% N. IR spectrum: 3 420 (N–H), 1 695 (C=O), 1 470 (NHCS). ^{1}H NMR spectrum: 5.70 m, 2 H (CH_2O); 5.42 m, 2 H (=CH_2); 6.00 m (=CH); 6.92 d, 1 H and 7.87 d, 1 H, J(A,B) = 4 Hz (=CH–CH=); 11.00 s, 1 H (NH).

General Procedure for Preparation of S-Allyl N-Acylmonothiocarbamates *25*, *29*, *31* – *33* and *35*

A solution of the corresponding O-allyl ester (3 mmol) in benzene (10 ml) was refluxed for 20 h (compound *25*), 11 h (compounds *29*, *31*, *32*), 15 h (compound *33*) or 12 h (compound *35*). The solvent was evaporated and the product crystallized from an appropriate solvent.

S-Allyl N-(2-chlorophenylacetyl)monothiocarbamate (**25**); yield 43%, m.p. 113 – 117 °C (tetrachloromethane). For $C_{12}H_{12}NO_2S$ (269.8) calculated: 53.42% C, 4.48% H, 5.19% N; found: 53.60% C, 4.56% H, 4.89% N. IR spectrum: 3 370 (N–H), 1 720 and 1 650 (CO–NH–CO). ^{1}H NMR spectrum: 3.53 m, 2 H (CH_2S); 3.88 s, 2 H (CH_2); 5.14 m, 2 H (=CH_2); 5.78 m, 1 H (=CH); 7.23 m, 4 H (C_6H_4); 8.78 s, 1 H (NH).

S-Allyl N-(2,6-difluorobenzoyl)monothiocarbamate (**29**). *A*) The product was obtained according to the above general procedure in 70% yield, m.p. 83 – 84 °C (heptane). For $C_{11}H_9F_2NO_2S$ (257.3) calculated: 51.35% C, 3.53% H, 5.44% N; found: 51.1% C, 3.70% H, 5.63% N. IR spectrum: 3 410 (N–H), 1 707 and 1 660 (CO–NH–CO). ^{1}H NMR spectrum: 3.57 m, 2 H (CH_2S); 5.25 m, 2 H (=CH); 5.87 m, 1 H (=CH); 7.18 m, 3 H (C_6H_3); 9.20 s, 1 H (NH). *B*) A mixture of 2,6-difluorobenzoyl chloride (7.02 g, 41 mmol) and potassium thiocyanate (4.03 g, 41 mmol) in anhydrous acetonitrile (60 ml) was stirred at room temperature for 5 min. Allyl alcohol (2.58 g, 3.02 ml, 45 mmol) was added, the stirred mixture was refluxed for 5 h, cooled to room temperature and with stirring poured in cold water (600 ml). Upon standing for 30 min, the separated oily product solidified and was filtered. Crystallization from heptane afforded 8.69 g (83%) of the product.

S-Allyl N-[3-(2-chlorophenyl)propenoyl]monothiocarbamate (**31**); yield 87%, m.p. 96 – 97 °C (tetrachloromethane). For $C_{13}H_{12}ClNO_2S$ (281.8) calculated: 55.42% C, 4.29% H, 4.97% N; found: 55.48% C, 4.43% H, 5.10% N. IR spectrum: 3 390 (N–H), 1 703 and 1 660 (CO–NH–CO). ^{1}H NMR spectrum: 3.57 m, 2 H (CH_2S); 5.20 m, 2 H (=CH_2); 5.87 m, 1 H (=CH); 6.87 d, 1 H and 8.20 d, 1 H, J(A,B) = 16 Hz (CH=CH); 7.44 m, 4 H (C_6H_4); 9.76 s, 1 H (NH).

S-Allyl N-[3-(4-chlorophenyl)propenoyl]monothiocarbamate (**32**); yield 91%, m.p. 175 °C (tetrachloromethane). For $C_{13}H_{12}ClNO_2S$ (281.8) calculated: 55.42% C, 4.29% H, 4.97% N; found: 55.28% C, 4.39% H, 4.88% N. IR spectrum: 3 380 (N–H), 1 710 and 1 660 (CO–NH–CO), 1 625 (C=C). ^{1}H NMR spectrum: 4.09 m, 2 H (CH_2S); 5.48 m, 2 H (=CH_2); 6.15 m, 1 H (=CH); 7.10 d, 1 H and 7.98 d, 1 H, J(A,B) = 16 Hz (CH=CH); 7.72 m, 4 H (C_6H_4); 11.62 s, 1 H (NH).

S-Allyl N-[3-(4-bromophenyl)propenoyl]monothiocarbamate (**33**); yield 72%, m.p. 155 – 156 °C (acetone–water). For $C_{13}H_{12}BrNO_2S$ (326.2) calculated: 47.87% C, 3.71% H, 4.29% N; found: 47.64% C, 3.78% H, 4.26% N. IR spectrum: 3 397 (N–H), 1 702 and 1 651 (C=O), 1 635 (C=C), 1 453 (NHCS). ^{1}H NMR spectrum: 3.52 m, 2 H (CH_2S); 5.50 m, 2 H (=CH_2); 5.81 m, 1 H (=CH); 6.81 d, 1 H and 7.68 d, 1 H, J(A,B) = 16 Hz (CH=CH); 7.48 m, 4 H (C_6H_4); 11.31 s, 1 H (NH).

S-Allyl N-(5-chloro-2-thienocarbonyl)monothiocarbamate (**35**); yield 88%, m.p. 131 – 133 °C (benzene). For $C_9H_8ClNO_2S_2$ (261.8) calculated: 41.29% C, 3.08% H, 5.35% N; found: 41.35% C, 3.19% H, 5.23% N. IR spectrum: 1 675 and 1 625 (CO–NH–CO). ^{1}H NMR spectrum: 3.72 m, 2 H (CH_2S); 5.40 m, 2 H (=CH_2); 6.03 m, 1 H (=CH); 7.48 d, 1 H and 8.25 d, 1 H, J(A,B) = 4 Hz (=CH–CH=); 12.18 s, 1 H (NH).

General Procedure for Preparation of N-Acyl-N'-substituted and N-Acyl-N',N'-disubstituted Ureas *37 – 48*, *53 – 120*

The corresponding amine (1 mmol) and triethylamine (14 μl, 0.1 mmol) were added to a solution of the given S-allyl N-acylmonothiocarbamate *25 – 27*, *29 – 36* (1 mmol) in benzene (8 ml). In the preparation of derivative *105*, D,L-serine methyl ester hydrochloride (1.0 mmol) and triethylamine (153 μl, 1.1 mmol) were used and water (1 ml) was added. The reaction mixture was refluxed for 2 h (or 1 h in the case of derivatives *37 – 45*, *47*, *78* and *79*). After cooling to room temperature, the separated product was filtered and crystallized from an appropriate solvent. Compound *105* was isolated by column chromatography of the crude product on silica gel (100 g, 100/160 mm) with benzene–acetone (7 : 1) as eluent. The yields, melting points, spectral data and elemental analyses are given in Table I.

General Procedure for Preparation of N-(2-Chloro-5-nitrobenzoyl)-N'-substituted and N-(2-Chloro-5-nitrobenzoyl)-N',N'-disubstituted Ureas *49* – *52*

Allyl alcohol (2.32 g, 40 mmol) was added to a solution of 2-chloro-5-nitrophenyl isothiocyanate (*4*) (10 g, 40 mmol) in anhydrous benzene (20 ml), the mixture was set aside for 3 days at room temperature and then refluxed for 6 h. The corresponding amine (40 mmol) and triethylamine (0.58 ml, 4 mmol) were added and reflux was continued for 2 h. After cooling, the separated product was collected on filter and crystallized. The yields, melting points, spectral data and elemental analyses are given in Table I.

REFERENCES

1. Addor R. W., Berkelhammer G.: Ann. Rep. Med. Chem. *17*, 311 (1982).
2. De Milo A. B., Ostromecky D. M., Cheng S. C., Redfern R. E., Fye R. L.: Agric. Food Chem. *26*, 164 (1978).
3. Petersen U. in: *Houben–Weyl, Methoden der Organischen Chemie* (H. Hageman, Ed.), Vol. E4, p. 392. Thieme, Stuttgart 1983.
4. Kutschy P., Dzurilla M., Košćík D., Kristian P.: Collect. Czech. Chem. Commun. *52*, 1764 (1987).
5. Uno T., Machida K., Hanai K., Saito Y.: Bull. Chem. Soc. Jpn. *42*, 1619 (1969).
6. Gatterman L., Kantzler A.: Ber. Dtsch. Chem. Ges. *25*, 1086 (1892).
7. Boeger M. Drabek J.: Cier. 3,504,016 (1985); Chem. Abstr. *103*, 215196z (1985).
8. Dixon A. E.: J. Chem. Soc. *67*, 1047 (1895).
9. Kristian P., Dzurilla M., Kováč Š.: Chem. Zvesti *23*, 173 (1969).

Translated by M. Tichý.