

Furan Derivatives. XXVIII.

Synthesis and Absorption Spectra of 2-(2-Furyl)- and 2-Phenyl-3-[5-(X-phenyl)-2-furyl]acrylonitriles

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2-(2-Furyl)-3-[5-(X-phenyl)-2-furyl]- and 2-phenyl-3-[5-(X-phenyl)-2-furyl]acrylonitriles (where X = 4-NO₂, 3-NO₂, 2-NO₂, 4-Cl, 3-Cl, 2-Cl, 4-Br, H, 4-CH₃ and 4-OCH₃) were prepared by condensation of substituted 5-phenyl-2-furaldehydes with furylacetonitrile and phenylacetonitrile, respectively. The infrared and ultraviolet spectra of the compounds synthesized are interpreted.

It is known that some furan derivatives exhibit an antibacterial activity [1—4]. Also the antibacterial activity which increases with compounds bearing two furan rings attached to the ethylenic group, has been reported [5]. From this point of view, some substituted 3-(5-phenyl-2-furyl)acrylic acids were prepared by Perkin's reaction starting from 5-phenyl-2-furaldehydes, or also by Meerwein's reaction from furylacrylic acid and diazonium salts [6]. All this, enforces our effort to synthesize related compounds in which the high biological activity might be expected. This work is a continuation of our previous work [7] dealing with the influence of the substituents bonded in position 2 of the benzene ring on the spectral data of compounds synthesized. Synthesized compounds have a structure similar to those used in practice as light stabilizers [8].

Experimental

Starting substituted phenylfuraldehydes were prepared according to [7, 9—14]. Furylacetonitrile was prepared in two ways according to [15, 16].

Preparation of 2-(2-furyl)-3-[5-(X-phenyl)-2-furyl]acrylonitriles

To a corresponding 5-phenyl-2-furaldehyde (0.01 mole) dissolved in absolute ethanol (15—125 ml depending on the solubility of starting aldehydes) 1.07 g (0.01 mole) of freshly distilled furylacetonitrile was added. Then, under vigorous stirring, a 10% ethanolic solution of sodium ethoxide (*ca.* 5 drops) was added. After a short time the solid was filtered off, washed with cold ethanol (*ca.* 10 ml) and crystallized from ethanol giving an appropriate nitrile.

Preparation of 2-phenyl-3-[5-(X-phenyl)-2-furyl]acrylonitriles

The appropriate 5-phenyl-2-furaldehyde (0.01 mole) was dissolved in absolute ethanol (15–125 ml) and to this solution phenylacetonitrile (1.17 g; 0.01 mol \pm) was added. Under stirring a 10% alcoholic solution of sodium ethoxide (*ca.* 5 drops) was added. The solid was filtered off, washed with cold ethanol and crystallized from ethanol or ethyl acetate.

Spectroscopy

Infrared spectra of the compounds investigated were recorded with the double-beam spectrophotometer UR-10 (Zeiss, Jena) in the 670–2400 cm $^{-1}$ range. Wave number measurements are believed to be accurate to ± 1 cm $^{-1}$; the spectra were measured in KBr discs (2 mg/1 g KBr).

Ultraviolet spectra were recorded with the double-beam spectropolarimeter ORD/UV-5 (Jasco, Tokyo) at room temperature using dioxan as a solvent (concentration 0.004–0.006 mg/1 ml and cells of 1.0 cm thickness).

Results and Discussion

A condensation of substituted 5-phenyl-2-furaldehydes with furylacetonitrile in absolute ethanol catalyzed by sodium ethoxide afforded substituted 2-(2-furyl)-3-[5-(X-phenyl)-2-furyl]acrylonitriles in 70–80% yields (Table 1). Similarly, by

Table 1

Survey of synthesized 2-(2-furyl)-3-[5-(X-phenyl)-2-furyl]acrylonitriles

No.	X	Formula	M	Calculated/found				Yield [%]	M.p. [°C] (Kofler)
				% C	% H	% N	% Hal.		
I	4-NO ₂	C ₁₇ H ₁₀ N ₂ O ₄	306.26	66.6	3.27	9.15		80	230–231
				66.4	3.30	9.18			
II	3-NO ₂	C ₁₇ H ₁₀ N ₂ O ₄	306.26	66.6	3.27	9.15		75	172–173
				66.7	3.34	9.35			
III	2-NO ₂	C ₁₇ H ₁₀ N ₂ O ₄	306.26	66.6	3.27	9.15		75	147–148
				66.5	3.35	9.25			
IV	4-Cl	C ₁₇ H ₁₀ ClNO ₂	295.71	68.0	3.39	4.74	11.98	77	157–158
				68.2	3.35	4.93	11.77		
V	3-Cl	C ₁₇ H ₁₀ ClNO ₂	295.71	68.0	3.39	4.74	11.98	75	98–99
				68.2	3.30	4.62	12.02		
VI	2-Cl	C ₁₇ H ₁₀ ClNO ₂	295.71	68.0	3.39	4.74	11.98	75	110–111
				68.3	3.25	4.61	11.90		
VII	4-Br	C ₁₇ H ₁₀ BrNO ₂	340.17	60.0	2.94	4.12	23.50	74	145–146
				59.8	2.86	4.39	23.65		
VIII	H	C ₁₇ H ₁₁ NO ₂	261.26	78.0	3.85	5.36		70	96–97
				77.8	3.70	5.43			
IX	4-CH ₃	C ₁₈ H ₁₃ NO ₂	257.29	78.5	4.76	5.09		72	85–86
				78.3	4.80	4.97			
X	4-OCH ₃	C ₁₈ H ₁₃ NO ₃	291.29	74.3	4.48	4.81		70	144–145
				74.0	4.35	5.00			

All compounds were crystallized from ethanol.

Table 2

Survey of synthesized 2-phenyl-3-[5-(X-phenyl)-2-furyl]acrylonitriles

No.	X	Formula	M	Calculated/found				Yield [%]	M.p. [°C] (Kofler)
				% C	% H	% N	% Hal.		
XI	4-NO ₂	C ₁₉ H ₁₂ N ₂ O ₃	316.0	72.2	3.92	8.85		98.0	221—222
				72.5	3.78	9.12			
XII	3-NO ₂	C ₁₉ H ₁₂ N ₂ O ₃	316.30	72.2	3.92	8.85		93.5	166—167
				72.4	3.84	9.05			
XIII	2-NO ₂	C ₁₉ H ₁₂ N ₂ O ₃	316.30	72.2	3.92	8.85		93.5	115—116
				72.4	3.84	8.97			
XIV	4-Cl	C ₁₉ H ₁₂ ClNO	305.75	74.8	3.96	4.60	11.60	94.5	147—148
				74.6	3.90	4.90	11.44		
XV	3-Cl	C ₁₉ H ₁₂ ClNO	305.75	74.8	3.90	4.60	11.60	92.5	98—99
				74.8	3.88	4.30	11.38		
XVI	2-Cl	C ₁₉ H ₁₂ ClNO	305.75	74.8	3.90	4.60	11.60	93.0	90—91
				74.7	3.82	4.66	11.64		
XVII	4-Br	C ₁₉ H ₁₂ BrNO	350.21	65.2	3.43	4.00	22.84	95.0	159—160
				65.1	3.40	3.91	22.82		
XVIII	H	C ₁₉ H ₁₃ NO	271.30	84.0	4.83	5.17		91.5	78—79
				83.9	4.73	5.22			
XIX	4-CH ₃	C ₂₀ H ₁₅ NO	285.32	84.2	5.31	4.91		87.0	121—122
				84.0	5.42	4.63			
XX	4-OCH ₃	C ₂₀ H ₁₅ NO ₂	301.32	79.9	5.08	4.65		85.0	101—102
				79.9	5.12	4.80			

Compound XI was crystallized from ethyl acetate, others from ethanol.

condensation of substituted 5-phenyl-2-furaldehydes with phenylacetonitrile substituted 2-phenyl-3-[5-(X-phenyl)-2-furyl]acrylonitriles in 85–98% yields were prepared (Table 2). The relatively lower yields (*ca.* 15%) of compounds listed in Table 1, than those of compounds listed in Table 2 can be ascribed to the fact that furylacetonitrile used in condensation is an unstable compound which was partially decomposed although it was carefully stored in dark-glass bottles.

The influence of substituents attached to the benzene ring on the yields of compounds synthesized has been observed. The highest yields were obtained with 4-substituted nitro derivatives (compounds I and XI; Tables 1 and 2).

Synthesized compounds were found to be relatively stable, well soluble in ethanol, in ethyl acetate and insoluble in water. All compounds prepared were yellow except 2- and 4-nitro derivatives, which were red.

From infrared spectral data of the compounds investigated (Table 3) it can be seen that the C≡N stretching vibrations are only slightly affected by the nature of the substituents. However, those are, in comparison with the unsubstituted derivative, slightly shifted to higher wave numbers with increasing electron-withdrawing power of substituents (compound VIII, $\nu(\text{C}\equiv\text{N})$ 2207 cm^{-1} ; compound XI $\nu(\text{C}\equiv\text{N})$ 2212 cm^{-1}).

The higher values of the C≡N stretching vibrations of 2-(2-furyl)-3-[5-(X-phenyl)-2-furyl]acrylonitriles (compounds I–X; Table 3) in comparison with those of 2-phenyl-3-[5-(X-phenyl)-2-furyl]acrylonitriles (compounds XI–XX; Table 4) suggest that the furan ring bonded on the same carbon atom as the C≡N group exhibit stronger electron-withdrawing power than the benzene ring.

Table 3

Ultraviolet and infrared spectral data of substituted 2-(2-furyl)-3-[5-(X-phenyl)-2-furyl]acrylonitriles

No.	X	λ_{\max} [nm]	$\log \epsilon$	λ_{\max} [nm]	$\log \epsilon$	λ_{\max} [nm]	$\log \epsilon$	λ_{\max} [nm]	$\log \epsilon$	λ_{\max} [nm]	$\log \epsilon$	λ_{\max} [nm]	$\log \epsilon$	$\nu(\text{C}\equiv\text{N})$ [cm ⁻¹]	$\nu(\text{CH}=\text{C})$ [cm ⁻¹]
<i>I</i>	4-NO ₂	422	4.52	410	4.51 sh	337	5.05 sh	245	4.15 sh	225	4.12 sh			2217(53)	1613(76)
<i>II^a</i>	3-NO ₂	397	4.55	303	3.68 sh	290	3.85 sh	275	3.90 sh	262	4.12	220	4.29	2222(53)	1627(76)
<i>III</i>	2-NO ₂	390	4.504	280	3.72 sh	265	3.87	235	4.14 sh					2212(52)	1620(36)
<i>IV^b</i>	4-Cl	403	4.64	395	4.62 sh	305	3.58	285	3.86	268	3.95	232	4.14	2219(72)	1614(50)
<i>V</i>	3-Cl	395	4.57	303	3.72 sh	288	3.91	263	4.08 sh	250	4.07 sh	235	4.11	2218(46)	1614(51)
<i>VI</i>	2-Cl	389	4.51	300	3.70	285	3.89	260	3.97	250	4.06	236	4.09	2226(66)	1617(49)
<i>VII</i>	4-Br	398	4.58	305	3.85 sh	287	4.05	269	4.05	257	4.08	228	4.16	2219(65)	1614(sh)
<i>VIII^c</i>	H	396	4.75	300	3.75 sh	288	3.95	282	3.94	264	4.04	253	4.09	2220(65)	1611(54)
<i>IX</i>	4-CH ₃	400	4.57	300	3.81	282	4.01	267	4.09	252	4.11	231	4.19	2218(55)	1617(44)
<i>X</i>	4-OCH ₃	410	4.57	300	3.84 sh	289	4.04 sh	276	4.15	268	4.09 sh	232	4.17	2218(81)	1620(74)

Additional bands: *a*) λ_{\max} 252 nm, $\log \epsilon$ 4.16; *b*) λ_{\max} 253 nm, $\log \epsilon$ 4.14; *c*) λ_{\max} 235 nm, $\log \epsilon$ 4.15; λ_{\max} 205 nm, $\log \epsilon$ 4.13. The asymmetrical (ν_{as}) and symmetrical (ν_{s}) stretching vibrations of the NO₂ groups of nitro derivatives [cm⁻¹]: *I*. 1522(76) and 1339(88); *II*. 1532(80) and 1363(85); *III*. 1537(74) and 1359(68).

The values in parenthesis are % of absorptions; sh — shoulder.

Table 4

Ultraviolet and infrared spectral data of substituted 2-phenyl-3-[5-(X-phenyl)-2-furyl]acrylonitriles

No.	X	λ_{\max} [nm]	$\log \epsilon$	λ_{\max} [nm]	$\log \epsilon$	λ_{\max} [nm]	$\log \epsilon$	λ_{\max} [nm]	$\log \epsilon$	$\nu(\text{CH}=\text{C})$ [cm^{-1}]	$\nu(\text{C}\equiv\text{N})$ [cm^{-1}]
XI	4-NO ₂	395	4.53	311	3.95	240	4.19 sh	229	4.22	1608(61)	2212(64)
XII ^a	3-NO ₂	365	4.47	268	4.18 sh	250	4.32 sh	243	4.33	1626(50)	2216(69)
XIII	2-NO ₂	370	4.42	260	3.99	234	4.14			1619(36)	2212(47)
XIV	4-Cl	369	4.49	257	4.21 sh	240	4.23			1621(50)	2209(61)
XV	3-Cl	370	4.50	245	4.22	240	4.21			1622(67)	2212(65)
XVI	2-Cl	378	4.59	245	4.19	238	4.18			1621(70)	2214(72)
XVII	4-Br	369	4.50	263	4.23	252	4.20	222	4.07	1618(61)	2208(46)
XVIII	H	366	4.44	255	4.17 sh	237	4.21			1625(50)	2207(56)
XIX	4-CH ₃	379	4.60	264	4.10	243	4.18	235	4.21	1617(65)	2207(79)
XX ^b	4-OCH ₃	382	4.48	269	4.30	265	4.28	240	4.11	1619(50)	2211(70)

Additional bands: *a*) λ_{\max} 238 nm, $\log \epsilon$ 4.32; λ_{\max} 225 nm, $\log \epsilon$ 4.29; *b*) λ_{\max} 222 nm, $\log \epsilon$ 4.07.

The asymmetrical (ν_{as}) and symmetrical (ν_{s}) stretching vibrations of the NO₂ groups [cm^{-1}]: XI. 1526(80) and 1340(88); XII. 1544(84) and 1366(91); XIII. 1534(86) and 1379(56).

The values in parenthesis are % of absorption; sh — shoulder.

The effect of substituents on the intensity of the $C\equiv N$ stretching band was observed to be more marked than that on the $C=N$ band positions.

The lower values of the $C\equiv N$ stretching vibrations in comparison with those of acrylonitrile ($\nu(C\equiv N)$ 2231 cm^{-1}) [17], suggest the mesomeric interaction between the $C\equiv N$ group and the rest of the molecule.

The $C\equiv N$ stretching vibrations of methyl-2-cyano-3-[5-(X-phenyl)-2-furyl]acrylates reported previously [7], are approximately the same. This points out that the final effect of furyl and carbomethoxy group on these vibrations is the same.



The highest values of λ_{max} observed with 4-substituted derivatives (Tables 3 and 4) point out the mesomeric interaction of substituents with the rest of molecules causing the extension of the conjugated system. This assumption is in accordance with the spectral data of methyl-2-cyano-3-[5-(X-phenyl)-2-furyl]acrylates reported in our previous work [7].

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