Preparation and NMR Spectra of Substituted 2-Phenyl-5,5-dialkylimidazolinones

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Dedicated to Professor Vojeslav Štěrba on the occasion of his 75th birthday

Eighteen substituted 2-phenyl-5,5-dialkylimidazolinones **2** have been prepared by cyclizations of substituted 2-(*N*-benzoylamino)alkanamides **1**. The cyclization of methylamides **1** proceeds at room temperature whereas primary amides are cyclized on boiling. The ^1H and ^{13}C nmr spectra of the imidazolinones are presented and the changes in their spectra connected with their protonation in hexadeuteriodimethyl sulfoxide-trifluoroacetic acid mixtures are discussed.

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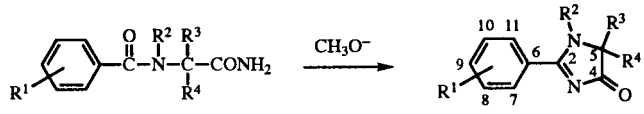
Introduction.

In the context of studies of compounds with potential herbicidal activity [1] a series of 26 substituted 2-(*N*-benzoylamino)alkanamides were prepared. Later they were cyclized to give the corresponding 2-(4-nitrophenyl)-5,5-dialkylimidazolinones [2] whose ^1H and ^{13}C nmr spectra were studied. It was found that the presence of tautomeric system -NH-C(Ar)=N-CO- substantially affects the nmr spectra of imidazolinones: signals of the carbon atoms involved in, or adjacent to, this system are broadened or even quite non-identifiable in the ^{13}C nmr spectra. The reason is obviously in the fact that the imidazolinone anion present in an only small amount exchanges proton with non-dissociated imidazolinone [2]. When measuring the ^{13}C nmr spectra in a (9:1 v/v) mixture of hexadeuteriodimethyl sulfoxide and trifluoroacetic acid we get sharp signals of all the carbon atoms, however, the protonation of the tautomeric system brings about changes in chemical shifts of both protons and carbon atoms (approximately 20% [2] and 100% of 2-(4-nitrophenyl)-5-methyl-5-isopropylimidazolinone is protonated in dimethyl sulfoxide-trifluoroacetic acid mixtures 99:1 and 9:1 v/v, respectively). In the *N*-methyl derivatives the signals of all the carbon atoms in ^{13}C nmr spectra are sharp, whether measured in hexadeuteriodimethyl sulfoxide or its mixture with 10% (v/v) trifluoroacetic acid, however the chemical shifts again are different [2] due to protonation.

The present paper describes the preparation and ^1H and ^{13}C nmr spectra of substituted 2-phenyl-5,5-dialkylimidazolinones.

Results and Discussion.

The cyclizations of 2-benzoylaminoalkanamides **1a-r** to 2-aryl-4-imidazolinones **2a-r** were carried out in methanolic solutions of sodium methoxide (Scheme 1). The substituted 2-aroylaminoalkanamides with a methyl group at nitrogen atom of aroylamino group (compounds **1a**, **1c**, **1d**, **1g**, **1i** ($R^2 = CH_3$)) are cyclized in methanolic methoxide several orders faster than the derivatives without methyl group (R^2 = H).



1 **2**

Compounds **1, 2**	R^1	R^2	R^3	R^4
a	H	CH_3	CH_3	CH_3
b	H	H	CH_3	i-C_3H_7
c	H	CH_3	CH_3	i-C_3H_7
d	H	CH_3	CH_3	i-C_4H_9
e	4-CH_3	H	CH_3	i-C_3H_7
f	2-CH_3	H	CH_3	i-C_3H_7
g	4-OCH_3	CH_3	CH_3	CH_3
h	4-OCH_3	H	CH_3	i-C_3H_7
i	4-OCH_3	CH_3	CH_3	i-C_3H_7
j	4-Cl	H	CH_3	i-C_3H_7
k	2-Cl	H	CH_3	i-C_3H_7
l	4-NO_2	H	CH_3	i-C_3H_7
m	2-NO_2	H	CH_3	i-C_3H_7
n	2-CO_2R [a]	H	CH_3	i-C_3H_7
o	4-CH_3	H	-$(CH_2)_5$-	
p	4-NO_2	H	-$(CH_2)_5$-	
q	4-C_6H_5	H	-$(CH_2)_5$-	
r	3,5-diNO_2	H	CH_3	i-C_3H_7

[a] **1**: R = CH_3, **2**: R = H

The *N*-methyl derivatives are cyclized in 1*M* methoxide on standing at room temperature already. Such behaviour agrees with the faster cyclization of *N*-methyl-*N*-(2-methoxycarbonylphenyl)sulfamide as compared with the cyclization of *N*-(2-methoxycarbonylphenyl)sulfamide [3] and is explained by favourable entropy factors. Replacement of hydrogen in the starting substance by a bulkier substituent entropically favours the formation of the cyclic intermediate by lowering the number of possible conformations of the starting molecule. At the same time also enthalpy factors can be more favourable after introducing the methyl group instead of hydrogen provided the formation of cyclic intermediate is connected with lowering of nonbonding interactions present in the starting molecule [4].

Table I

Melting Points and Elemental Analyses of Compounds **2**

Compound	M.p., °C Yield, %	Formula M. W.	Elemental analysis Calcd./Found (%) C	H	N	Cl
2a	151-153	$C_{12}H_{14}N_2O$	71.25	6.98	13.86	
	88	202.3	71.41	7.00	13.86	
2b [a]	176-181 [b]	$C_{13}H_{17}ClN_2O$	61.77	6.78	11.09	14.03
	58	252.7	62.11	6.43	10.95	13.80
2c [a]	76-80 [b]	$C_{14}H_{19}ClN_2O$	63.13	7.20	10.52	13.14
	60	266.8	62.89	7.33	10.49	13.10
2d	104-106	$C_{15}H_{20}N_2O$	73.72	8.26	11.47	
	63	244.3	73.89	8.26	11.49	
2e [a]	163-166 [b]	$C_{14}H_{19}ClN_2O$	63.13	7.20	10.52	13.14
	67	266.8	63.21	7.18	10.58	13.21
2f [a]	222-226 [b]	$C_{14}H_{19}ClN_2O$	63.13	7.20	10.52	13.14
	75	266.8	62.98	7.28	10.49	13.26
2g [a]	224-228 [b]	$C_{13}H_{17}ClN_2O_2$	58.19	6.39	10.45	13.04
	78	268.7	57.99	6.42	10.39	13.10
2h [a]	182-187 [b]	$C_{14}H_{19}ClN_2O_2$	59.55	6.79	9.93	12.40
	76	282.8	59.38	6.75	9.89	12.44
2i	183-185	$C_{15}H_{20}N_2O_2$	69.19	7.75	10.77	
	72	260.3	69.09	7.74	10.70	
2j	169-171	$C_{13}H_{15}ClN_2O$	62.38	6.04	11.20	13.98
	54	250.7	62.29	6.05	11.15	14.00
2k [a]	213-218 [b]	$C_{13}H_{16}Cl_2N_2O$	54.53	5.64	9.79	24.45
	74	287.2	54.64	5.65	9.77	24.46
2l	200-202	$C_{13}H_{15}N_3O_3$	59.76	5.79	16.08	
	69	261.3	60.10	5.84	15.96	
2m [a]	213-216 [b]	$C_{13}H_{16}ClN_3O_3$	52.44	5.42	14.11	11.91
	71	297.7	52.53	5.48	14.14	11.80
2n	110-113	$C_{14}H_{16}N_2O_3$	64.60	6.20	10.76	
	64	260.3	64.53	6.27	10.68	
2o [a]	212-216 [b]	$C_{15}H_{19}ClN_2O$	64.72	6.89	10.07	12.57
	47	278.8	64.82	6.85	9.96	12.62
2p	275-277	$C_{14}H_{15}N_3O_3$	61.53	5.53	15.38	
	55	273.3	61.14	5.52	15.28	
2q	234-236	$C_{20}H_{20}N_2O$	78.91	6.63	9.21	
	61	304.4	79.05	6.65	9.23	
2r[a]	195-200 [b]	$C_{13}H_{15}ClN_4O_5$	45.56	4.41	16.35	10.34
	34	342.7	45.61	4.45	16.30	10.35

[a] Hydrochloride. [b] melting point with decomposition.

Table II

Chemical Shifts δ (^{1}H) (ppm) of Compounds **2** in Hexadeuteriodimethyl Sulfoxide at 25 °C

Compound	NCH_3 (*s*)	Ar (*m*)	C-CH_3 (*s*)	CH (*m*)	$CH(CH_3)_2$, (J) (*2x d*)	Further signals
2a [a]	3.18	7.81 (*o*) 7.62 (*m*) 7.68(*p*)	1.35	-	-	
2a [b]	3.44	7.96(*o*) 7.76(*m*) 7.85(*p*)	1.65	-	-	
2b [a] [c]	-	8.48(*o*) 7.77(*m*) 7.93(*p*)	1.59	2.22	1.10 (6.89) 0.97 (6.82)	
2b [b]	-	8.32(*o*) 7.77(*m*) 7.93(*p*)	1.60	2.21	1.09 (6.90) 0.97 (6.81)	
2c [a]	3.46	8.06(*o*) 7.77(*m*) 7.90(*p*)	1.70	2.41	1.13 (6.78) 0.92 (6.82)	
2c [b]	3.45	8.00(*o*) 7.76(*m*) 7.88(*p*)	1.69	2.40	1.14 (6.83) 0.93 (6.86)	

Table II (Continued)

Compound	NCH_3 (*s*)	Ar (*m*)	C-CH_3 (*s*)	CH (*m*)	$CH(CH_3)_2$, (J) (*2x d*)	Further signals
2d [a]	3.17	7.80(*o*) 7.63(*m*) 7.69(*p*)	1.32	1.46	0.88 (6.67) 0.81 (6.61)	δ (CH_AH_B) 1.82, 1.68, J_{AB} = 14.49, J_{AX} = 5.60, J_{BX} = 7.11
2d [b]	3.48	8.00(*o*) 7.78(*m*) 7.90(*p*)	1.66	1.66	0.93 (6.65) 0.87 (6.56)	δ (CH_AH_B) 2.17, 1.89, J_{AB}=15.02, J_{AX} = 4.94, J_{BX} = 7.86
2e [a]	-	8.40 7.60 AA'XX'	1.59	2.21	1.10 (6.64) 0.96 (6.63)	δ ($ArCH_3$) 2.51
2e [b]	-	8.28 7.57 AA'XX'	1.59	2.20	1.08 (6.88) 0.95 (6.84)	δ ($ArCH_3$) 2.51
2f [a]	-	[d]	1.58	2.20	1.11 (6.88) 0.98 (6.84)	δ ($ArCH_3$) 2.60
2f [b]	-	[e]	1.63	2.22	1.10 (6.89) 1.00 (6.80)	δ ($ArCH_3$) 2.58
2g [b]	3.45	7.96 7.29 AA'XX'	1.61	-	-	δ(OCH_3) 3.94
2h [a]	-	8.51 7.33 AA'XX'	1.59	2.20	1.10 (6.90) 0.96 (6.79)	δ (OCH_3) 3.98
2h [b]	-	8.40 7.31 AA'XX'	1.58	2.18	1.08 (6.89) 0.95 (6.80)	δ (OCH_3) 3.96
2i [a]	3.19	7.82 7.16 AA'XX'	1.35	2.07	1.04 (6.83) 0.84 (6.77)	δ (OCH_3) 3.90
2i [b]	3.48	8.01 7.31 AA'XX'	1.67	2.39	1.14 (6.83) 0.92 (6.85)	δ (OCH_3) 3.96
2j [b]	-	8.21 7.90 AA'XX'	1.58	2.18	1.08 (6.91) 0.96 (6.80)	
2k [a]	-	[f]	1.53	2.15	1.10 (6.86) 0.97 (6.78)	
2k [b]	-	[g]	1.61	2.20	1.10 (6.83) 1.00 (6.79)	
2l [a], [c]	-	8.40 8.26 AA'XX'	1.30	1.98	1.02 (6.79) 0.81 (6.79)	
2l [b] [c]	-	8.50 8.34 AA'XX'	1.44	2.09	1.06 (6.80) 0.89 (6.80)	
2m [a]	-	[h]	1.46	2.11	1.09 (6.86) 0.97 (6.82)	
2m [b]	-	[i]	1.58	2.21	1.12 (6.89) 1.02 (6.82)	
2n [a]	-	[j]	1.25	1.93	1.02 (6.83) 0.85 (6.77)	
2n [b]	-	[k]	1.59	2.22	1.11 (6.90) 1.04 (6.83)	
2o [b]	-	8.26 7.58 AA'XX'	-	-	-	δ (CH_3) 2.49 (*s*), δ (CH_2) 2.0-1.4 (10H, *m*)
2p [a] [c]	-	8.41 8.27 AA'XX'	-	-	-	δ (CH_2) 1.78-1.60 (8H, *m*), 1.53-1.45 (2H, *m*)
2q [b]	-	8.35 8.13 AA'XX'	-	-	-	δ (Ar): 7.89 (*o*), 7.58 (*m*), 7.52 (*p*); δ (CH_2) 2.03-1.47 (10H, *m*)

Table II (Continued)

Compound	NCH_3 (*s*)	Ar (*m*)	$C\text{-}CH_3$ (*s*)	CH (*m*)	$CH(CH_3)_2$, (J) (*2x d*)	Further signals
2r [b]	-	9.28 (*d*) 9.05 (*t*)	1.41	2.07	1.07 (6.84) 0.87 (6.82)	

[a] In hexadeuteriodimethyl sulfoxide; [b] In hexadeuteriodimethyl sulfoxide with 10% trifluoroacetic acid; [c] From ref [2]; [d] δ (Ar): 7.77 (H-6), 7.69 (H-4), 7.53 (H-3), 7.51 (H-5); [e] δ (Ar): 7.79 (H-6), 7.72 (H-4), 7.55 (H-3), 7.53 (H-5); [f] δ (Ar): 7.90 (H-6), 7.82-7.76 (H-3, H-4), 7.67 (H-5); [g] δ (Ar): 7.98 (H-6), 7.85- 7.81 (H-3, H-4), 7.70 (H-5); [h] δ (Ar): 8.35 (H-3), 8.10-7.95 (H-4, H-5, H-6); [i] δ (Ar): 8.45 (H-3), 8.15-8.05 (H-4, H-5, H-6); [j] δ (Ar): 7.89 (H-6), 7.72-7.63 (H-3, H-4, H-5); [k] δ (Ar): 8.22 (H-6), 7.97-7.90 (H-3, H-4, H-5).

We have found that the isolated cyclization product from *N*-(2-methoxycarbonylphenyl)-2-amino-2,3-dimethylbutanamide **1n** is the corresponding carboxylic acid **2n**. So far it is not clear whether the hydrolysis by the traces of water present in methanol accompanies the cyclization or forms a subsequent process of hydrolysis of 2-(2-methoxycarbonylphenyl)-5-methyl-5-isopropyl-4-imidazolinone. The hydrolysis process can also be affected by anchimeric effect of the adjacent imidazolinone cycle [5]. The kinetics of these reactions is being studied now. The importance of steric effect for the cyclization course is also indicated by the fact that two Cl substituents at ortho positions in 2-(2,6-dichlorobenzoylamino)-2,3-dimethylbutanamide completely prevent the cyclization. This compound does not cyclize even after 100 hours' boiling in methanolic 1*M* sodium methoxide. The structures of all the substances were confirmed by their ^1H and ^{13}C nmr spectra. In the compounds containing isopropyl group, both the methyl groups are anisochronous in ^1H as well as ^{13}C nmr spectra since the molecules of these compounds possess no plane of symmetry in any of their conformations. Nevertheless, the protons as well as carbon atoms of *p*-disubstituted benzene ring of the above-mentioned compounds at *o,o'* and/or *m,m'* positions are isochronous.

The chemical shifts δ (^1H) of the imidazolinones synthesized are summarized in Table II. The compounds prepared in the form of their hydrochlorides show very close chemical shifts in hexadeuteriodimethyl sulfoxide and its mixture with trifluoroacetic acid. The least basic *o*-nitro derivative **2m**, which was also isolated as the hydrochloride, is partially dissociated in hexadeuteriodimethyl sulfoxide alone to give the neutral base which is protonated by added trifluoroacetic acid. This is obvious from the increase of about 0.1 ppm in chemical shifts of $C\text{-}CH_3$ and CH groups in the mixture of hexadeuteriodimethyl sulfoxide and trifluoroacetic acid. In the compounds isolated as bases, the protonation is connected with increases of about 0.3 ppm in chemical shifts of $N\text{-}CH_3$, $C\text{-}CH_3$, and CH groups. The change in chemical shifts is smaller in 4-nitro derivative **2p**.

In the case of compound **2a**, which served as the basic skeleton for application of substituent chemical shifts and interpretation of ^{13}C nmr spectra of other substances, the signals of quaternary carbon atoms were assigned on the basis of ^{13}C selective INEPT. In the measurements carried out in hexadeuteriodimethyl sulfoxide alone, two signals with the chemical shifts δ (^{13}C) 65.4 (C-5) and 193.8 (C-4) were detected due to the polarization transfer from the methyl groups at 5 position (δ (^1H) 1.35). The polarization transfer from the methyl group $N\text{-}CH_3$ (δ (^1H) 3.18) again was connected with detection of two signals with δ (^{13}C) 65.4 (C-5) and 176.9 (C-2). Analogous experiments with compound **2a** dissolved in a hexadeuteriodimethyl sulfoxide plus trifluoroacetic acid mixture revealed the following pairs of chemical shifts: δ (^{13}C) 68.7 (C-5), 178.6 (C-4), and δ (^{13}C) 68.7 (C-5), 167.4 (C-2). The chemical shifts of carbon atoms of carbonyl group (C-4) as well as carbon C-5 in the basic form of substances with $N\text{-}CH_3$ group depend little on the substitution of benzene ring (δ (^{13}C) *ca* 193 and 178, respectively). The protonation brings about a lowering of chemical shift of the carbonyl group in compound **2a** by about 15 ppm, the chemical shift of C-2 carbon atom being decreased by about 9.5 ppm by the protonation. Similar changes in chemical shifts δ (^{13}C) with changing medium like those in compound **2a** can also be observed in other compounds which were isolated as free bases and carry a methyl group at N^1 nitrogen atom (Table III).

The compounds containing NH group in the amidine grouping behave somewhat differently in the protonation. The carbonyl group of base has the chemical shift δ (^{13}C) about 187-189 and again its chemical shift is lowered on protonation, however, the change is smaller (approximately to the value of δ (^{13}C) 179-184), particularly with the nitro derivative **2l**. On the other hand, however, the chemical shift of C-2 carbon atom is increased on protonation, by 9 ppm at most (compound **2j**). The interval containing the signals of C-2 carbon atoms in the bases of these compounds is broader (δ (^{13}C) 157-164, see also [2]), which can be caused by a stronger dependence on the substituents in the benzene nucleus. However, the set of compounds investigated is too small for any unambiguous evaluation of this possibility. After the protonation, the chemical shift of carbon atom C-2 increases to the value δ (^{13}C) 162-172, the change again being smaller (*ca* 5

Table III

Chemical Shifts δ(^{13}C) (ppm) of Compounds **2** in Hexadeuteriodimethyl Sulfoxide and its Mixture with Trifluoroacetic Acid at 25°C

Compound	C-4	C-2	C-5	C-6	C-7	C-8	C-9	C-10	C-11	NCH_3	CH	CCH_3	$CHCH_3$	Additional signals
2a [a]	193.8	176.9	65.4	129.0	129.1	128.6	131.8	128.6	129.1	29.8	-	21.7	-	
2a [b]	178.6	167.4	68.6	121.9	130.5	129.3	134.9	129.3	130.5	31.2	-	20.9		
2b [a] [c]	179.9	166.5	70.4	122.0	130.0	129.5	136.2	129.5	130.0	-	34.8	19.4	16.5 16.4	
2b [b]	179.5	167.6	70.6	121.8	130.2	129.9	136.8	129.9	130.2	-	35.2	19.4	16.5 16.5	
2c [a]	177.1	168.1	74.2	121.3	130.4	129.4	135.1	129.4	130.4	31.8	33.4	18.1	16.3 15.0	
2c [b]	177.1	168.3	74.5	121.6	130.4	129.6	135.3	129.6	130.4	31.8	33.6	18.2	16.3 15.0	
2d [a]	193.3	177.5	68.5	129.0	128.9 [d]	128.7 [d]	131.8	128.7 [d]	128.9 [d]	30.1	24.3 [e]	23.0 [e]	23.4 [e] 23.1 [e]	δ (CH_3) 43.4
2d [b]	178.3	168.2	71.7	121.6	130.4	129.6	135.3	129.6	130.4	31.7	24.0 [f]	23.6 [f]	23.1 [f] 21.6 [f]	δ (CH_3) 43.4
2e [b]	179.4	167.1	70.4	118.8	130.4 [g]	130.5 [g]	148.4	130.5 [g]	130.4 [g]	-	35.2	19.5	16.5 16.5	δ ($ArCH_3$) 21.7
2f [b]	179.3	169.6	70.9	122.8	138.1	131.9 [h]	134.5	126.7	130.5 [h]	-	34.8	19.8 [i]	16.6 16.4	δ ($ArCH_3$) 19.3 [i]
2g [b]	178.4	166.4 [j]	68.5	113.4	133.3	114.9	164.7 [j]	114.9	133.3	31.4	-	21.0	-	δ ($ArOCH_3$) 56.2
2h [a]	179.3	165.8 [k]	69.7	113.1	132.7	115.2	165.4 [k]	115.2	132.7	-	34.8	19.5	16.4 16.3	δ ($ArOCH_3$) 56.2
2h [b]	179.2	166.4 [l]	70.0	113.2	133.0	115.5	166.0 [l]	115.5	133.0	-	35.2	19.6	16.5 16.4	δ ($ArOCH_3$) 56.4
2i [a]	192.3	177.2	70.9	120.9	131.4	114.1	162.1	114.1	131.4	30.6	33.0	19.3	16.7 15.5	δ ($ArOCH_3$) 55.6
2i [b]	177.0	167.2 [m]	74.2	113.0	133.1	115.1	164.9 [m]	115.1	133.1	31.8	33.6	18.2	16.3 15.0	δ($ArOCH_3$) 56.2
2j [a]	187.8	157.6	73.9	127.7	129.0 [n]	128.7 [n]	136.5	128.7 [n]	129.0 [n]	-	34.3	21.1	16.9 16.8	
2j [b]	179.7	166.7	70.8	121.0	131.7 [o]	130.1 [o]	141.8	130.1 [o]	131.7 [o]	-	35.1	19.2	16.5 16.3	
2k [b]	179.7	167.2	71.6	123.0	132.1	131.0	135.9	128.1	132.3	-	35.0	19.4	16.6 16.4	
2l [a] [c]	187.6	157.1	74.3	134.4	128.3	124.0	149.3	124.0	128.3	-	34.3	21.0	16.8 16.7	
2l [b] [c]	184.5	162.5	72.7	131.5	129.8	124.3	150.4	124.3	129.8	-	34.6	20.2	16.7 16.5	
2m[a]	182.9	163.0	72.5	121.3	147.1	125.3	134.5 [p]	133.8 [p]	131.5 [p]	-	34.2	19.8	16.9 16.6	
2m [b]	180.2	167.3	72.0	119.6	146.9	125.9	135.2 [q]	135.1 [q]	132.2 [q]	-	34.6	19.4	16.9 16.5	
2n [a]	188.9	164.5	72.6	130.1	134.1	129.5 [r]	130.8 [r]	130.7 [r]	130.0 [r]	-	34.0	20.6	17.1 16.9	δ (COOH) 168.4
2n [b]	179.0	171.9	71.2	124.5	131.0	131.2 [s]	134.0 [t]	133.3 [t]	130.5 [s]	-	34.3	18.9	16.9 16.3	δ (COOH) 166.3
2o [b]	179.0	166.7	67.0	119.2	130.3 [u]	130.2 [u]	147.9	130.2 [u]	130.3 [u]	-	-	-	-	δ ($ArCH_3$) 21.7, δ (CH_2) 32.0 (C- 2,2'), 24.2 (C-4), 20.3 (C-3,3')
2p [b] [c]	182.9	163.4	69.0	130.6	130.4	124.3	150.7	124.3	130.4	-	-	-	-	δ (CH_2) 32.2 (C- 2,2)), 24.4 (C-4), 20.8 (C-3,3')
2q [b]	179.3	166.7	67.2	120.9	130.8	127.7	147.8	127.7	130.8	-	-	-	-	δ (CH_2) 32.0 (C- 2,2'), 24.2 (C-4) 20.4 (C-3,3'); δ (Ar) 138.3 (*i*), 127.6 (*o*),129.5 (*m*),130.8 (*p*)

[a] In hexadeuteriodimethyl sulfoxide. [b] In hexadeuteriodimethyl sulfoxide with 10% trifluoroacetic acid. [c] From ref [2]. [d]-[u] The assignmenst may be reversed.

ppm) in the case of compound **2l**. The hydrochlorides of imidazolinones have very similar chemical shifts δ (^{13}C) in hexadeuteriodimethyl sulfoxide and its mixture with trifluoroacetic acid, except for o-nitro derivative **2m** exhibiting the same effect like that in the proton spectra (see above).

The assignment of signal of carboxyl carbon atom in compound **1n** was also carried out with the help of ^{13}C selective INEPT by the polarization transfer from the proton at C-3 position of benzene nucleus.

EXPERIMENTAL

Syntheses of Substances.

The synthesis of substituted 2-aroylaminoalkanamides **1a-r** is described in literature [1]. The cyclizations of the 2-aroylaminoalkanamides were carried out in methanolic 1*M* sodium methoxide. Compounds **2a**, **2c**, **2d**, **2g**, and **2i** were prepared by the cyclization realized by standing overnight at room temperature whereas compounds **2b**, **2e**, **2f**, **2h**, **2j-r** required 1.5 hours' boiling. After the cyclization was complete, the mixture was neutralized with methanolic hydrochloric acid and the solvent was evaporated to dryness from a water bath. The evaporation residue was washed with water, dried, and recrystallized. Imidazolinones **2b**, **2c**, **2e**, **2f**, **2g**, **2h**, **2k**, **2m**, **2o**, and **2r** were isolated as hydrochlorides after an addition of methanolic hydrochloric acid to chloroform extract of the evaporation residue. The yields, melting points, and elemental analyses of the substances prepared are given in Table I.

NMR Spectra.

The ^{1}H and ^{13}C nmr spectra were measured at 360.14 and 90.57 MHz, respectively, at 25° using a Bruker AMX 360 spectrometer. For the measurements, the substances were dissolved in hexadeuteriodimethyl sulfoxide or its mixture with trifluoroacetic acid (10% v/v). The chemical shift are referred to the middle signal of solvent multiplet (δ (^{1}H) 2.55 and δ (^{13}C) 39.6). The CH, CH_3, and C_q, CH_2 groups in ^{13}C nmr spectra were differentiated by means of the APT pulse sequence. The ^{13}C nmr signals were assigned with the help of substituent chemical shifts [6] and unambiguous assignment of signals of quaternary carbon atoms in ^{13}C nmr spectra of compounds **2a**, **2n** was carried on the basis of ^{13}C selective INEPT [7], [8].

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REFERENCES AND NOTES

[1] M. Sedlák, A. Halama, J. Kaválek, V. Macháček and V. Štěrba, *Collect. Czech. Chem. Commun.*, **60**, 150 (1995).

[2] M. Sedlák, A. Halama, J. Kaválek, V. Macháček, P. Mitaš and V. Štěrba,*Collect. Czech. Chem. Commun.*, **61**, 910 (1996).

[3] M. Sedlák, J. Kaválek, V. Macháček and V. Štěrba, *Molecules*, **1**, 170 (1996).

[4] B. Capon and S. P. McManus, Neighbouring Group Participation, Vol **1**, Chapter 2, Plenum Press, New York, 1976.

[5] G. A. Rogers and T. C. Bruice, *J. Am. Chem. Soc.*, **96**, 2463 (1974).

[6] H.-O. Kalinowski, S. Berger and S. Braun, ^{13}C-NMR-Spektroskopie, Georg Thieme Verlag, Stuttgart, 1984, p 284.

[7] A. Bax, *J. Magn. Reson.*, **57**, 314 (1984).

[8] S. Braun, H.-O. Kalinowski and S. Berger, 100 and More Basic NMR Experiments, VCH Publishers, New York, 1996, p 203.