PREPARATION OF DERIVATIVES OF 2-CYANO-3-(5-*N*-ARYLAMINO- OR 5-*N*-ALKYL-*N*-PHENYLAMINO-2-FURYL)PROPENOIC ACIDS

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(5-Bromo-2-furyl)methylidenemalonodinitrile (**1**) reacted with substituted aromatic amines under formation of (5-*N*-arylamino-2-furyl)methylidenemalonodinitriles **2a–2h** whereas no reaction was observed with *N*-alkyl-*N*-phenylamines. Derivatives of 2-cyano-3-(5-*N*-alkyl-*N*-phenylamino-2-furyl)-propenoic acid **5a–5o** were prepared by reaction of the corresponding *N*-alkylanilines with 5-bromo-2-furancarbaldehyde, followed by hydrolysis of the obtained Eiji salts and reaction with malonic acid derivatives.

Key words: 3-(5-Amino-2-furyl)propenoic acid.

3-(5-*N*-Substituted amino-2-furyl)propenoic acids are usually prepared by reaction of the corresponding 5-amino-2-furancarbaldehydes with active methylene compounds or by nucleophilic substitution of activated 3-(5-*N*-substituted-2-furyl)propenoic acids with aliphatic secondary amines[1–5]. So far, only little attention has been paid to the preparation of 3-(5-*N*-arylamino- or 5-*N*-alkylphenylamino-2-furyl)propenoic acids because the starting 5-*N*-arylamino- or 5-*N*-alkyl-*N*-phenylamino-2-furancarbaldehydes are not very stable and they are therefore unsuitable as precursors for obtaining propene derivatives. 5-*N*-Phenylamino-2-furancarbaldehyde, is stable only as its acetyl derivative[6], 5-*N*-methylphenylamino- or 5-*N*-ethylphenylamino-2-furancarbaldehyde were isolated in low yields using a complicated procedure[7,8]. Nucleophilic substitution reaction of 3-(5-bromo-2-furyl)propenoic acids with *N*-alkylamines does not take place.

RESULTS AND DISCUSSION

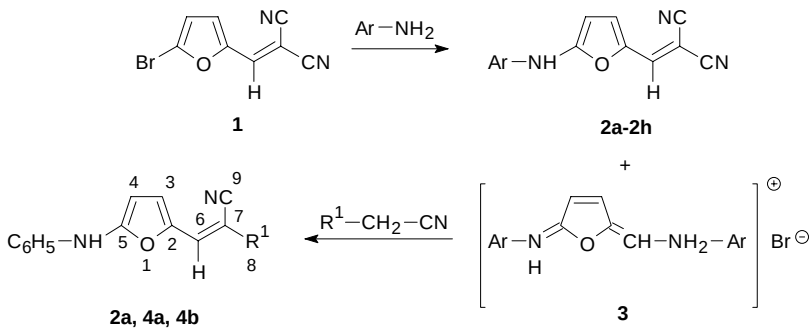
Reaction of compound **1** with two moles of aniline (Scheme 1) afforded two products which were identified by ^{1}H NMR analysis as (5-*N*-phenylamino-2-furyl)methylidenemalonodinitrile (**2a**) and ketimine **3** (Eiji product). The latter had identical physical and spectral properties as the compound prepared according to the literature[6]. The ratio of

these products depended on the molar quantity of the aniline used. We assumed that originally the reaction gives the product **2a** which on addition of aniline and elimination of malonic acid affords the Eiji product **3**.

We have found that addition of a small amount of malonodinitrile suppressed the formation of the Eiji product **3** and the reaction afforded exclusively the product **2a**. Compound **1** reacted with substituted anilines in the presence of malonodinitrile to give various substituted *N*-arylamino derivatives **2a–2g**. The reaction course was influenced by the solvent. The ketimine **3** was not formed in nonpolar solvents such as 1,4-dioxane or 1,2-dimethoxyethane, however, the reaction time was extremely long (several days to several weeks). In protic, as well as polar aprotic, solvents (acetonitrile, dimethylformamide, ethyl acetate) the reaction gave both compounds **2a** and **3**. No reaction with aliphatic amines was observed, except with benzylamine which gave (5-*N*-benzylamino-2-furyl)methylidenemalonodinitrile (**2h**) in high yield (Scheme 1). In contrast, compound **1** did not react with *N*-alkyl-*N*-phenylamines.

Compound **3** was alkali hydrolyzed and, without isolation, subjected to reaction with compounds containing active methylene group (malonodinitrile, methyl cyanoacetate or cyanoacetamide) which resulted in aromatization of the 2,5-dihydrofuran nucleus and gave compounds **2a**, **4a**, **4b** (Scheme 1).

Derivatives **5a–5o** were prepared by reaction of 5-bromo-2-furancarbaldehyde with two moles of an *N*-alkyl-*N*-phenylamine (Scheme 2). However, we were not able to

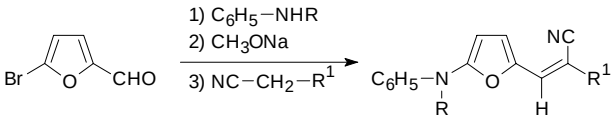


In formulae **2a**, R^1 = CN
4a, R^1 = $COOCH_3$
4b, R^1 = $CONH_2$

2	Ar
a	C_6H_5
b	4-Br-C_6H_4
c	2-Cl-C_6H_4
d	3-Cl-C_6H_4
e	4-Cl-C_6H_4
f	3,4-diCl-C_6H_3
g	4-F-C_6H_4
h	C_6H_5-CH_2

SCHEME 1

isolate the arising ketimine **3** even in the form of its perchlorate, as described in the case of secondary aliphatic amines[9]. Therefore, we hydrolyzed the ketimine directly in the reaction mixture and the liberated 5-*N*-alkyl-*N*-phenylamino-2-furancarbaldehyde was treated *in situ* with malonic acid derivatives under formation of the corresponding derivatives **5a–5o**.



5a-5o

5	R	R^1
a	CH_3	CN
b	CH_3CH_2	CN
c	$CH_3(CH_2)_2$	CN
d	$CH_3(CH_2)_3$	CN
e	$(CH_3)_2CH$	CN
f	CH_3	$COOCH_3$
g	CH_3CH_2	$COOCH_3$
h	$CH_3(CH_2)_2$	$COOCH_3$
i	$CH_3(CH_2)_3$	$COOCH_3$
j	$(CH_3)_2CH$	$COOCH_3$
k	CH_3	$CONH_2$
l	CH_3CH_2	$CONH_2$
m	$CH_3(CH_2)_2$	$CONH_2$
n	$CH_3(CH_2)_3$	$CONH_2$
o	$(CH_3)_2CH$	$CONH_2$

SCHEME 2

The reaction mixture was hydrolyzed using various bases. Hydrolysis with 10% NaOH, followed by reaction with malonic acid derivatives, afforded products **5a–5o** in yields of 10–18%, with triethylamine the yields amounted to 20–32%. Although hydrolysis with morpholine gave good yields (66–84%), the desired products were accompanied by the corresponding (5-morpholin-4-yl-2-furyl)methylidenemalonodinitrile which could be removed only by chromatography. The reagent of choice appeared to be sodium methoxide that gave yields 58–94% (Table I). The low yields found for *N*-isopropylaniline are apparently due to the bulkiness of the nucleophile.

The ^{1}H NMR spectra of compounds **2a**, **4a** and **4b** exhibit signals of protons H-3 and H-4. Compared with the spectrum of (5-amino-2-furyl)methylidenemalonodinitrile[10] (7.38, H-3; 5.66, H-4 and 7.06, H-6), the signals of the corresponding protons in compounds **2a**, **4a** and **4b** are considerably shifted. Similar spectral characteristics were observed also for substituted (5-*N*-arylamino-2-furyl)methylidenemalonodinitrile derivatives (Table II). The H-6 proton signal was observed at 7.51–7.29, H-3 proton signals

TABLE I
Characteristic data of compounds **2a–2g**, **4a**, **4b**, **5a–5o**

Compound	M.p., °C Yield, %	Formula M.w.	Calculated/Found		
			% C	% H	% N
2a	188–190	$C_{14}H_9N_3O$	71.48	3.86	17.86
	88	235.2	71.38	3.79	18.01
2b[a]	201–204	$C_{14}H_8BrN_3O$	53.53	2.57	13.38
	73	314.1	53.48	2.55	13.51
2c[b]	200–202	$C_{14}H_8ClN_3O$	62.35	2.99	15.58
	72	269.7	62.26	2.93	15.69
2d[c]	182–183	$C_{14}H_8ClN_3O$	62.35	2.99	15.58
	70	269.7	62.22	2.91	15.68
2e[d]	168–170	$C_{14}H_8ClN_3O$	62.35	2.99	15.58
	70	269.7	62.29	3.02	15.70
2f[e]	200–202	$C_{14}H_7Cl_2N_3O$	55.29	2.32	13.82
	71	304.1	55.18	2.29	13.90
2g	201–204	$C_{14}H_8FN_3O$	66.40	3.18	16.59
	74	253.2	66.28	2.99	16.71
4a	172–174	$C_{15}H_{12}N_2O_3$	67.16	4.51	10.44
	90	268.3	67.08	4.52	10.50
4b	209–211	$C_{14}H_{11}N_3O_2$	66.40	4.38	16.59
	91	253.3	66.31	4.33	16.71
5a	134–135	$C_{15}H_{11}N_3O$	72.28	4.45	16.86
	86	249.3	72.10	4.56	16.73
5b	96–98	$C_{16}H_{13}N_3O$	72.99	4.98	15.96
	80	263.3	72.83	4.83	15.87
5c	103–105	$C_{17}H_{15}N_3O$	73.63	5.45	15.15
	90	277.3	73.48	5.50	15.02
5d	228–230	$C_{18}H_{17}N_3O$	74.20	5.88	14.42
	84	291.4	73.98	5.71	14.29
5e	123–125	$C_{17}H_{15}N_3O$	73.63	5.45	15.15
	57	277.3	73.81	5.51	15.37
5f	109–110	$C_{16}H_{14}N_2O_3$	68.07	5.00	9.92
	90	282.3	67.91	4.92	9.78

TABLE I
(*Continued*)

Compound	M.p., °C Yield, %	Formula M.w.	Calculated/Found		
			% C	% H	% N
5g	139–141	$C_{17}H_{16}N_2O_3$	68.91	5.44	9.45
	82	296.3	69.03	5.49	9.58
5h	142–144	$C_{18}H_{18}N_2O_3$	69.66	5.85	9.03
	81	310.4	69.51	5.91	8.96
5i	104–106	$C_{19}H_{20}N_2O_3$	70.35	6.21	8.64
	93	324.4	70.41	6.10	8.77
5j	106–108	$C_{18}H_{18}N_2O_3$	69.66	5.85	9.03
	64	310.4	69.53	5.94	8.95
5k	201–203	$C_{15}H_{13}N_3O_2$	67.40	4.90	15.72
	94	267.3	67.32	4.98	15.80
5l	197–199	$C_{16}H_{15}N_3O_2$	68.31	5.37	14.94
	87	281.3	68.19	5.46	14.81
5m	202–204	$C_{17}H_{17}N_3O_2$	69.14	5.80	14.23
	92	295.3	69.91	5.72	14.10
5n	174–175	$C_{18}H_{19}N_3O_2$	69.88	6.19	13.58
	89	309.4	69.71	6.26	13.66
5o	217–219	$C_{17}H_{17}N_3O_2$	69.14	5.80	14.23
	71	295.3	69.27	5.71	14.37

[a] Calculated: 25.44% Br, found: 25.39% Br. [b] Calculated: 13.14% Cl, found: 13.19% Cl. [c] Calculated: 13.14% Cl, found: 13.29% Cl. [d] Calculated: 13.14% Cl, found: 13.21% Cl. [e] Calculated: 23.31% Cl, found: 23.25% Cl.

TABLE II
^{1}H NMR spectra of compounds **2a–2g**, **4a**, **4b**, **5a–5o**

Compound	H-3, d	H-4, d	H-6, s	^3J(3,4)	Aromatic protons
2a	7.54	6.08	7.48	4.0	7.05–7.46 m, 5 H
2b	7.46	6.03	7.40	4.0	7.30–7.43 m, 4 H
2c[a]	7.57	6.06	7.48	4.1	7.40–7.55 m, 4 H
2d	7.48	6.06	7.51	4.0	7.01–7.45 m, 4 H
2e[b]	7.46	6.03	7.49	4.0	7.01–7.83 m, 4 H
2f[c]	7.59	6.09	7.44	4.1	7.38–7.58 m, 3 H
2g[d]	7.47	6.00	7.44	4.2	7.08–7.56 m, 4 H
4a[e]	7.64	6.01	7.65	4.0	6.25–7.62 m, 5 H
4b[f]	7.60	5.86	7.60	4.0	6.75–7.38 m, 7 H
5a[g]	7.44	5.73	7.31	4.2	7.50–7.60 m, 5 H
5b[h]	7.13	5.58	7.95	4.2	7.40–7.71 m, 5 H
5c[i]	7.40	5.55	7.26	4.2	7.53 s, 5 H
5d[j]	7.40	5.68	7.53	4.2	7.71 s, 5 H
5e[k]	6.95	5.18	7.55	4.0	7.32–7.62 m, 5 H
5f[l]	7.40	5.70	7.65	4.2	7.51–7.63 m, 5 H
5g[m]	7.28	5.53	7.61	4.2	7.50 s, 5 H
5h[n]	7.41	5.49	7.59	4.2	7.51 s, 5 H
5i[o]	7.40	5.48	7.58	4.2	7.52 s, 5 H
5j[p]	6.91	5.21	8.03	4.0	7.41–7.61 m, 5 H
5k[r]	7.38	5.69	7.70	4.2	7.53–7.70 m, 5 H
5l[s]	7.31	5.48	7.66	4.2	7.51 s, 5 H
5m[t]	7.28	5.44	7.64	4.2	7.52 s, 5 H
5n[u]	7.25	5.41	7.61	4.2	7.41 s, 5 H
5o[v]	6.88	5.01	7.88	4.0	7.10–7.62 m, 5 H

Other signals: [a] 11.19 brs, 1 H (NH); [b] 10.50 brs, 1 H (NH); ; [c] 11.21 brs, 1 H (NH); [d] 11.10 brs, 1 H (NH); [e] 3.71 s, 3 H (OCH_3); 10.80 brs, 1 H (NH); [f] 10.31 brs, 1 H (NH); [g] 3.69 s, 1 H (CH_3N); [h] 1.30 t, 3 H, ^3J = 7.0 (CH_3CH_2N); 4.08 q, 2 H, ^3J = 7.0 (CH_3CH_2N); [i] 1.70 m, 2 H (CH_2); 0.96 t, 3 H (CH_3); 1.23–1.88 m, 2 H (CH_2); [j] 1.70 m, 2 H (CH_2); 0.96 t, 3 H (CH_3); 1.23–1.80 m, 2 H (CH_2); 4.15 t, 2 H (CH_2); [k] 1.26–1.34 d, 6 H (2 × CH_3); 4.60–4.92 m, 1 H (CH); [l] 3.68 s, 3 H (CH_3N); 4.79 s, 3 H (CH_3O); [m] 3.80 s, 3 H (CH_3O); 1.30 t, 3 H, ^3J = 7.0 (CH_3CH_2N); 4.08 q, 2 H, ^3J = 7.0 (CH_3CH_2N); [n] 3.77 s, 3 H (CH_3O); 4.03 t, 2 H (CH_2); 1.73 m, 2 H (CH_2); 0.96 t, 3 H (CH_3); [o] 3.75 s, 3 H (CH_3O); 4.05 t, 2 H (CH_2); 1.30–1.91 m, 4 H (2 × CH_2); 0.89 t, 3 H (CH_3); [p] 3.77 s, 3 H (CH_3O); 4.60–4.91 m, 1 H (CH); 1.28–1.35 d, 6 H (2 × CH_3); [r] 3.65 s, 3 H (CH_3N); 6.72 m, 2 H (NH_2); [s] 1.30 t, 3 H, ^3J = 7.0 (CH_3CH_2N); 4.08 q, 2 H, ^3J = 7.0 (CH_3CH_2N); 7.08 m, 2 H (NH_2); [t] 0.96 t, 3 H (CH_3); 1.65 m, 2 H (CH_2); 4.00 t, 2 H (CH_2); 7.08 m, 2 H (NH_2); [u] 0.89 t, 3 H (CH_3); 6.60 m, 2 H (NH_2); [v] 1.13–1.21 d, 6 H (2 × CH_3); 4.31–4.73 m, 1 H (CH).

at 7.59–7.40 and H-4 proton signals at 6.09–5.86. For compounds **2a**, **2h** and **5k** we measured also ^{13}C NMR spectra. The signals of protons C-2 to C-9 were assigned on the basis of ref.[10] and a standard NOE spectrum.

The *trans*-relation of the H-6 atom and the CN group in compounds **5f–5o** can be derived from the vicinal coupling constants ^3J(C≡N,H-6) = 12.4 and ^3J(C=O,H-6) = 5.6

TABLE III
Spectral properties of compounds **2a–2g**, **4a**, **4b**, **5a–5o**

Compound	UV spectra		IR spectra		
			ν(NH)	ν(CN)	ν(C=C)
2a	236 (3.25)	465 (3.87)	3 280	2 190	1 635
2b	266 (3.32)	468 (3.65)	3 250	2 210	1 640
2c	255 (3.28)	458 (3.72)	3 303	2 200	1 628
2d	263 (3.36)	469 (3.70)	3 290	2 201	1 640
2e	258 (3.18)	472 (3.56)	3 230	2 195	1 635
2f	252 (3.22)	466 (3.62)	3 235	2 205	1 645
2g	261 (3.31)	469 (3.71)	3 255	2 195	1 635
4a	267 (3.59)	464 (3.95)	3 280	2 210	1 610
4b	269 (3.57)	458 (3.27)	3 310	2 200	1 620
5a	220 (2.46)	462 (3.02)	2 220[a]	2 218	1 625
5b	229 (2.44)	464 (2.95)	2 198[a]	2 210	1 642
5c	231 (2.47)	464 (3.13)	2 196[a]	2 202	1 625
5d	273 (2.63)	465 (3.02)	2 197[a]	2 202	1 628
5e	254 (2.53)	461 (3.10)	2 196[a]	2 210	1 631
5f	228 (2.43)	462 (3.14)	1 698[b]	2 205	1 621
5g	230 (2.47)	461 (3.10)	1 690[b]	2 204	1 620
5h	228 (2.43)	462 (3.07)	1 691[b]	2 202	1 622
5i	274 (2.49)	462 (3.11)	1 701[b]	2 208	1 626
5j	249 (2.53)	461 (3.02)	1 730[b]	2 200	1 620
5k	229 (2.41)	457 (3.03)	1 684[b]	2 202	1 638
5l	231 (2.43)	458 (3.02)	1 680[b]	2 210	1 628
5m	229 (2.46)	458 (3.04)	1 676[b]	2 220	1 627
5n	273 (2.51)	459 (3.11)	1 672[b]	2 221	1 630
5o	271 (2.46)	458 (3.01)	1 672[b]	2 200	1 630

[a] Related to the absorption of CN group, ν(CN). [b] Related to the absorption of CO group, ν(CO).

in the spectrum of compound **5k**. The marked downfield shift of the H-4 proton signal in compounds **5e**, **5j** and **5o** as compared with compounds **5d**, **5i** and **5n** is probably connected with the bulkiness of the isopropyl group.

Electron spectra of compounds **5a–5o** (Table III) exhibit an absorption band at 220–274 nm due to the $\pi \rightarrow \pi^*$ electron transition of the aromatic and furan nuclei. Another intense band, in the visible region, at 457–464 nm, corresponds to the $n \rightarrow \pi^*$ transition of the whole system. The IR spectra display characteristic vibrational bands of CN groups at 2 196–2 218 cm^{-1}. In some cases this band is split, showing a nonequivalence of the CN groups in the molecule, probably due to their orientation in the solid state (KBr technique).

EXPERIMENTAL

The melting points were determined on a Boetius block and are uncorrected. Infrared spectra were recorded on a PU 9800 FTIR Philips spectrometer using KBr technique (0.3 mg of compound/300 mg KBr), calibration with polystyrene foil. Ultraviolet spectra (λ_{max}, log ε) were measured on an M-40 (Zeiss, Jena) spectrophotometer in methanol, concentration 2 . 10^{-5} mol/dm^3. ^1H and ^{13}C NMR spectra (δ, ppm; *J*, Hz) were taken on a Varian VXR-300 spectrometer at 25 °C in hexadeuteriodimethyl sulfoxide with tetramethylsilane as internal standard. The purity of the products and the reaction course were monitored by TLC on Silufol (Merck), detection with iodine vapours and UV light.

(5-*N*-Benzylamino-2-furyl)methylidenemalonodinitrile (**2h**)

A mixture of (5-bromo-2-furyl)methylidenemalonodinitrile (**1**; 1.95 g, 0.01 mol), benzylamine (2.15 g, 0.02 mol) and methanol (20 ml) was refluxed for 1 h. After addition of water (10 ml) the mixture was set aside for 12 h at room temperature. The deposited compound was collected, washed with aqueous methanol and dried. Crystallization from methanol afforded 2.14 g (86%) of compound **2h**, m.p. 200–202 °C. UV spectrum: 455 (3.87). IR spectrum: 1 635 (CO), 2 190 (CN), 3 280. For $C_{15}H_{11}N_3O$ (249.3) calculated: 72.28% C, 4.45% H, 16.86% N; found: 72.03% C, 4.37% H, 16.98% N. ^1H NMR spectrum: 4.50 brs, 2 H (CH_2N); 5.79 d, 1 H, $^3J(3,4)$ = 4.2 (H-4); 7.13 s, 1 H (H-6); 7.36 d, 1 H, $^3J(4,3)$ = 4.2 (H-3); 7.18–7.40 m, 5 H (phenyl). ^{13}C NMR spectrum: 46.0 (Ar-CH_2), 53.5 (C-7), 96.4 (C-4), 117.3 (C-9), 118.5 (C-8), 133.9 (C-3), 136.5 (C-6), 139.5 (C-2), 165.6 (C-5), 127.6, 127.8, 128.6 and 137.7 (phenyl).

(5-*N*-Arylamino-2-furyl)methylidenemalonodinitriles **2a–2g**

Nitrile **1** (1.95 g, 0.01 mol) and malonodinitrile (0.2 g, 0.003 mol) were dissolved in boiling methanol (20 ml) and a solution of the corresponding aromatic amine (0.02 mol) in methanol (5 ml) was added in one portion. The mixture was refluxed until the starting compounds reacted completely (2–5 h, monitoring by TLC). Water (10 ml) was added and the mixture was allowed to stand at room temperature for 12 h. The product was collected by filtration, washed with aqueous methanol, dried and purified by crystallization from methanol. The physicochemical characteristics of the obtained derivatives are given in Tables I–III. ^{13}C NMR spectrum of compound **2a**: 57.1 (C-7), 96.4 (C-4), 116.6 (C-9), 117.8 (C-8), 135.1 (C-3), 135.6 (C-6), 140.6 (C-2), 161.0 (C-5), 118.8, 123.6, 129.4 and 137.5 (phenyl).

Nitrile, Methyl Ester and Amide of 2-Cyano-3-(5-*N*-phenylamino-2-furyl)propenoic Acid (**2a**, **4a** and **4b**)

The corresponding derivative of malonic acid (0.0021 mol; 138 mg of malonodinitrile, 208 mg of methyl cyanoacetate or 177 mg of cyanoacetamide) was added in one portion to a vigorously stirred solution of compound **3** (hydrate; 0.75 g, 0.002 mol; prepared according to ref.[6]) in 80% methanol (10 ml). After stirring at room temperature for 5 h, the precipitate was filtered, washed with dilute methanol, dried and purified by crystallization from dimethyl sulfoxide. The physicochemical characteristics of the products **2a**, **4a** and **4b** are given in Tables I–III.

Nitriles, Methyl Esters and Amides of 2-Cyano-3-(5-*N*-Alkyl-*N*-phenylamino-2-furyl)propenoic Acids **5a–5o**

The appropriate secondary amine (0.022 mol; 2.36 g of *N*-methyl-*N*-phenylamine; 2.67 g of *N*-ethyl-*N*-phenylamine; 2.97 g of *N*-phenyl-*N*-propylamine; 2.97 g of *N*-phenyl-*N*-isopropylamine or 3.28 g of *N*-butyl-*N*-phenylamine) was added to a solution of 5-bromo-2-furancarbaldehyde (1.75 g, 0.01 mol) in methanol (10 ml) and the mixture was refluxed until the 5-bromo-2-furancarbaldehyde reacted completely (1–5 h, monitored by TLC). The reaction mixture was cooled to 5 °C and sodium methoxide (0.56 g, 0.011 mol) in methanol (5 ml) and water (2 ml) was added. After stirring at room temperature for 1 h, the corresponding malonic acid derivative (0.012 mol; 0.79 g of malonodinitrile; 1.19 g of methyl cyanoacetate; 1.0 g of cyanoacetamide) was added and stirring was continued for 2 h. The reaction mixture was then set aside at 0 °C for 5 h, the precipitate was collected, washed with ice-cold methanol, dried and purified by crystallization from methanol. The physicochemical characteristics of the products **5a–5o** are given in Tables I–III. ^{13}C NMR spectrum of compound **5k**: 34.8 (CH_3N); 89.3 (C-7); 91.7, ^1J(C-H) = 181.9 (C-4); 118.4, ^3J(C-H,CN) = 12.4 (C-9); 130.6, ^1J(C-H) = 179.9 (C-3); 130.0, ^1J(C-H) = 161.3 (C-6); 142.9 (C-2); 160.8 (C-5); 164.2, ^3J(C=O,H-6) = 5.6 (C-8); 123.2; 125.5; 129.5 and 139.9 (phenyl).

REFERENCES

1. Knoppova V., Kada R., Kovac J.: Collect. Czech. Chem. Commun. *44*, 2417 (1979); *51*, 879 (1986).
2. Kada R., Knoppova V., Kovac J.: Synth. Commun. *7*, 157 (1977).
3. Kada R., Knoppova V., Kovac J.: Collect. Czech. Chem. Commun. *43*, 3409 (1978); *45*, 1831 (1980).
4. Kada R., Knoppova V., Kovac J., Mackova N.: Collect. Czech. Chem. Commun *49*, 2141 (1984).
5. Berkes D., Kovac J.: Collect. Czech. Chem. Commun. *43*, 579 (1978).
6. Eiji N.: Chem. Ber. *103*, 2992 (1970).
7. Nazarova Z. N., Pustovarov V. S.: Khim. Geterotsikl. Soedin. *1969*, 586; Chem. Abstr. *72*, 31523 (1970).
8. Pustovarov V. S., Nazarova Z. N., Kravchenko O. B.: Zh. Org. Khim. *7*, 835 (1971); Chem. Abstr. *75*, 48788 (1971).
9. Gracza T., Arnold Z., Kovac J.: Collect. Czech. Chem. Commun. *49*, 1600 (1984); *51*, 879 (1986).
10. Kriz M.: *Ph.D. Thesis*. Slovak Technical University, Bratislava 1984.