THE SYNTHESIS AND SOME PROPERTIES OF *N,N′*-BIS(3-ALKOXYPHENYL)UREAS

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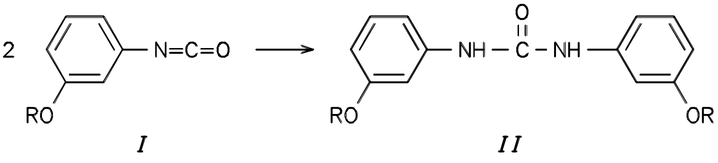
Symmetrical *N,N′*-diarylureas can be prepared by heating arylisocyanates with water[1]. *N,N′*-Diarylureas are also formed as by-products during the preparation of arylcarbamoic acid esters by adding of tertiary alcohols to arylisocyanates[2,3].

We prepared *N,N′*-bis(3-alkoxyphenyl)ureas *IIa* – *IIh* by adding of water to 3-alkoxyphenylisocyanates *I* in the presence of sodium hydroxide (Scheme 1) aaccording to the literature[1].



For R see Table I

SCHEME 1

As shown in Table I, which lists analytical data and some physical properties of the compounds *II*, the yields range from 72 to 83%. We found that in contrast with alkoxyphenylcarbamoic acid esters[4,5], all the *N,N′*-bis(3-alkoxyphenyl)ureas prepared (including those with a higher number of carbons in the alkoxy group) are practically insoluble in nonpolar solvents (e.g., hexane). The structures of compounds *II* were confirmed by their ^{1}H and ^{13}C NMR spectra (Tables II and III) and by IR spectroscopy. The chemical shifts were in keeping with the proposed chemical structures. In the IR spectra of all the compounds *IIa* – *IIh*, the following characteristic absorption bands were observed[6 – 8]: a band of medium intensity at 3 420 cm^{-1} due to the N–H stretching vibration, an intense band at 1 677 – 1 679 cm^{-1} (C=O stretching), and a medium intensity band at 1 600 – 1 605 cm^{-1} (aromatic C–C stretching).

TABLE I
Physical properties and elemental analyses of compounds *IIa* – *IIh*

Compound	R	Formula	M. p., °C Yield, %	R_F[a] R_M[b]	Calculated/Found		
					% C	% H	% N
IIa	CH_3	$C_{15}H_{16}N_2O_3$	173 – 175 83	0.590 –0.158	66.18 66.40	5.92 6.20	10.28 10.51
IIb	CH_2CH_3	$C_{17}H_{20}N_2O_3$	158 – 159 81	0.503 –0.005	68.00 67.86	6.71 6.58	9.32 8.98
IIc	$(CH_2)_2CH_3$	$C_{19}H_{24}N_2O_3$	159 – 161 77	0.359 0.252	69.50 69.20	7.37 7.67	8.53 8.20
IId	$(CH_2)_3CH_3$	$C_{21}H_{28}N_2O_3$	138 – 139 76	0.249 0.497	70.77 70.34	7.92 8.21	7.86 8.12
IIe	$(CH_2)_4CH_3$	$C_{23}H_{32}N_2O_3$	133 – 134 73	0.183 0.650	71.86 71.52	8.39 8.19	7.28 7.62
IIf	$(CH_2)_5CH_3$	$C_{25}H_{36}N_2O_3$	132 – 133 75	0.123 0.853	72.80 72.71	8.80 8.69	6.79 7.12
IIg	$(CH_2)_6CH_3$	$C_{27}H_{40}N_2O_3$	130 – 132 73	0.079 1.067	73.60 73.20	9.15 9.42	6.36 6.09
IIh	$(CH_2)_7CH_3$	$C_{29}H_{44}N_2O_3$	130 – 131 72	0.061 1.187	74.33 74.58	9.46 9.17	5.98 6.20

[a] TLC Silufol UV-254 in 1 M HCl–acetone. [b] $R_M = \log (1/R_F - 1)$.

TABLE II
Selected ^1H NMR spectral parameters (δ, ppm) of compounds *IIa* – *IIh*

Compound	H-2	H-4	H-5	H-6	NH	Alkyl
IIa	7.17	6.55	7.17	6.93	8.50	3.73
IIb	7.16	6.53	7.15	6.90	8.58	3.99, 1.32
IIc	7.19	6.53	7.15	6.88	8.60	3.88, 1.72, 0.98
IId	7.19	6.53	7.15	6.88	8.61	3.93, 1.68, 1.43, 0.93
IIe	7.18	6.53	7.15	6.87	8.61	3.93, 1.77, 1.40, 1.35, 0.90
IIf	7.18	6.53	7.15	6.87	8.61	3.92, 1.70, 1.41, 1.30 (4 H), 0.88
IIg	7.19	6.53	7.14	6.87	8.62	3.93, 1.70, 1.41, 1.35, 1.28 (4 H), 0.90
IIh	7.19	6.53	7.14	6.87	8.61	3.92, 1.70, 1.41, 1.35, 1.27 (6 H), 0.86

TABLE III
Selected ^{13}C NMR spectral parameters (δ, ppm) of compounds *IIa* – *IIh*

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C=O	Alkyl
IIa	140.9	104.0	159.7	107.2	129.6	110.6	152.4	54.9
IIb	140.8	104.5	158.9	107.8	129.5	110.4	152.4	62.8, 14.7
IIc	140.8	104.5	159.1	107.8	129.5	110.4	152.4	68.8, 22.1, 10.4
IId	140.8	104.5	159.1	107.8	129.5	110.4	152.4	67.0, 30.8, 18.8, 13.7
IIe	140.8	104.5	159.1	107.8	129.5	110.4	152.3	67.2, 28.3, 27.8, 22.1, 13.9
IIf	140.8	104.5	159.1	107.8	129.5	110.4	152.3	67.2, 28.7, 25.2, 31.0, 22.1, 13.9
IIg	140.8	104.5	159.1	107.8	129.5	110.4	152.3	67.2, 28.7, 25.5, 28.4, 31.2, 22.0, 13.9
IIh	140.8	104.5	159.1	107.8	129.5	110.4	152.3	67.2, 28.8, 25.5, 28.7, 28.7, 31.2, 22.1, 13.9

The products were also studied using thin-layer partition chromatography. We have found experimental conditions which afford satisfactory resolution of the separate members of series *II*, with the R_F values ranging from 0.06 (compound *IIa*) to 0.59 (compound *IIh*) (Table I). As expected and similarly to other homologous series[9,10], there is a linear relationhip between R_M [$R_M = \log(1/R_F - 1)$] (ref.[10]) and the number of carbons (n) in the alkoxy group:

$$R_M = 0.199\, n - 0.353 \qquad (r = 0.997,\ s = 0.030),$$

where r is the correlation coefficient and s the residual scattering.

EXPERIMENTAL

The melting points were determined with a Boetius block and are unceorrected. IR spectra were measured in chloroform solution on a Specord M-80 (Zeiss) spectrophotometer. NMR spectra (^{1}H at 300 MHz and ^{13}C at 75 MHz) were obtained on a Varian VXR-300 spectrometer in $CDCl_3$, using tetramethylsilane as an internal reference. All the compounds were checked for purity by partition TLC on silica gel Silufol UV-254 (Kavalier Votice, The Czech Republic) plates impregnated with a 5% solution of silicon oil in heptane, using 1 M HCl–acetone (1 : 1) as the mobile phase (detection by 254 nm UV light).

General Procedure for the Preparation of *N,N′*-Bis(3-alkoxyphenyl)ureas *IIa – IIh*

A mixture of 3-alkoxyphenylisocyanate *I* (30 mmol), sodium hydroxide (600 mg, 15 mmol) and water (10 ml) was heated under stirring for 2 h at boiling temperature. After slow cooling to room temperature (within 30 min) the solid product that appeared was collected by filtration, washed with water and dried. The obtained colourless product was finally crystallized from 2-propanol–water (1 : 1).

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