PREPARATION, ^{1}H AND ^{13}C NMR SPECTRA OF SUBSTITUTED 2-BENZOYLAMINOCARBOXAMIDES

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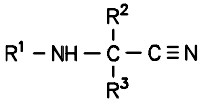
A new type of herbicides based on imidazolinones has been introduced into agriculture under commercial names of Arsenal, Pursuit, Scepter, Assert etc. by American Cyanamid Company since 1983 (ref.[1]). These compounds destroy diocotyledonous weeds and are almost nontoxic for mammals and fish (LD_{50} rat – 500 mg/kg, LD_{50} trout – 300 mg/kg) and nonmutagenic according to the AMES test[2].

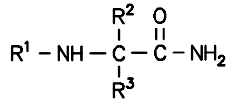
The aim of the present work is to synthesize substituted 2-benzoylaminocarboxamides as starting materials for preparation of imidazolinones and potential biologically active substances (Formulae *I* – *III*).

The nitriles *I* were prepared by the Strecker synthesis from the respective ketones, potassium cyanide, and aqueous ammonia or methylamine. In the syntheses of nitriles *Ii* and *Ij*, 4-nitroacetophenone was added to the reaction mixtures in benzene solution, and the reaction mixture contained a phase transfer catalyst. Even at these conditions, however, the yields of nitriles *Ii* and *Ij* were lower (Table I).

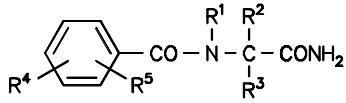
The subsequent hydrolysis of nitriles *I* to amides *II* was performed either in 98% sulfuric acid by heating on a water bath or in alkaline medium of aqueous ammonia by action of hydrogen peroxide at 40 °C. The conditions of hydrolysis were chosen according to the state of nitrile at 40 °C. The liquid nitriles *Ia* – *Ih* were hydrolyzed in alkaline medium, the nitriles *Ii* and *Ij* in acidic medium. Nitrile *Ib* was also hydrolyzed in sulfuric acid because its hydrolysis yields in ammoniacal peroxide were very low. The hydrolysis of α-aminonitriles in ammoniacal medium is accompanied by reversible exchange of amino group with the medium[3,4]. Therefore, the hydrolysis was carried out in the solution of the corresponding amine. The acylation of aminoamides *II* to benzoylamino derivatives *IIIa* – *IIIz* was carried out using the respective substituted benzoyl chlorides in anhydrous chloroform in the presence of one equivalent of triethylamine. The reaction has high yields (Table I) and the products can easily be purified by recrystallization from a mixture of chloroform and acetone or benzene and methanol.



I



II



III

I, *II*	R^1	R^2	R^3
a	H	CH_3	CH_3
b	CH_3	CH_3	CH_3
c	H	CH_3	CH_3CH_2
d	H	CH_3	i-C_3H_7
e	CH_3	CH_3	i-C_3H_7
f	CH_3	CH_3	i-C_4H_9
g	H	$-(CH_2)_5-$	
h	H	CH_3	C_6H_5
i	H	CH_3	4-NO_2-C_6H_4
j	CH_3	CH_3	4-NO_2-C_6H_4

III	R^1	R^2	R^3	R^4	R^5
a	H	CH_3	CH_3	4-NO_2	H
b	CH_3	CH_3	CH_3	H	H
c	CH_3	CH_3	CH_3	4-NO_2	H
d	H	CH_3	CH_3CH_2	4-NO_2	H
e	H	CH_3	i-C_3H_7	H	H
f	H	CH_3	i-C_3H_7	2-CH_3	H
g	H	CH_3	i-C_3H_7	4-CH_3	H
h	H	CH_3	i-C_3H_7	4-OCH_3	H
i	H	CH_3	i-C_3H_7	2-Cl	H
j	H	CH_3	i-C_3H_7	4-Cl	H
k	H	CH_3	i-C_3H_7	2-$COOCH_3$	H
l	H	CH_3	i-C_3H_7	2-Cl	6-Cl
m	H	CH_3	i-C_3H_7	2-F	6-F
n	H	CH_3	i-C_3H_7	2-NO_2	H
o	H	CH_3	i-C_3H_7	4-NO_2	H
p	H	CH_3	i-C_3H_7	3-NO_2	6-NO_2
q	CH_3	CH_3	i-C_3H_7	H	H
r	CH_3	CH_3	i-C_3H_7	4-NO_2	H
s	CH_3	CH_3	i-C_3H_7	4-OCH_3	H
t	CH_3	CH_3	i-C_4H_9	4-NO_2	H
u	H	$-(CH_2)_5-$		4-CH_3	H
v	H	$-(CH_2)_5-$		4-NO_2	H
w	H	CH_3	C_6H_5	4-NO_2	H
x	H	CH_3	4-NO_2-C_6H_4	4-NO_2	H
y	CH_3	CH_3	4-NO_2-C_6H_4	4-NO_2	H
z	CH_3	CH_3	i-C_4H_9	H	H

TABLE I
Physico-chemical data of compounds *I*, *II* and *III*

Compound	M.p., °C Yield, %	Formula (M.w.)	Calculated/Found		
			% C	% H	% N
Id	70[a] 56	$C_6H_{12}N_2$ (112.2)	–	–	–
Ii	109 – 111 28	$C_9H_9N_3O_2$ (191.2)	–	–	–
Ij	186 – 190 (dec.)[b] 31	$C_{10}H_{11}N_3O_2$ (205.2)	–	–	–
IIa	101 – 103 15	$C_4H_{10}N_2O$ (102.1)	–	–	–
IIb	79 – 81 21	$C_5H_{12}N_2O$ (116.2)	–	–	–
IIi	115 – 116 54	$C_9H_{11}N_3O_3$ (209.2)	–	–	–
IIj	123 – 124 50	$C_{10}H_{13}N_3O_3$ (223.2)	–	–	–
IIIa	229 – 232 72	$C_{11}H_{13}N_3O_4$ (251.2)	52.58 53.03	5.22 5.39	16.72 17.00
IIIb	156 – 157 67	$C_{12}H_{16}N_2O_2$ (220.3)	65.43 65.66	7.32 7.46	12.72 12.98
IIIc	208 – 209 67	$C_{12}H_{15}N_3O_4$ (265.3)	54.33 54.57	5.70 5.84	15.84 16.07
IIId	173 – 176 78	$C_{12}H_{15}N_3O_4$ (265.3)	54.33 54.56	5.70 5.87	15.84 15.59
IIIe	142 – 144 64	$C_{13}H_{18}N_2O_2$ (234.3)	66.64 66.71	7.74 7.85	11.96 11.72
IIIf	125 – 127 75	$C_{14}H_{20}N_2O_2$ (248.3)	67.72 67.66	8.12 8.09	11.28 11.32
IIIg	154 – 155 70	$C_{14}H_{20}N_2O_2$ (248.3)	67.72 68.11	8.12 7.91	11.28 10.93
IIIh	167 – 170 53	$C_{14}H_{20}N_2O_3$ (264.3)	63.62 63.86	7.63 7.80	10.60 10.46
IIIi	110 – 111 75	$C_{13}H_{17}ClN_2O_2$ (268.7)	58.10 58.28	6.38 6.57	10.42 10.50

TABLE I
(*Continued*)

Compound	M.p., °C Yield, %	Formula (M.w.)	Calculated/Found		
			% C	% H	% N
IIIj	151 – 152 81	$C_{13}H_{17}ClN_2O_2$ (268.7)	58.10 57.91	6.38 6.59	10.42 10.65
IIIk	168 – 169 67	$C_{15}H_{20}N_2O_4$ (292.3)	61.63 61.40	6.90 7.17	9.58 10.22
IIIl	169 – 171 61	$C_{13}H_{16}Cl_2N_2O_2$ (303.2)	51.50 51.76	5.32 5.15	9.24 9.50
IIIm	152 – 154 68	$C_{13}H_{16}F_2N_2O_2$ (270.3)	57.77 58.00	5.97 6.11	10.36 10.01
IIIn	168 – 170 98	$C_{13}H_{17}N_3O_4$ (279.3)	55.90 55.62	6.13 6.02	15.05 14.78
IIIo	181 – 183 81	$C_{13}H_{17}N_3O_4$ (279.3)	55.90 55.56	6.13 5.96	15.05 14.80
IIIp	204 – 206 94	$C_{13}H_{16}N_4O_6$ (324.3)	48.15 48.40	4.97 5.06	17.28 17.03
IIIq	171 – 172 65	$C_{14}H_{20}N_2O_2$ (248.3)	67.72 68.02	8.12 8.01	11.28 10.96
IIIr	216 – 218 68	$C_{14}H_{19}N_3O_4$ (293.3)	57.33 57.60	6.53 6.64	14.33 14.54
IIIs	139 – 142 61	$C_{15}H_{22}N_2O_3$ (278.3)	64.73 64.50	7.97 8.10	10.06 9.89
IIIt	180 – 183 71	$C_{15}H_{21}N_3O_4$ (307.4)	58.62 58.49	6.89 7.07	13.67 14.01
IIIu	182 – 184 87	$C_{15}H_{20}N_2O_2$ (260.3)	69.20 69.50	7.74 7.48	10.76 11.02
IIIv	201 – 202 70	$C_{14}H_{17}N_3O_4$ (291.3)	57.72 57.49	5.88 5.71	14.42 14.22
IIIw	125 – 128 79	$C_{16}H_{15}N_3O_4$ (313.3)	61.34 61.54	4.83 4.92	13.41 13.14
IIIx	198 – 201 90	$C_{16}H_{14}N_4O_6$ (358.3)	53.63 53.41	3.94 3.70	15.64 15.99
IIIy	206 – 208 86	$C_{17}H_{16}N_4O_6$ (372.3)	54.84 54.50	4.33 4.45	15.05 15.26
IIIz	80 – 82 57	$C_{15}H_{22}N_2O_2$ (262.4)	68.67 68.90	8.45 8.18	10.68 11.00

[a] B.p. at 1.06 kPa; [b] hydrochloride.

Due to the presence of an asymmetrical carbon atom, the molecules of compounds *Id*, *IIId – IIIt*, *IIIz* do not possess a plane of symmetry which would halve the angle between the paired groups ($CH(\mathbf{CH}_3)_2$, $\mathbf{CH}_2CH_3$). Hence these groups are anisochronous in ^1H and, as the case may be, also ^{13}C NMR spectra. The coupling constants $^3J(CH–CH_3)$ are the same, within the experimental error, for both anisochronous methyl groups. The paired groups in the molecules *IIId*, *IIIe*, *IIIg*, *IIIh*, *IIIj*, *IIIo*, *IIIq – IIIt*, *IIIw*, *IIIz* are also represented by pairs of protons and carbons in the benzene nuclei. However, no anisochronism of these groups was observed in the ^1H and ^{13}C NMR spectra.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra (δ, ppm; *J*, Hz) were measured at 400.13 and 100.62 MHz, respectively, using a Bruker AM 400 spectrometer, or at 360.14 and 90.57 MHz, respectively, using a Bruker AMX apparatus at 25 °C. For the measurements, the compounds *III* were dissolved in hexadeuteriodimethyl sulfoxide (ca 5% solutions). The chemical shifts refer to the middle signal of the solvent multiplet (δ(^1H) 2.55 and δ(^{13}C) 39.6). If not otherwise stated, the NMR spectra of compounds *I* and *II* were measured in $CDCl_3$, and the chemical shifts refer to hexamethyldisiloxane (δ(^1H) 0.05) and the solvent signal (δ(^{13}C) 77.0). The groups CH, CH_3 and C_q, CH_2 were resolved by the APT pulse sequence. For compound *IIIc*, the assignment of chemical shifts of the carbonyl groups was confirmed by the ^{13}C selective INEPT method. The TLC analyses were carried out on Silufol (Kavalier, The Czech Republic).

Preparation of Aminonitriles *Ia – Ih*

2-Amino-2-methylpropanenitrile (*Ia*), 2-methylamino-2-methylpropanenitrile (*Ib*), 2-amino-2-methylbutanenitrile (*Ic*), 2-methylamino-2,3-dimethylbutanenitrile (*Ie*), 2-methylamino-2,4-dimethylpentanenitrile (*If*), 1-aminocyclohexanecarbonitrile (*Ig*), and 2-amino-2-phenylpropanenitrile (*Ih*) were prepared according to ref.[5]. 2-Amino-2,3-dimethylbutanenitrile (*Id*) was prepared by an analogous Strecker synthesis from the corresponding ketone. ^1H NMR spectrum: 1.81 br, 2 H (NH_2); 1.77 m, 1 H (CH); 1.41 s, 3 H (CCH_3); 1.06 d, 3 H, *J* = 6.79 ($CHC\mathbf{H}_3$); 1.05 d, 3 H, *J* = 6.87 ($CHCH_3$). ^{13}C NMR spectrum: 123.62 (CN), 53.71 (C_q), 36.96 (CH), 24.63 ($C\mathbf{C}H_3$), 17.07 and 16.73 ($CH(\mathbf{C}H_3)_2$).

2-Amino- and 2-Methylamino-2-(4-nitrophenyl)propanenitriles (*Ii* and *Ij*)

A 250 ml flask equipped with a high-speed mixer was charged with benzene (50 ml) and 4-nitroacetophenone (10 g, 61 mmol). The solution formed was treated with a solution prepared from potassium cyanide (8 g, 123 mmol), ammonia (40 ml), glacial acetic acid (40 ml), and benzyltriethylammonium chloride (0.1 g). The mixture was vigorously stirred at 40 °C 24 h. The upper benzene layer was separated and dried with sodium sulfate. The first portion of product (2.5 g in the form of hydrochloride) was isolated by introducing gaseous hydrogen chloride. The aqueous phase was cooled to 5 °C, the separated crystals were collected by suction (2 g) and recrystallized from a cyclohexane–chloroform mixture. TLC: R_F(chloroform) = 0.07, R_F(chloroform–methanol 3 : 1) = 0.68. ^1H NMR spectrum: 8.31 and 7.93, 4 H (C_6H_4); 3.31 br, 2 H (NH); 1.73 s, 3 H (CH_3). ^{13}C NMR spectrum: 149.96 (C-1), 147.29 (C-4), 126.71 (C-2), 123.97 (CN), 123.81 (C-3), 53.18 (C_q), 30.89 (CH_3).

TABLE II
^{1}H NMR spectra of substituted 2-benzoylaminocarboxamides *III*

Compound	NH_2 (2 × brs)	R^1 = H (brs)	R^1 = CH_3 (s)	C–CH_3 (s)	CH (m)	CH(C**H**$_3$) (2 × d)	Ar[a]	Others
IIIa	6.92 7.30	8.59	–	1.50	–	–	8.35, 2 H; 8.14, 2 H	
IIIb	6.69 7.15	–	2.90	1.43	–	–	7.56 m, 5 H	
IIIc	6.76 7.31	–	2.88	1.45	–	–	8.34, 2 H; 7.82, 2 H	
IIId	7.08 7.39	8.31	–	1.53	–	–	8.34, 2 H; 8.10, 2 H	2.05 m (CH_2); 0.82 t, *J* = 7.4 (CH_2C**H**$_3$)
IIIe	7.22 6.99	7.83	–	1.45	2.29	0.98, 0.92 *J* = 6.7	7.82 d, 2 H; 7.56 t, 1 H; 7.49 t, 2 H	–
IIIf	7.15 7.08	7.78	–	1.49	2.27	0.98, 0.94 *J* = 6.8	7.42 d, 2 H; 7.36 t, 1 H; 7.27 t, 2 H	2.38 s ($ArCH_3$)
IIIg	7.20 7.05	7.76	–	1.47	2.33	0.98, 0.92 *J* = 6.7	7.75, 2 H; 7.30, 2 H	2.39 s ($ArCH_3$)
IIIh	7.18 6.98	7.67	–	1.47	2.33	0.98, 0.93 *J* = 6.8	7.82, 2 H 7.03, 2 H	3.84 s ($ArOCH_3$)
IIIi	7.16 7.09	8.08	–	1.50	2.24	0.99, 0.93 *J* = 6.7	7.57 d, 1 H; 7.53 d, 1 H; 7.48 t, 1 H; 7.44 t, 1 H	–
IIIj	7.19 7.00	7.92	–	1.45	2.28	0.98, 0.93 *J* = 6.8	7.87, 2 H; 7.56, 2 H	–
IIIk	7.13 7.11	8.09	–	1.46	2.15	0.96, 0.94 *J* = 6.9	7.83 d, 1 H; 7.67 t, 1 H; 7.59 t, 1 H; 7.57 d, 1 H	3.82 s ($COOCH_3$)
IIIl	7.26 6.72	8.37	–	1.51	2.20	0.98, 0.95 *J* = 6.8	7.53, 2 H; 7.47, 1 H (AB_2)	–
IIIm	7.18 6.93	8.39	–	1.45	2.24	0.96, 0.91 *J* = 6.8	7.54 m, 1 H 7.18 t, 2 H	–
IIIn	7.12 7.04	8.34	–	1.46	2.13	0.96, 0.93 *J* = 6.8	8.09 d, 1 H; 7.84 t, 1 H; 7.75 m, 2 H	–
IIIo	7.22 7.05	8.18	–	1.48	2.28	1.00, 0.95 *J* = 6.8	8.35, 2 H; 8.09, 2 H	–

TABLE II
(*Continued*)

Compound	NH_2 (2 × brs)	R^1 = H (brs)	R^1 = CH_3 (s)	C–CH_3 (s)	CH (m)	CH(C**H**$_3$) (2 × d)	Ar[a]	Others
IIIp	7.31 6.98	8.59	–	1.47	2.27	1.02, 1.00 *J* = 6.9	9.05 d, 2 H; 8.99 t, 1 H (A_2X)	–
IIIq	7.13 6.74	–	2.90	1.39	2.89	1.07, 0.89 *J* = 7.0	7.52 m, 2 H; 7.47 m, 3 H	–
IIIr	7.23 6.76	–	2.88	1.41	2.86	1.08, 0.91 *J* = 7.0	8.34, 2 H; 7.79, 2 H	–
IIIs	7.08 6.73	–	2.93	1.38	2.85	1.06, 0.87 *J* = 6.9	7.52, 2 H; 7.01, 2 H	3.83 s ($ArOCH_3$)
IIIt	7.25 6.73	–	2.91	1.48	2.09	0.99, 0.95 *J* = 6.5	8.34, 2 H; 7.76, 2 H	1.78 m (CH_2)
IIIu	7.01 6.83	7.82	–	–	–	–	7.80, 2 H; 7.31, 2 H	[b]
IIIv	7.12 6.78	8.25	–	–	–	–	8.35, 2 H; 8.13, 2 H	[c]
IIIw	7.43 7.30	8.68	–	1.98	–	–	8.32, 2 H; 8.07, 2 H	7.54 d, 2 H; 7.39 t, 2 H; 7.31 t, 1 H
IIIx	7.60 7.52	9.09	–	2.06	–	–	8.25, 2 H; 7.85, 2 H	8.36, 2 H; 8.15, 2 H[a]
IIIy	7.58 7.20	–	2.88	1.94	–	–	8.25, 2 H; 7.84, 2 H	8.39, 2 H; 7.99, 2 H[a]
IIIz	7.12 6.68	–	2.94	1.47	2.10	0.99, 0.95 *J* = 6.5	7.51 – 7.46 m, 5 H	1.77 m (CH_2)

[a] If no multiplicity is given, the signal is the AA′XX′ system; [b] 2.40 s ($ArCH_3$), 2.23 brd (H-2); 1.73 dt (H-2′); 1.51 m (H-3, H-3′, H-4); 1.28 m (H-4′); [c] 2.23 brd (H-2); 1.78 dt (H-2′); 1.55 m (H-3, H-3′, H-4); 1.28 m (H-4′).

TABLE III
^{13}C NMR spectra of substituted 2-benzoylaminocarboxamides *III*

Compound	$CONH_2$	Ar**C**ON	Ar						C_q	N–CH_3	CH	$CH(\mathbf{C}H_3)_2$ and C–$\mathbf{C}H_3$	Others
			C-1	C-2	C-3	C-4	C-5	C-6					
IIIa	176.03	164.31	140.71	129.22	123.37	149.01	123.37	129.22	56.69	–	–	25.16	–
IIIb	175.93	170.75	137.69	128.25	127.23	129.51	127.23	128.25	61.11	33.80	–	23.11	–
IIIc	175.50	168.75	143.82	128.37	123.61	147.75	123.61	128.37	61.39	33.56	–	23.04	–
IIId	175.43	163.97	140.82	128.85	123.47	149.00	123.47	128.85	60.18	–	–	22.16	28.89 ($\mathbf{C}CH_2$) 8.16 ($CH_2\mathbf{C}H_3$)
IIIe	175.73	166.81	135.43	127.66	128.67	131.56	128.67	127.66	63.14	–	34.14	17.80, 17.60 17.23	–
IIIf	175.17	169.14	135.20	137.74	130.39[a]	129.21[a]	127.19[a]	125.49[a]	63.02	–	33.78	17.55, 17.34 17.05	19.42 ($ArCH_3$)
IIIg	175.27	166.15	132.58	127.49	128.83	141.06	128.83	127.49	62.76	–	33.84	17.68, 17.46 17.13	21.08 ($ArCH_3$)
IIIh	175.51	165.92	127.60	129.37	113.57	161.73	113.57	129.37	62.82	–	33.90	17.68, 17.47 17.15	55.53 ($ArOCH_3$)
IIIi	174.83	166.10	137.25	129.96	130.78[a]	129.60[a]	129.33[a]	127.13[a]	63.30	–	34.03	17.56, 17.35 17.18	–
IIIj	175.14	165.46	134.05	128.46	129.55	136.04	129.55	128.46	62.96	–	33.93	17.67, 17.45 17.05	–
IIIk	174.96	167.35	138.98	129.25	131.94[a]	129.27[a]	129.07[a]	128.32[a]	63.12	–	34.32	17.70, 17.48 17.31	168.04 (COO) 52.46 (OCH_3)
IIIl	174.53	163.44	136.61	131.35	128.24	131.03	128.24	131.35	63.65	–	34.40	17.33, 17.21 17.09	–
IIIm	174.72	160.31	115.82[b]	159.11[c]	111.90[d]	131.56[e]	111.90[d]	159.11[c]	63.79	–	33.79	17.31, 17.12 17.06	–

TABLE III
(*Continued*)

Compound	$CONH_2$	Ar**C**ON	Ar						C_q	N–CH_3	CH	$CH(CH_3)_2$ and C–CH_3	Others
			C-1	C-2	C-3	C-4	C-5	C-6					
IIIn	174.57	165.34	133.24	146.64	124.01	130.51	133.77	129.63	63.29	–	34.33	17.45, 17.25 17.06	–
IIIo	174.55	164.78	141.09	129.08	123.34	148.94	123.34	129.08	63.10	–	33.85	17.58, 17.36 17.12	–
IIIp	174.27	162.81	138.17	128.22	147.90	120.61	147.90	128.22	63.46	–	33.95	17.82, 17.57 17.33	–
IIIq	175.17	171.64	138.11	127.06	128.42	129.54	128.42	127.06	66.69	30.65	35.51	19.06, 17.90 17.48	–
IIIr	174.66	169.44	144.15	128.16	123.79	147.72	123.79	128.10	66.82	30.54	35.15	18.99, 17.85 17.51	–
IIIs	174.99	171.61	130.02	129.29	113.51	160.26	113.51	129.29	66.71	30.69	35.68	18.94, 17.83	55.37 ($ArOCH_3$)
IIIt	175.18	168.84	144.05	128.11	123.69	147.68	123.69	128.11	64.28	25.35	34.56	24.58, 23.27 21.19	43.54 (CH_2)
IIIu	176.68	166.44	132.42	127.82	128.27	141.09	128.72	127.82	59.10	–	–	–	[f]
IIIv	176.12	165.07	141.04	129.34	123.25	148.97	123.25	129.34	59.91	–	–	–	[g]
IIIw	174.96	164.70	140.95	129.34	124.17	149.66	124.17	129.34	62.70	–	–	22.88	[h]
IIIx	173.10	164.06	140.19	129.12	123.68	149.32	123.68	129.12	62.19	–	–	23.00	[i]
IIIy	170.21	168.24	140.99	127.22[a]	121.87[a]	146.35[a]	121.87[a]	127.22[a]	66.16	34.06	–	21.27	[j]
IIIz	175.61	170.79	138.02	128.27	126.90	129.31	126.90	128.27	63.95	25.11	34.82	24.60, 23.33 21.29	43.66 (CH_2)

[a] Not assigned; [b] $^2J_{CF}$ = 23.1; [c] $^1J_{CF}$ = 248.1, $^4J_{CF}$ = 8.2; [d] $^2J_{CF}$ = 19.2, $^4J_{CF}$ = 5.3; [e] $^3J_{CF}$ = 10.0; [f] 31.78 (C-2′), 25.35 (C-3′), 21.48 (C-4′), 21.10 ($ArCH_3$); [g] 31.69 (C-2′), 25.25 (C-3′), 21.43 (C-4′); [h] 124.12 (C-1′), 126.45 (C-2′, C-6′), 128.83 (C-3′, C-5′), 128.93 (C-4′); [i] 146.66 (C-1′), 127.89 (C-2′, C-6′), 123.23 (C-3′, C-5′), 149.48 (C-4′); [j] 144.52 (C-1′), 126.95 (C-2′, C-6′), 120.86 (C-3′,C-5′), 146.26 (C-4′).

2-Methylamino-2-(4-nitrophenyl)propanenitrile (*Ij*) was prepared in the same way. The physical characteristics are given in Table I.

Preparation of Aminoamides *IIa*, *IIc – IIh*

The aminoamides *IIa*, *IIc*, *IId*, *IIg*, *IIh* were prepared by hydrolyses of the aminonitriles *Ia*, *Ic*, *Id*, *Ig*, *Ih* using hydrogen peroxide in aqueous ammonia[5]. The hydrolyses of *N*-methylaminonitriles *Ie*, *If* were carried out similarly in aqueous methylamine. ^{1}H NMR spectrum of *IIa*: 7.34 and 6.21 2 bs, 2 H (NH_2CO); 1.7 bs, 2 H (NH_2); 136, 6 H (CH_3). ^{13}C NMR spectrum of *IIa*: 181.07 (CO), 54.70 (C_q), 29.05 (CH_3).

2-Amino- and 2-Methylamino-2-(4-nitrophenyl)propanamides (*IIi* and *IIj*) and 2-Methylamino-2-methylpropanamide (*IIb*)

1-Cyano-1-(4-nitrophenyl)ethylammonium chloride (*Ii* . HCl; 10 g, 44 mmol) was heated on a boiling water bath with 98% sulfuric acid (35 ml) 80 min. The solution was cooled and poured onto 250 g crushed ice and neutralized with 40% sodium hydroxide solution to ca pH 9. The separated tarry portions were filtered off with charcoal, and the raw product *IIi*, precipitated on cooling, was recrystallized from a chloroform–benzene mixture (Table I). TLC: R_F(chloroform–methanol 3 : 1) = 0.35. ^{1}H NMR spectrum ($(CD_3)_2SO$): 8.23 and 7.82, 4 H (C_6H_4); 7.47 and 7.23, 2 × bs, 2 H ($CONH_2$); 2.56 bs, 2 H (NH_2); 1.60 s, 3 H (CH_3). ^{13}C NMR spectrum ($(CD_3)_2SO$): 177.11 (CO), 154.34 (C-1), 146.25 (C-4), 127.08 (C-2), 123.04 (C-3), 60.55 (C_q), 27.99 (CH_3).

Similar procedure was used to prepare 2-methylamino-2-(4-nitrophenyl)propanamide (*IIj*) and 2-methylamino-2-methylpropanamide (*IIb*). *IIj*: ^{1}H NMR spectrum ($(CD_3)_2SO$): 8.24 and 7.77, 4 H (C_6H_4); 7.42 and 7.29, 2 × br, 2 H ($CONH_2$); 2.82 bs, 1 H (NH); 2.19 s, 3 H (NCH_3); 1.55 s, 3 H (CCH_3). ^{13}C NMR spectrum ($(CD_3)_2SO$): 175.68 (CO), 152.42 (C-1), 146.34 (C-4), 127.75 (C-2), 123.13 (C-3), 65.27 (C_q), 29.87 (NCH_3), 22.91 (CCH_3). *IIb*: ^{1}H NMR spectrum: 7.09 and 6.39, 2 br, 2 H (NH_2); 2.24 s, 3 H (CH_3N); 1.23 s, 6 H ($C(CH_3)_2$). ^{13}C NMR spectrum: 180.22 (CO), 58.82 (C_q), 30.02 (CH_3N), 24.90 (CCH_3).

Preparation of Substituted 2-Benzoylaminocarboxamides *III*. A General Procedure

A solution of respective benzoyl chloride (20 mmol) in chloroform (10 ml) was treated with a solution of corresponding derivative *II* (20 mmol) and triethylamine (20 mmol) in chloroform (35 ml). After 1 h standing, the mixture was heated to boiling 30 min, cooled, extracted with 3 × 30 ml water, and dried with sodium sulfate. The solvent was distilled off, and the residue was recrystallized from benzene. The yields, melting points, and elemental analyses of the compounds *III* prepared are given in Table I. The substances were identified by means of ^{1}H and ^{13}C NMR spectra (Tables II and III).

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