SYNTHESIS AND SPECTRAL PROPERTIES OF 2-(5-R-2-FURYLMETHYLENE)-3-OXOBUTANENITRILES

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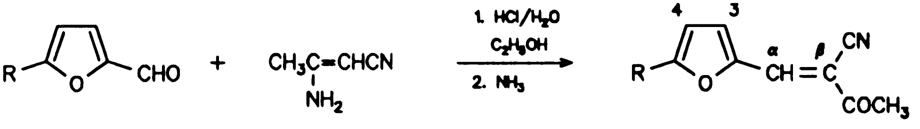
Substituted 2-(5-R-2-furylmethylene)-3-oxobutanenitriles *IIa* – *III* were obtained by condensation of the corresponding 5-R-2-furaldehydes *Ia* – *Il* with 3-amino-2-butenenitrile in acid medium. Relation between the structure and spectral properties (NMR, IR, UV, MS) is presented and the influence of substituents in position 5 of the furan ring on the conjugated 2-furylethylene system is discussed.

Our preceding papers[1–5] reported the synthesis of 5-R-furylmethylenepropanedinitriles and 3-(5-R-2-furylmethylene)-2,4-pentanediones, their spectra and utilization as precursors for the synthesis of six-membered heterocycles.

This paper concerns the preparation of 2-(5-R-2-furylmethylene)-3-oxobutanenitriles *II* of which only the unsubstituted 2-(2-furylmethylene)-3-oxobutanenitrile was synthesized[6] from 2-furaldehyde (*Ia*) and 5-methylisoxazole.

A modified procedure published[7] for the preparation of 2-benzylidene-3-oxobutanenitriles was applied for the synthesis of 2-(5-R-2-furylmethylene)-3-oxobutanenitriles *II* (Scheme 1); 3-amino-2-butenenitrile was first hydrolyzed by dilute hydrochloric acid in ethanol to yield cyanoacetone, which, on Knoevenagel condensation with 5-R-2-furaldehydes and neutralization afforded the crystalline *IIa* – *III* in 33 – 91% yields (Table I). This procedure is more advantageous than that[7] because it requires only 4 h reaction time instead of 4 days. Neutralization of the nitro derivative *IIb* must be very careful to prevent its polymerization.

*NMR spectra.*The ^{1}H NMR spectra of 2-(5-R-furyl)-3-oxobutanenitriles *IIa* – *III* (Table II) revealed H_α signals at δ 7.40 – 8.01, the position of which depended on the substituent nature. The H_α resonance appeared at lower field[3] when compared with that of 5-R-2-furylmethylenepropanedinitrile derivatives. Protons at the furan ring of 5-furylsubstituted derivatives appeared as doublets with coupling constant $^3J(3,4)$ = 3.6 – 4.2 Hz; δ 7.16 – 7.64 (H-3) and 5.53 – 7.46 (H-4). Because no considerable long-range coupling constants $^4J(H_\alpha,3)$, $^5J(H_\alpha,4)$ were seen in the ^1H NMR spectra of compounds *II* we believe that an *s-trans* conformation between the furan ring and the exocyclic double bond is preferred. The same conformation was also ascribed to 5-R-2-furylmethylenepropanedinitriles, 5-R-2-furaldehydes *I* (ref.[8]) and α-halogen-3-(5-R-2-furyl)acrylonitriles[9] in contrast to e.g. β-(5-R-2-furyl)acrylonitriles[10] having $^5J(H_\alpha, 4) \sim 1.0$ Hz and *s-cis* conformation.



Ia – Il *IIa – IIl*

I, II	R	*I, II*	R
a	H	*g*	I
b	NO_2	*h*	C_6H_5S
c	CN	*i*	C_6H_5
d	CO_2CH_3	*j*	CH_3
e	Cl	*k*	C_6H_5O
f	Br	*l*	$(CH_3)_2N$

SCHEME 1

The *E* or *Z* geometry of compounds *II* was unambiguosly attributed by means of ^{13}C NMR spectrometry. *Trans* arrangement of H_α and CN groups was inferred from vicinal long-range spin–spin constants $^3J(H_\alpha$, CN) 13.32 Hz (*IIc*), 13.20 Hz (*IIe*), 12.70 (*IIk*), and 11.08 (*IIl*). Similar values of $^3J(H_\alpha$, CN) 12 – 14 Hz were found with (*E*)-α-cyanochalcones[11] and 5-R-2-methylenepropanedinitriles[3]. This finding evidenced the *E* isomerism of the above-mentioned series *II*.

The ^{13}C NMR spectra of coumpounds *IIa* – *IIl* (Table III) have the C-α and C-β signals at δ 135.15 – 137.35 and 91.46 – 111.89, respectively. The measured chemical shifts reflected the polarisability of the double bond bearing two electron-accepting groups (CN, $COCH_3$), which caused a decrease of the electron density at C-α. It is worth noting that the effect of substituent at C-β is much more significant (Δδ 20.43) than at C-α (Δδ 2.2). Also the CN group seems to be more sensitive against the substituent effect (Δδ 5.17) than the CO one (Δδ 2.73).

Infrared spectra. Characteristic wave numbers belonging to stretching vibration of CO and CN groups are listed in Table IV. The electron-donating substituents lower the frequency of ν(CO) and ν(CN) stretching vibrations, the electron-accepting ones rise them. The substituent R effect in position 5 of the furan ring is more pronounced with ν(CO) ($\Delta\tilde{\nu}$ 52 cm^{-1}) than with ν(CN) ($\Delta\tilde{\nu}$ 22.4 cm^{-1}).

As known, the α,β-unsaturated ketones can exist in *s-cis* or *s-trans* conformations. These conformations can be seen in the IR spectra at different frequencies of the CO

TABLE I
2-(5-R-2-Furylmethylene)-3-oxobutanenitriles *IIa* – *III*

Compound (R)	M. p., °C (Yield, %)	Formula (M. w.)	Calculated/Found		
			% C	% H	% N
IIa	64 – 65[a]	$C_9H_7NO_2$	67.07	4.39	8.69
(H)	(70)	(161.2)	67.22	4.44	8.39
IIb	142 – 144	$C_9H_6N_2O_4$	52.43	2.94	13.59
(NO_2)	(44)	(206.2)	52.21	3.05	13.69
IIc	141 – 143	$C_{10}H_6N_2O_2$	64.51	3.25	15.05
(CN)	(66)	(186.2)	64.35	3.26	15.14
IId	147 – 149	$C_{11}H_9NO_4$	60.27	4.15	6.39
(CO_2CH_3)	(60)	(219.2)	60.24	4.30	6.22
IIe	120 – 122	$C_9H_6ClNO_2$	55.26	3.10	7.16
(Cl)	(71)	(195.6)	55.07	3.08	7.21
IIf	122 – 123	$C_9H_6BrNO_2$	45.02	2.52	5.84
(Br)	(84)	(240.1)	45.20	2.70	5.85
IIg	136 – 138	$C_9H_6INO_2$	37.65	2.11	4.88
(I)	(38)	(287.1)	37.55	2.30	5.00
IIh	62 – 63	$C_{15}H_{11}NO_2S$	66.89	4.12	5.20
(C_6H_5S)	(43)	(269.3)	66.92	4.36	5.32
IIi	153 – 155	$C_{15}H_{11}NO_2$	75.93	4.68	5.90
(C_6H_5)	(91)	(237.3)	75.64	4.80	6.08
IIj	128 – 129	$C_{10}H_9NO_2$	68.55	5.19	8.00
(CH_3)	(88)	(175.2)	68.53	4.90	7.89
IIk	82 – 84	$C_{15}H_{11}NO_3$	71.13	4.39	5.53
(C_6H_5O)	(42)	(253.3)	71.05	4.40	5.63
III	154 – 157	$C_{11}H_{12}N_2O_2$	64.68	5.93	13.72
($(CH_3)_2N$)	(40)	(204.3)	64.30	5.80	14.00

[a] Ref.[6], m.p. 65 °C.

TABLE II
^1H NMR chemical shifts of compounds *IIa – IIl* (δ, ppm; $CDCl_3$; 25 °C)

Compound	H_α[a]	H-3[b]	H-4[b]	J(3, 4), Hz	CH_3[a]	R
IIa	7.93	7.43[c]	6.69[c]	3.60	2.54	7.79 dd[d]
IIb	7.97	7.64	7.46	3.90	2.60	–
IIc	7.93	7.54	7.30	3.90	2.59	–
IId	8.01	7.59	7.34	3.90	2.57	3.97
IIe	7.84	7.45	6.52	3.90	2.54	–
IIf	7.85	7.41	6.64	3.60	2.54	–
IIg	7.87	7.32	6.85	3.90	2.54	–
IIh	7.82	7.41	6.58	3.60	2.50	7.49 – 7.53 m, 2 H (H-2′, 6′) 7.36 – 7.39 m, 3 H (H-3′, 4′, 5′)
IIi	7.88	7.35	6.93	3.90	2.55	7.33 – 7.36 m, 1 H (H-4′) 7.40 – 7.88 m, 5 H (H arom)
IIj	7.84	7.34	6.34	3.90	2.51	2.47
IIk	7.75	7.29	5.61	3.90	2.47	7.19 – 7.45 m, 6 H (H arom)
IIl	7.40	7.16	5.53	4.20	2.41	3.21

[a] Singlet; [b] doublet; [c] dd; [d] J(4,5) = 1.5 Hz.

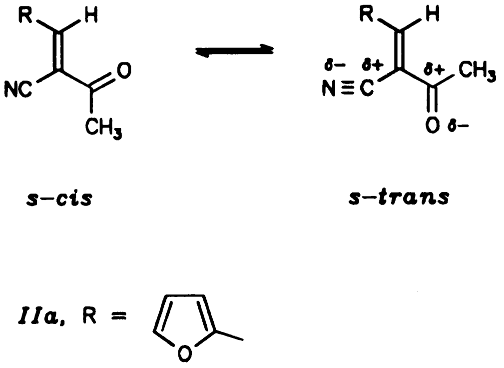
TABLE III
^{13}C NMR chemical shifts of compounds *IIa – IIl* (δ, ppm; $CDCl_3$)

Compound	CO	C-5	C-2	C-3	C-4	C-α	C-β	CN	CH_3
IIa	190.96	148.73	148.96	122.72	114.15	137.35	105.41	117.13	27.80
IIb	189.36	149.23	149.23	120.65	112.77	135.93	111.89	115.70	27.88
IIc[a]	189.77	129.49	151.94	119.91	123.95	135.70	110.26	115.92	27.91
IId[b]	190.18	147.82	150.89	120.88	119.83	137.22	109.39	116.27	27.75
IIe	190.66	144.08	148.42	124.12	111.37	136.04	105.33	116.81	27.82
IIf	190.61	130.99	150.76	123.93	116.29	135.94	105.36	116.80	27.84
IIg	190.65	99.17	154.11	124.96	123.76	135.67	105.41	116.79	27.87
IIh[c]	190.89	150.74	155.36	123.93	117.36	136.16	104.65	117.15	27.79
IIi[d]	191.28	160.38	148.09	126.12	109.39	136.08	103.90	117.86	27.93
IIj[e]	191.29	160.86	147.79	125.20	111.51	136.89	103.18	117.55	27.76
IIk[f]	191.19	163.58	140.90	127.35	91.61	136.24	101.31	117.83	27.72
IIl[g]	192.09	164.94	140.69	130.99	92.00	135.15	91.46	120.87	27.44

[a] 110.45 (CN); [b] 158.20 (CO_2), 52.69 (CH_3); [c] 132.25 (C-2′,6′), 130.72 (C-1′), 129.63 (C-3′,5′), 128.85 (C-4′); [d] 130.06 (C-4′), 129.18 (C-3′), 125.47 (C-2′), 128.61 (C-′1); [e] 14.39 (CH_3); [f] 153.73 (C-1′), 130.22 (C-3′,5′), 126.30 (C-4′), 119.41 (C-2′,6′); [g] 38.19 (CH_3).

stretching vibrations; the more conjugated conformer (*s-trans*) appeared at lower frequencies[12 – 16]. The IR spectra of compounds *II* in chloroform disclosed an intensive band at about 1 700 cm^{-1} with a shoulder at the side of the band with lower frequencies. We presume that the band at higher frequency belongs to the *s-cis* conformer and shoulders at lower frequency to the *s-trans* conformer.

A more detailed study with the unsubstituted derivative *IIa* (Scheme 2) in various solvents showed that the shape of the ν(CO) absorption band in tetrachloromethane



SCHEME 2

TABLE IV
IR and UV spectra of compounds *IIa* – *IIl*

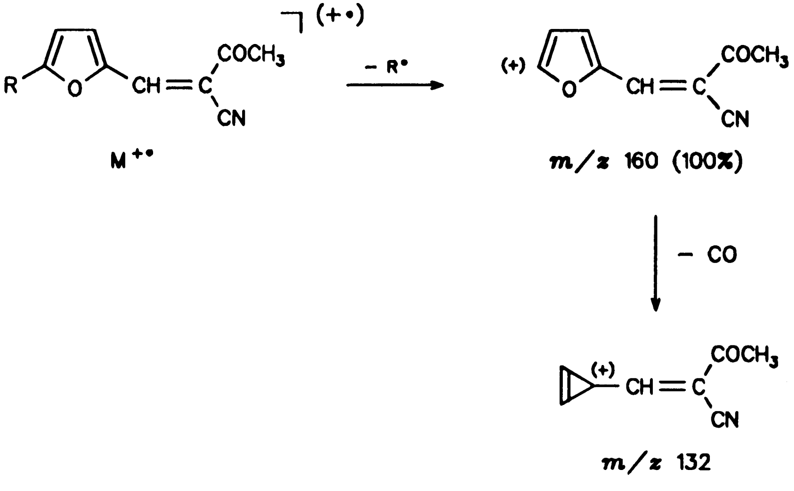
Compound	UV spectrum[a]		$\tilde{\nu}_{max}$, cm^{-1} [b]	
	λ_{max}, nm (log ε)		ν(CN)	ν(CO)
IIa	201 (2.77)	345 (3.12	2 216.0	1 699.2
IIb	248 (2.86)	350 (3.27)	2 218.4	1 712.0
IIc	219 (2.97)	333 (3.41)	2 218.4	1 708.0
IId	226 (2.94)	342 (3.42)	2 217.6	1 705.6
IIe	204 (2.95)	351 (3.44)	2 214.4	1 700.0
IIf	206 (2.93)	356 (3.43)	2 214.4	1 700.0
IIg	206 (2.93)	368 (3.35)	2 214.4	1 700.8
IIh	202 (3.24)	383 (3.22)	2 213.6	1 697.6
IIi	203 (2.99)	406 (3.35)	2 212.0	1 693.6
	254 (3.04)			
IIj	206 (2.94)	365 (3.48)	2 213.6	1 692.8
IIk	203 (3.12)	389 (3.44)	2 211.2	1 690.4
IIl	234 (3.16)	481 (3.87)	2 196.0	1 660.0

[a] Methanol; [b] chloroform.

with an intense maximum at 1 703 cm^{-1} was similar to that in chloroform. The spectra in more polar solvents revealed separation of both absorption bands appearing at 1 702 and 1 686 cm^{-1} (benzene), 1 700 and 1 682 cm^{-1} (1,2-dichloroethane), 1 702 and 1 684 cm^{-1} (tetrahydrofuran) and 1 702 and 1 682 cm^{-1} in acetonitrile, where, in contrast to other solvents, the more intense band lied at lower frequency (1 682 cm^{-1}). This can be rationalized by an enhanced stabilization of the more polar *s-trans* conformer.

Ultraviolet spectra. Conjugation of the furan ring with the polarized ethylene bond was also corroborated by UV spectroscopy (Table IV). The most long-wave band λ_{max} at 333 – 481 nm corresponding to π–π^* transition of the whole conjugated system is very sensitive against the change of a substituent R in position 5 of the furan ring. The greatest bathochromic shift with respect to the light-yellow unsubstituted derivative *IIa* showed the dark-red dimethylamino derivative *IIl* ($\Delta\lambda$ 136 nm). Intensity of this band was only little influenced and varied within log ε 3.12 – 3.87 m^2 mol^{-1}.

Mass spectra of 2-arylmethylene-3-oxobutanenitriles have so far not been studied. The mass spectra of 2-(5-R-2-furylmethylene)-3-oxobutanenitriles (Table V) with the exception of derivatives *IIa*, *IIc* and *IIi* can be interpreted according to the general fragmentation scheme (Scheme 3). The parent peak of compounds *IIb* (R = NO_2), *IId* (R = CO_2CH_3), *IIe* (R = Cl), *IIf* (R = Br), *IIg* (R = I), *IIh* (R = C_6H_5S), *IIk* (R = C_6H_5O) and *IIl* (R = $(CH_3)_2N$) is a stable fragment ion of *m*/*z* 160 formed by elimination of the radical R from position 5 of the furan ring. This ion underwent further fragmentation to remove the CO molecule under origination of the *m*/*z* 132 ion. This removal is characteristic of mass spectra of furan and its derivatives[17 – 19]. Halogen derivatives *IIe* – *IIg* also displayed the diagnostic elimination of CO from the molecular radical ion follo-



R = NO_2, I, Br, Cl, CO_2CH_3, C_6H_5O, C_6H_5S

SCHEME 3

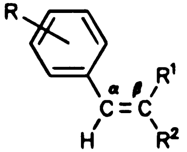
wed by removal of the radical $^{\bullet}COCH_5$ to yield ions of *m/z* 124 (*IIe*), 168 (*IIf*) and 216 (*IIg*). Compounds *IIa*, *IIc* and *IIi* are characterized by their parent peak of molecular radical ions; further fragmentation proceeded in various directions the most important of which is the elimination of $^{\bullet}CH_3$ radical to furnish the respective $[M - CH_3]^+$ ions at *m/z* 222 (*IIi*), 171 (*IIc*) and 146 (*IIa*).

Hammett correlation was employed for a more detailed study of the transition substituent effect through the furan ring to the side chain $-CH=C(CN)-COCH_3$; one-parameter Hammett correlation and a two-parameter correrlation equation were the tools for this examination. Table VI shows that a more tense correlations were obtained[20] with parameter σ_p^+ better reflecting the behaviour of electron-donating substituents at the furan ring. Correlations of the ^{13}C NMR chemical shift data with σ_p^+ disclosed that the

TABLE V
Mass spectral data of compounds *II*

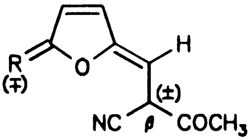
Compound	*m/z* (rel. intensity, %)
IIa	161 ($M^{+\bullet}$, 100), 160 (9), 147 (4), 146 (30), 133 (9), 132 (3), 120 (4), 119 (26), 118 (5), 92 (6), 90 (7), 63 (3), 43 (14)
IIb	206 ($M^{+\bullet}$, 31), 191 (7), 161 (12), 160 (100), 133 (3), 132 (20), 118 (3), 117 (6), 105 (3), 90 (4), 89 (9), 88 (5), 77 (6), 63 (5), 62 (5), 43 (22)
IIc	186 ($M^{+\bullet}$, 100), 172 (5), 171 (46), 160 (5), 159 (14), 158 (4), 144 (6), 143 (8), 117 (8), 115 (10), 89 (5), 88 (13), 64 (7), 63 (3), 62 (3), 43 (20)
IId	219 ($M^{+\bullet}$, 13), 204 (7), 188 (6), 161 (11), 160 (100), 145 (4), 132 (52), 117 (4), 89 (3)
IIe	197 (M^{+}, 6), 195 ($M^{+\bullet}$, 17), 182 (3), 180 (12), 168 (3), 167 (11), 161 (10), 160 (100), 132 (10), 126 (4), 125 (3), 124 (10), 88 (3), 43 (5)
IIf	241 (M^{+}, 10), 239 ($M^{+\bullet}$, 10), 226 (4), 224 (4), 170 (7), 168 (7), 161 (10), 160 (100), 132 (14), 90 (4), 89 (5), 88 (4), 77 (3), 62 (3), 43 (4)
IIg	287 ($M^{+\bullet}$, 36), 272 (11), 216 (10), 161 (11), 160 (100), 132 (22), 128 (5), 118 (4), 117 (6), 90 (5), 89 (7), 88 (4), 77 (4), 62 (3), 43 (3)
IIh	269 ($M^{+\bullet}$, 26), 171 (3), 161 (11), 160 (100), 132 (10)
IIi	237 ($M^{+\bullet}$, 100), 236 (3), 221 (9), 222 (52), 209 (3), 208 (4), 195 (14), 194 (9), 168 (6), 167 (10), 166 (12), 145 (3), 160 (22), 140 (8), 139 (10), 115 (11), 105 (11), 91 (4), 89 (5), 77 (10), 63 (3), 61 (3), 43 (10)
IIj	253 ($M^{+\bullet}$, 28), 238 (4), 182 (4), 161 (10), 160 (100), 132 (9), 77 (6), 43 (3)
IIk	175 ($M^{+\bullet}$, 57), 160 (100), 133 (10), 132 (8),106 (6), 104 (4), 77 (6), 43 (7)
IIl	204 ($M^{+\bullet}$, 56), 203 (4), 189 (13), 161 (4), 160 (100), 133 (7), 132 (9), 118 (3)

most sensitive of the ethylene bond atom against the substitution effect ($\rho = 7.90$, $N = 11$) was the C-β atom with which also the best correlation coefficient ($r = 0.994$) was obtained. Similar behaviour showed[11,21 – 23] the C-β atom also with related benzene derivatives *III* – *VIII*.



III, $R^1 = R^2 = CN$
IV, $R^1 = R^2 = CO_2C_2H_5$
V, $R^1 = CN$; $R^2 = CO_2C_2H_5$
VI, $R^1 = CN$; $R^2 = CONH_2$
VII, $R^1 = CN$; $R^2 = C_6H_5CO$
VIII, $R^1 = CN$; $R^2 = p\text{-}C_6H_5C_6H_4CO$

In contrast, no correlation was found with the C-α atom bonded directly to the furan ring. The noticeable transition of the substituent effect to C-β and minimal one to the C-α atoms can be explained by the mesomeric structure *IX* reflecting changes in electronic distribution of the furylethylene system by electron-accepting and electron-donating substituents.



IX

Good correlations with negative slopes were obtained with CN and CO groups at C-β; the less sensitive ($\rho \sim -1$) were the carbonyl shifts. Conversely, correlations of stretching vibrations ν(CO), and ν(CN) with σ_p^+ (Table VII) have a positive slope ρ and ν(CO) seemed to be more sensitive against the substitution effect. Correlation only for carbon C-3 ($r = 0.992$, $N = 12$) was observed of all furan carbon atoms.

A two-parameter correlation employing parameters[20] σ_I and σ_R was carried out in order to obtain information on the formal resonance and inductive (polar) effects of the substituent R to ^{13}C NMR chemical shifts and CO and CN stretching vibrations (Table VIII). Repeatidly, the more tense correlations were found with σ_R^+ excepting δ(CO).

The most tense correlation (r = 0.98) was again obtained for C-β. Correlations with σ_I and σ_R^+ showed that preferentially the inductive effect contributed to ^{13}C NMR chemical shifts of the carbonyl (λ = 2.55) and cyano (λ = 1.27) groups. The dominant resonance effect should preferentially come into effect with ν(CN) wave numbers.

EXPERIMENTAL

The infrared spectra in chloroform were measured with a Specord M-80 (Zeiss, Jena), styrene foil calibrated spectrophotometer. Compounds *II* were measured at the highest recording mode in the 1 600 to 2 300 cm^{-1} region. The ultraviolet spectra in methanol (c 10^{-4} mol dm^{-3}, 0.2 cm cell width) were recorded with a Specord M-40 (Zeiss, Jena) apparatus. The ^{1}H and ^{13}C NMR spectra of $CDCl_3$ solution containing tetramethylsilane as an internal reference were taken with Varian VXR 300 apparatus at 298.15 K; measured were saturated solutions in 5 mm (^{1}H) or 10 mm (^{13}C) multinuclear probes. Measuring conditions: 299.93 MHz operating frequency, spectral width 4 kHz, 16 000 points, pulse 8.7 μs, 41° flip angle for ^{1}H NMR measurements and 75.426 MHz, spectral width 16 502 Hz, pulse 8.7 μs, 54° flip angle and 32 000 points for ^{13}C measurements. Carbon signals of the furan ring were ascribed by comparison with the ^{13}C NMR spectral data of 5-R-2-furylethylene derivatives[3,20,21]. Mass spectra were measured with an MS 25 RPA (Kratos, Manchester) instrument at 70 eV electron energy.

TABLE VI
Correlations of ^{13}C NMR chemical shifts of compounds *II* with Hammett constants (σ_p, σ_p^+), $\delta = \delta_\Phi + \rho\sigma_p$

Carbon	Parameter	ρ^a	$\delta_\Phi{}^b$	r^c	S^d	N^e
C-3	σ_p^+	−4.34 ± 0.54	123.92 ± 0.34	0.932	1.40	12
	σ_p	−7.22 ± 1.23	125.50 ± 0.49	0.881	2.36	12
C-4	σ_p^+	14.59 ± 2.92	114.24 ± 1.87	0.845	41.24	12
	σ_p	22.76 ± 6.35	109.20 ± 2.56	0.750	63.21	12
	σ_p^+	13.77 ± 1.60	114.77 ± 1.07	0.950	11.38	10[f]
C-β	σ_p^+	7.65 ± 0.50	105.32 ± 0.32	0.979	1.21	12
	σ_p	12.82 ± 1.56	102.52 ± 0.63	0.933	3.82	12
	σ_p^+	7.90 ± 0.28	105.07 ± 0.19	0.994	0.38	11[g]
CN	σ_p^+	−1.95 ± 0.16	117.09 ± 0.10	0.967	0.13	12
	σ_p	−3.25 ± 0.44	117.80 ± 0.18	0.920	0.30	12
	σ_p^+	−2.02 ± 0.11	117.16 ± 0.07	0.987	0.06	11[g]
CO	σ_p^+	−1.02 ± 0.13	190.67 ± 0.08	0.928	0.08	12
	σ_p	−1.89 ± 0.14	191.08 ± 0.06	0.975	0.03	12

[a] Line slope and standard deviation; [b] intercept on the δ axis and standard deviation; [c] correlation coefficient; [d] standard deviation; [e] number of substituents in regression analysis; [f] C_6H_5S and C_6H_5O neglected; [g] C_6H_5S neglected.

Starting materials for the preparation of substituted 2-(5-R-2-furylmethylene)-3-oxobutanenitriles *IIa* – *IIl* were the corresponding 5-R-2-furaldehydes *Ia* – *Il*. Substituents in position 5 of the furan ring were chosen as to cover the whole range of Hammett constants. The 5-R-2-furaldehydes were synthesized according to procedures described in the literature[3,24 – 28].

TABLE VII
Correlations of stretching vibrations ν(CO) and ν(CN) with Hammett constants (σ_p, σ_p^+), $\nu = \nu_\phi + \rho\sigma$

ν	Parameter	ρ	ν_ϕ[a]	*r*	*S*	*N*
(CO)	σ_p^+	19.16 ± 1.59	1 698.0 ± 1.0	0.967	12.26	12
	σ_p	31.59 ± 4.64	1 691.0 ± 1.9	0.907	33.76	12
	σ_p^+	19.89 ± 1.06	1 697.3 ± 0.7	0.988	5.23	11
(CN)	σ_p^+	8.38 ± 0.98	2 213.9 ± 0.6	0.938	4.67	12
	σ_p	13.29 ± 2.64	2 211.0 ± 1.1	0.846	10.97	12

[a] Intercept on the ν axis and standard deviation.

TABLE VIII
Correlation parameters in the equation $a = \rho_I\sigma_I + \rho_R\sigma_R + b$. For σ_I σ_R see ref.[20]

Parameter	σ_R	ρ_I	ρ_R	λ[a]	*b*	*r*[b]	*S*
δ(C-3)	R^Φ	−6.42 ± 1.67	−13.15 ± 1.86	0.48	123.75 ± 0.73	0.936	1.02
	R^+	−4.28 ± 1.72	−4.58 ± 0.66	0.93	123.45 ± 0.76	0.935	1.21
δ(C-β)	R^Φ	12.22 ± 2.76	21.29 ± 3.07	0.57	104.93 ± 1.20	0.938	1.98
	R^+	8.58 ± 1.61	7.83 ± 0.62	1.10	105.71 ± 0.71	0.980	1.14
δ(CN)	R^Φ	−3.34 ± 0.99	−4.77 ± 1.10	0.70	117.38 ± 0.43	0.876	0.71
	R^+	−2.45 ± 0.54	−1.93 ± 0.21	1.27	117.10 ± 0.24	0.966	0.38
δ(CO)	R^Φ	−2.50 ± 0.18	−2.47 ± 0.21	1.01	191.10 ± 0.08	0.986	0.13
	R^+	−2.12 ± 0.28	−0.83 ± 0.11	2.55	191.40 ± 0.13	0.969	0.20
$\tilde{\nu}$(CN)	R^Φ	10.11 ± 5.10	22.86 ± 5.63	0.44	2 214.50 ± 2.00	0.833	3.63
	R^+	5.77 ± 2.80	9.38 ± 1.07	0.62	2 215.90 ± 1.20	0.953	1.99
$\tilde{\nu}$(CO)	R^Φ	30.52 ± 9.89	48.56 ± 11.02	0.63	1 696.30 ± 4.30	0.872	7.11
	R^+	21.44 ± 5.22	19.60 ± 2.00	1.09	1 699.00 ± 2.10	0.967	3.70

[a] $\lambda = \rho_I/\rho_R$; [b] correlation coefficient.

2-(5-R-2-Furylmethylene)-3-oxobutanenitriles *IIa – IIl*

Dilute hydrochloric acid (1 : 1, 20 ml) was poured into the solution of 3-amino-2-butenenitrile (8.2 g, 0.1 mol) in dry ethanol (60 ml) with stirring. Ammonium chloride separated and after 15 min 5-R-2-furaldehyde (0.1 mol) was added at room temperature. The mixture was left standing for 30 min, cold water was added (200 ml), neutralized with ammonia to pH 7.5 and the vigorous stirring was continued for 30 min. The precipitate was filtered off, washed with water and dried in air. The products were twice crystallized from ethanol.

Products prepared and their characteristic data lists Table I.

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