

Furan Derivatives. XXVII.

Synthesis and Absorption Spectra of Methyl-2-cyano-3-[5-(X-phenyl)-2-furyl]acrylates

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Received June 22, 1970

By condensation of substituted 5-phenyl-2-furaldehydes with methyl cyanoacetate in ethanol catalyzed by sodium ethoxide ten substituted methyl-2-cyano-3-[5-(X-phenyl)-2-furyl]acrylates (where X = 4-NO₂, 3-NO₂, 2-NO₂, 4-Cl, 3-Cl, 2-Cl, 4-Br, H, 4-CH₃ and 4-OCH₃) were prepared. The infrared and ultraviolet spectra of the compounds synthesized and also starting aldehydes are interpreted in terms of configurational effects.

Some phenylfuran derivatives obtained by condensation of substituted phenylfuraldehyde with various nitrogen bases [1–4] have been reported to exhibit an antimicrobiological, mainly a tuberculostatic activity [5–8]. It is also known that some similar compounds have a practical use as light stabilizers [9–15]. From this point of view, we synthesized related compounds having acidic hydrogens.

In the present work we report a synthesis of 5-(2-chlorophenyl)-2-furaldehyde not yet described in literature and a condensation of substituted 5-phenyl-2-furaldehydes with methyl cyanoacetate.

Experimental

Starting phenylfuraldehydes used in condensation were prepared according to [16–21]. However, the synthesis of 5-(2-chlorophenyl)-2-furaldehyde has not yet been described.

Preparation of 5-(2-chlorophenyl)-2-furaldehyde

2-Chloroaniline (27.4 g; 0.25 mole) was dissolved in 15% hydrochloric acid (120 ml). The solution was cooled to –5°C and treated with NaNO₂ (16 g in 80 ml of water). A solution of diazonium salt was filtered, stirred and added into an aqueous solution of freshly distilled furaldehyde (27 g; 0.28 mole in 50 ml of H₂O). To the reaction mixture heated to 25–30°C 15 ml of an aqueous solution of CuCl₂ (11 g CuCl₂ · 5H₂O) was added in small portions under stirring.

After 4 hours of stirring the reaction mixture was allowed to stand for 15 hours at room temperature. The solid was filtered off, washed with water and steam — distilled to remove volatile compounds. The residual solid crystallized from ethanol yielded 5-(2-chlorophenyl)-2-furaldehyde; m.p. 76.5–77.5°C (65%).

For $C_{11}H_7O_2Cl$ (206.62) calculated: 63.8% C, 3.41% H, 17.15% Cl; found: 63.6% C, 3.32% H, 17.1% Cl.

5-(2-Chlorophenyl)-2-furaldehyde was found to be a stable compound, well soluble in ethanol and ether, and insoluble in water.

Preparation of methyl-2-cyano-3-[5-(X-phenyl)-2-furyl]acrylates

To the solution of substituted 5-(X-phenyl)-2-furaldehyde (0.02 mole) in absolute ethanol (25—250 ml depending on the solubility of aldehyde) a freshly distilled methyl cyanoacetate (1.98 g; 0.02 mole) was added. A 10% solution of sodium ethoxide (*ca.* 5 drops) was added to the reaction mixture under stirring. After a short time fine crystals formed were filtered off, washed with cold ethanol (10—20 ml) and crystallized from ethanol or ethyl acetate.

Spectroscopy

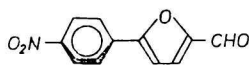
Ultraviolet spectra were recorded with the double-beam spectropolarimeter ORD/UV-5 (Jasco, Tokyo) at $20 \pm 2^\circ C$, using dioxan as a solvent (concentration 0.004—0.006 mg/ml and cells of 1.0 cm thickness). The λ_{max} are believed to be accurate to ± 1 nm.

Infrared spectra were recorded with the double-beam spectrophotometer UR-10 (Zeiss, Jena) in the 670—2400 cm^{-1} region. Wave number measurements are believed to be accurate to ± 1 cm^{-1} . The spectra were recorded in $CHCl_3$ (concentration 0.1 mole, cells of 0.4 mm thickness). With respect to the insolubility of nitro derivatives studied in $CHCl_3$, the spectra of those were measured in KBr discs (2 mg/1 g KBr).

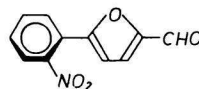
Results and Discussion

The yields of substituted methyl-2-cyano-3-[5-(X-phenyl)-2-furyl]acrylates obtained by condensation of 5-phenyl-2-furaldehydes with methyl cyanoacetate in absolute ethanol were found to be higher than 90% (Table 1). The highest yield was obtained with compound *I* what is in accordance with our conclusions previously made [7, 18, 19]. All compounds synthesized were found to be stable, well soluble in ethanol and ethyl acetate, and insoluble in water.

From ultraviolet spectra of aldehydes used in condensation (Table 2) it can be seen that the highest value of λ_{max} having been observed for 4-substituted derivatives whilst the lowest ones for 2-substituted derivatives which might be explained by configurational effects suggesting that 2-substituted derivatives are twisted more than 4-substituted ones [7], *e.g.*



λ_{max} 340 nm



λ_{max} 291 nm

A coplanar structure, however, is impossible, since it would involve a large measure of compression between the *ortho*-hydrogens in the benzene and furan rings. Thus, the bulky substituents in position 2 of the benzene ring will enforce twisted configuration. The lower differences in the values of λ_{max} of chloro derivatives in com-

parison with those of nitro derivatives can be due to the mass effects *e.g.* the twisted configuration is less enforced by chloro atom attached in position 2 of the benzene ring than that by nitro group. This assumption seems to be reasonable and it is also supported by the result reported in our previous work [7].

Table 1

Survey of methyl-2-cyano-3-[5-(X-phenyl)-2-furyl]acrylates synthesized

No.	X	Formula	M	Calculated/found				Yield [%]	M.p. [°C] (Kofler)
				% C	% H	% N	% Hal.		
I	4-NO ₂	C ₁₅ H ₁₀ N ₂ O ₅	298.24	60.4	3.36	9.40		98	264–266
				60.5	3.40	9.37			
II	3-NO ₂	C ₁₅ H ₁₀ N ₂ O ₅	298.24	60.4	3.36	9.40		94	210–211
				60.7	3.29	9.27			
III	2-NO ₂	C ₁₅ H ₁₀ N ₂ O ₅	298.24	60.4	3.36	9.40		93	142
				60.3	3.39	9.19			
IV	4-Cl	C ₁₅ H ₁₀ ClNO ₃	287.69	62.6	3.48	4.77	12.35	95	165
				62.8	3.42	4.90	12.37		
V	3-Cl	C ₁₅ H ₁₀ ClNO ₃	287.69	62.6	3.48	4.77	12.35	93	167–168
				62.5	3.54	4.77	12.11		
VI	2-Cl	C ₁₅ H ₁₀ ClNO ₃	287.69	62.6	3.48	4.77	12.35	94	121–122
				62.8	3.49	4.70	12.11		
VII	4-Br	C ₁₅ H ₁₀ BrNO ₃	332.15	54.2	3.02	4.22	24.10	92	145
				54.1	3.08	4.15	24.15		
VIII	H	C ₁₅ H ₁₁ NO ₃	253.24	71.0	4.35	5.53		92	105–106
				71.2	4.40	5.83			
IX	4-CH ₃	C ₁₆ H ₁₃ NO ₃	267.27	72.0	4.91	5.24		90	163–164
				71.9	5.01	5.26			
X	4-OCH ₃	C ₁₆ H ₁₃ NO ₄	283.27	67.8	4.62	4.94		91	159–161
				67.9	4.73	5.09			

Compounds I and II crystallized from ethyl acetate, others from ethanol.

Table 2

Ultraviolet and infrared spectral data of 5-(X-phenyl)-2-furaldehydes

No.	X	λ_{\max} [nm]	log ϵ	λ_{\max} [nm]	log ϵ	λ_{\max} [nm]	log ϵ	λ_{\max} [nm]	log ϵ	λ_{\max} [nm]	log ϵ	$\nu(\text{C}=\text{O})$ [cm ⁻¹]
XI*	4-NO ₂	340	4.48	290	3.09	230						1693
		309	4.48	262	3.09	230						1690
XII*	3-NO ₂	331	4.43			230						1690
		291	4.43			230						1690
XIII*	2-NO ₂	330	4.44	319	4.51	236	4.00	226	4.16			1680
		327	4.41	314	4.48	239	3.86	233	4.02	225	4.16	1678
XIV	4-Cl	325	4.31	312	4.42	240	3.65	232	3.99	233	4.10	1686
		332	4.41	320	4.51	235	3.96	225	4.10			1679
XV	3-Cl	328	4.34	316	4.41	233	3.94	222	4.16			1676
		340	4.40	322	4.48	262	3.46	234	3.98	224	4.15	1679
XVI	2-Cl	348	4.38	333	4.29	274	3.86	237	3.95	226	4.08	1677

Data taken from [7]; $\lambda_{\text{as}}(\text{NO}_2)$ and $\nu_s(\text{NO}_2)$: 1529 and 1349 cm⁻¹ (XI); 1524 and 1354 cm⁻¹ (XII); 1539 and 1357 cm⁻¹ (XIII).

Table 3

Ultraviolet and infrared spectral data of methyl-2-cyano-3-[5-(X-phenyl)-2-furyl]acrylates

No.	λ_{\max} [nm]	$\log \epsilon$	λ_{\max} [nm]	$\log \epsilon$	λ_{\max} [nm]	$\log \epsilon$	λ_{\max} [nm]	$\log \epsilon$	λ_{\max} [nm]	$\log \epsilon$	$\nu(\text{CH}=\text{C})$ [cm^{-1}]	$\nu(\text{C}=\text{O})$ [cm^{-1}]	$\nu(\text{C}=\text{N})$ [cm^{-1}]
<i>I</i> ^a	410	4.54		4.61		3.82	321	4.20			1621(73)	1737(72)	2227(55)
<i>II</i> ^b	379	4.57	275	3.96	246	4.34	229	4.27			1613(96)	1725(94)	2221(41)
<i>III</i> ^c	381	4.62		4.33							1619(87)	1734(88)	2222(64)
<i>IV</i>	391	4.60	263	4.19	256	4.24	245	4.18	228	4.14	1618(86)	1728(84)	2217(46)
<i>V</i>	384	4.57	255	4.13	248	4.17	230	3.98			1623(90)	1728(86)	2221(44)
<i>VI</i>		4.53	246	4.23	226	4.17					1620(80)	1728(82)	2220(40)
<i>VII</i>	390	4.59	265	4.18	259	4.20	245	4.14	227	4.10	1621(82)	1725(80)	2219(40)
<i>VIII</i> ^d	389	4.52	292	3.63	281	3.63	249	4.20	225	4.99	1620(94)	1725(87)	2221(59)
<i>IX</i>	398	4.60	263	4.17	256	4.24	226	4.12			1626(88)	1729(86)	2219(61)
<i>X</i>	414	4.59	300	3.60	273	4.23	243	4.08	226	4.11	1615(81)	1727(75)	2219(53)

The values in parenthesis are % of absorption; the asymmetrical (ν_{as}) and symmetrical (ν_{s}) stretching vibrations of the NO_2 groups.

a) 1518 and 1336 cm^{-1} ; *b*) 1536 and 1375 cm^{-1} ; *c*) 1529 and 1351 cm^{-1} ; *d*) compounds *VIII* shows additional bands (shoulders) at 305 and 269 nm and 260 nm an inflex maximum.

The C=O stretching vibrations of aldehydes investigated (Table 2) are shifted to higher wave numbers with increasing electron-withdrawing power of substituents as expected.

From ultraviolet spectral data of final compounds (Table 3) it can be seen that the values of λ_{\max} of absorption bands are higher than those observed for aldehydes studied (Table 2) suggesting that the conjugated system with these compounds was extended. The different course of absorption bands observed for 2- and 4-substituted derivatives can be explained by configurational effects analogously as for aldehydes studied. Also the C=O stretching vibrations (Table 3) are influenced by the nature of substituents approximately in the same way as in the case of aldehydes. The C≡N stretching vibrations are also influenced by substituents in such a way that electron-releasing substituents (CH₃, -OCH₃) as well as halogens (+M effect) independently of their position on the benzene ring, shift those to lower values while electron-withdrawing substituents do the reverse.

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Translated by Š. Kováč