

Furan derivatives. XXXI.

α,β -Unsaturated ketones of the phenylfuran series

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1-(2-Furoyl)-2-[5-(X-phenyl)-2-furyl]ethylenes, 1-benzoyl-2-[5-(X-phenyl)-2-furyl]ethylenes, and 4-[5-(4-nitrophenyl)-2-furyl]-3-butene-2-ones (X = = 4-NO₂, 3-NO₂, 4-Cl, 4-Br, 4-CH₃, 4-OCH₃, H) have been synthesized by the condensation of 5-(X-phenyl)-2-furaldehydes with 2-acetylfuran, acetophenone, and acetone. The preparation of 5-(X-phenyl)-2-furaldehydes (X = = 4-CH₃, 4-OCH₃, H) and the arylation of 2-acetylfuran by the modified Meerwein's reaction is also described. Infrared spectra of the synthesized compounds are interpreted.

α,β -Unsaturated ketones of general formula R₁-CH=CH-CO-R₂ (chalcones), where R₁ and R₂ are aromatic groups, have been extensively investigated by many workers. Recently, more attention have received heterocyclic analogs of chalcones, *i.e.* compounds containing one or two heteroatoms in the molecule, as *e.g.* chalcone analogs containing five-membered rings with one heteroatom [1-5].

Arylation of 2-furaldehyde with benzenediazonium salts was conducted under the conditions of Meerwein's reaction [6-13]. By finding suitable reaction conditions for the arylation and for the preparation of new aryl 2-furaldehydes [6-9] it was possible to synthesize new α,β -unsaturated ketones [14-18] of the phenylfuran series.

Experimental

Infrared spectra (3600-700 cm⁻¹) were measured in chloroform at a concentration of 0.025 M using a double-beam UR-10 Zeiss spectrometer. In the range of 1750-1500 cm⁻¹ the spectra of compounds IV-VIII and XII-XVI were measured also in carbon tetrachloride. Some spectra were taken using KBr technique. Calibration of the instrument was done with standard polystyrene foil (thickness 20 μ m). The reading of the wave numbers was done with the accuracy of ± 1 cm⁻¹.

5-(4-X-Phenyl)-2-furaldehyde

(X = CH₃, OCH₃, H)

To a mixture containing the corresponding aryl amine (0.5 mole), concentrated hydrochloric acid (135 ml), and water (50 ml) a solution of NaNO₂ (36.2 g in 100 ml of water) was added at 10°C. The solution of the diazonium salt was filtered and 2-furaldehyde (0.64 mole) in acetone (100 ml) was added. The temperature of the reaction mixture

was raised to 25°C followed by the portionwise addition of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (23 g) in water (100 ml) while the mixture was vigorously stirred. The reaction was allowed to proceed at 40°C for 4 hours and then at room temperature for 16 hours. The oily layer was extracted with chloroform and the chloroform solution was washed with water and 5% sodium hydroxide. Evaporation of the organic solvent was followed by steam distillation of the crude product and the residue was extracted with ether. The ethereal solution was dried with sodium sulfate, concentrated, and the product was vacuum distilled.

5-Phenyl-2-furaldehyde (yield 40%, b.p. 145°C/5 torr) was obtained as a yellow oil which darkened on standing. Ref. [10–13] b.p. 90–92°C/30 torr; Ref. [19] 146°C/5 torr.

5-(4-Tolyl)-2-furaldehyde (yield 32%, b.p. 160°C/8 torr) was obtained as an orange oil which solidified on standing. M.p. 55–56°C (from *n*-hexane).

For $\text{C}_{12}\text{H}_{10}\text{O}_2$ (186.21) calculated: 77.38% C, 5.40% H; found: 77.65% C, 5.48% H.

5-(4-Methoxyphenyl)-2-furaldehyde (yield 25%, b.p. 175°C/0.5 torr) was a yellow viscous oil. Ref. [10–13] b.p. 100–105°C/50 torr.

For $\text{C}_{12}\text{H}_{10}\text{O}_3$ (202.21) calculated: 71.25% C, 4.99% H; found: 71.12% C, 4.96% H.

5-(4-Nitrophenyl)-2-acetylfuran (XVIII)

p-Nitroaniline (0.1 mole) was dissolved with little warming in 15% hydrochloric acid (60 ml), the solution was diluted with water (80 ml), cooled to 0–3°C and diazotized with a 30% solution of sodium nitrite (24 ml). The filtered solution of the diazonium salt was diluted with water (50 ml) and 2-acetylfuran (0.1 mole) in acetone (50 ml) was added, followed by a dropwise addition of a water solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (2.55 g; 0.015 mole) and the reaction mixture was left at 25–35°C for 4–5 hours and then at room temperature for 16 hours. The precipitated product was filtered, washed with water and a solution of sodium carbonate and water until neutral. Yield 53%, m.p. 165–166°C (from ethanol).

For $\text{C}_{12}\text{H}_9\text{NO}_4$ (231.2) calculated: 62.20% C, 3.68% H, 6.00% N; found: 62.01% C, 3.75% H, 6.27% N.

1-(2-Furoyl)-2-[5-(*X*-phenyl)-2-furyl]ethylenes and 1-benzoyl-2-[5-(*X*-phenyl)-2-furyl]ethylenes (I–XVI)

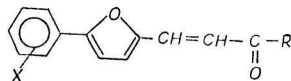
5-(*X*-Phenyl)-2-furaldehyde (0.01 mole) and 2-acetylfuran (0.01 mole), or acetophenone (0.01 mole) was dissolved with heating in ethanol and, under stirring, 10% sodium hydroxide (2–3 drops) was added. The stirring was continued for 2 hours and the reaction mixture was then left at room temperature for 24 hours. The precipitated product was filtered, washed with ethanol and crystallized from ethanol.

4-[5-(4-Nitrophenyl)-2-furyl]-3-butene-2-one (XVII)

5-(4-Nitrophenyl)-2-furaldehyde (1.01 g; 0.005 mole) was dissolved in hot ethanol and at 30°C acetone (20 ml) and 25% solution of sodium hydroxide (5–7 drops) was added. The mixture was stirred for 2 hours and then concentrated to the half of the original volume. The separated product was filtered and crystallized from ethanol.

Results and discussion

The boiling points found for the synthesized 5-phenyl-, 5-(4-totyl)-, and 5-(4-methoxy)-2-furaldehydes did not agree with the reported values [10–13]. The identity as well

Table 1. Synthesized α,β -unsaturated ketones

No.	X	R	Formula	M	Calculated/found				Yield [%]	M.p. [°C]
					% C	% H	% N	% Hal.		
<i>I</i>	4-NO ₂	2-furyl	C ₁₈ H ₁₁ NO ₅	309.27	69.82 69.70 69.71	3.58 3.50 3.49	4.53 4.40 4.65		71	224-226
<i>II</i>	3-NO ₂	2-furyl	C ₁₈ H ₁₁ NO ₅	309.27	69.82 69.71	3.58 3.49	4.53 4.65		68.5	182-186
<i>III</i>	2-NO ₂	2-furyl	C ₁₈ H ₁₁ NO ₅	309.26	69.82 69.63	3.58 3.49	4.53 4.55		69	107-109
<i>IV</i>	4-Cl	2-furyl	C ₁₈ H ₁₁ ClO ₃	298.71	72.37 72.17	3.71 3.67		11.86 11.90	79	135
<i>V</i>	4-Br	2-furyl	C ₁₈ H ₁₁ BrO ₃	343.17	66.49 66.32	3.82 3.78		23.28 23.20	75.7	162-163
<i>VI</i>	H	2-furyl	C ₁₇ H ₁₂ O ₃	264.27	77.25 77.4	4.58 4.54			71	99-100
<i>VII</i>	4-CH ₃	2-furyl	C ₁₈ H ₁₄ O ₃	278.29	77.68 77.64	5.06 5.31			65	114-115
<i>VIII</i>	4-OCH ₃	2-furyl	C ₁₈ H ₁₄ O ₄	294.29	73.45 73.40	4.79 4.95			73	111-112
<i>IX</i>	4-NO ₂	phenyl	C ₁₉ H ₁₃ NO ₄	319.30	71.48 71.30	4.10 4.00	4.41 4.30		75	174-175
<i>X</i>	3-NO ₂	phenyl	C ₁₉ H ₁₃ NO ₄	319.30	71.46 71.5	4.10 4.22	4.41 4.51		72	149
<i>XI</i>	3-NO ₂	phenyl	C ₁₉ H ₁₃ NO ₄	319.30	71.46 71.27	4.10 3.99	4.41 4.59		73	101
<i>XII</i>	4-Cl	phenyl	C ₁₉ H ₁₃ ClO ₂	308.74	73.91 73.96	4.25 4.26		11.48 11.60	82	133
<i>XIII</i>	4-Br	phenyl	C ₁₉ H ₁₃ BrO ₂	353.20	64.60 64.40	3.71 3.48		22.93 22.68	80	144-145
<i>XIV</i>	H	phenyl	C ₁₉ H ₁₄ O ₂	274.30	83.15 82.81	5.14 5.09			73	115
<i>XV</i>	4-CH ₃	phenyl	C ₂₀ H ₁₆ O ₂	288.33	83.30 83.64	5.58 5.22			68	124-125
<i>XVI</i>	4-OCH ₃	phenyl	C ₂₀ H ₁₆ O ₃	304.33	78.92 78.96	5.30 5.11			62	116-117
<i>XVII</i>	4-NO ₂	CH ₃	C ₁₄ H ₁₁ NO ₄	257.25	65.30 65.05	4.27 4.27	5.45 5.35		75	183-185

Table 2

Infrared data of the synthesized compounds

No.	$\bar{\nu}(\text{C}=\text{C})$ [cm ⁻¹]	$\bar{\nu}(\text{C}=\text{O})$ [cm ⁻¹]	No.	$\bar{\nu}(\text{C}=\text{C})$ [cm ⁻¹]	$\bar{\nu}(\text{C}=\text{O})$ [cm ⁻¹]
<i>I</i>	1605 (78) 1597 (92) ^b	1662 (50) 1653 (82) ^b	<i>X</i>	1608 (82)	1665 (57)
<i>II</i>	1605 (80)	1662 (63)	<i>XI</i>	1608 (82)	1665 (58)
<i>III</i>	1607 (92)	1662 (82)	<i>XII</i>	1602 (84)	1662 (60)
<i>IV</i>	1599 (80)	1660 (61)	<i>XIII</i>	1604 (80)	1661 (73)
<i>V</i>	1599 (76)	1660 (50)	<i>XIV</i>	1604 (80)	1663 (58)
				1608 (68) ^a	1670 (56) ^a
<i>VI</i>	1600 (86) 1606 (87) ^a 1595 (95) ^b	1661 (68) 1666 (64) ^a 1649 (88) ^b	<i>XV</i>	1594 (95) ^b 1603 (83) 1606 (83) ^a 1597 (92) ^b	1654 (80) ^b 1664 (60) 1669 (55) ^a 1654 (84) ^b
<i>VII</i>	1601 (88) 1604 (90) ^a 1590 (95) ^b	1660 (70) 1663 (67) ^a 1648 (91) ^b	<i>XVI</i>	1601 (85) 1604 (90) ^a 1600 (66) ^b	1660 (55) 1669 (56) ^a 1655 (62) ^b
<i>VIII</i>	1598 (92) 1603 (93) ^a 1590 (97) ^b	1658 (68) 1664 (65) ^a 1653 (90) ^b	<i>XVII</i>	1597 (84)	1667 (60) 1688 (47)
<i>IX</i>	1607 (87) 1598 (95) ^b	1667 (56) 1655 (69) ^b	<i>XVIII</i>	1609 (57)	1680 (75)

a) Measured in CCl₄; *b*) measured in KBr.

The values in parentheses refer to the absorption in %.

as the purity of the products were ascertained by elemental analysis, infrared and ultra-violet spectrometry [21] and thin-layer chromatography [22]. Similar problems were encountered by *Davis et al.* [19] in identification of 5-phenyl-2-furaldehyde obtained by formylation of phenylfuran.

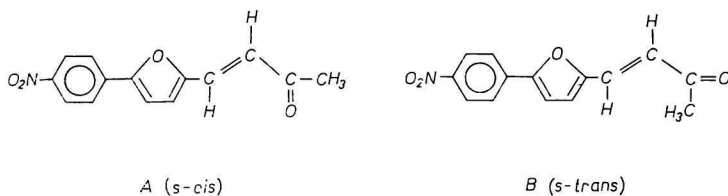
α,β -Unsaturated ketones were prepared according to the procedure described in Experimental Section at the boiling point of ethanol. An exception was the condensation of 5-(4-nitrophenyl)-2-furaldehyde with acetone, which was conducted at $\sim 30^\circ\text{C}$ since compound *XVII* undergoes at elevated temperatures condensation through its second methyl group.

Infrared spectra of the investigated chalcone analogs show intense absorption bands at 1670–1648 cm⁻¹ corresponding to the stretching vibrations of C=O bonds. The wave numbers of C=O bonds found in chloroform are, as expected, lower by 5–9 cm⁻¹ than those found in carbon tetrachloride. When the measurements were carried out in solid state the wave numbers found for all compounds were at lower values (by 11–17 cm⁻¹) than those found with the solutions in carbon tetrachloride, which is obviously due to dipolar interactions.

It further follows from the spectrometric data that the decrease of $\bar{\nu}(\text{C}=\text{O})$ values of *I–VIII* compared to those of *IX–XVI* can be accounted for by the electron-donor effects of the furan cycle [20]. The substituent X has but little effect upon $\bar{\nu}(\text{C}=\text{O})$. Compound *XVIII* shows more pronounced –M effect of the nitrophenyl residue upon the frequencies of C=O bonds than that of the compounds *I* and *IX*.

The introduction of the vinylene group into the molecule of *XVIII* (between the

C=O group and the 5-(4-nitrophenyl)-2-furyl residue; compound *XVII*) resulted in the splitting of the absorption band of the C=O group which indicates the presence of two rotation isomers [23] (Scheme 1).



Scheme 1

The more intense absorption band (at 1667 cm^{-1}) probably corresponds to the structure *B*, and the less intense one (at 1688 cm^{-1}) to the structure *A*.

The stretching vibrations of the vinylic groups and those of aromatic C=C bonds are pictured by bands at 1610–1500 cm^{-1} in the spectra.

The frequencies of NO_2 groups of compounds *I–III* and *IX–XI* are at

4- NO_2 derivatives:	$\tilde{\nu}_{\text{as}}(\text{NO}_2)$	1535 cm^{-1} ;	$\tilde{\nu}_{\text{s}}(\text{NO}_2)$	1345 cm^{-1} ,
3- NO_2 derivatives:	$\tilde{\nu}_{\text{as}}(\text{NO}_2)$	1544 cm^{-1} ;	$\tilde{\nu}_{\text{s}}(\text{NO}_2)$	1361 cm^{-1} ,
2- NO_2 derivatives:	$\tilde{\nu}_{\text{as}}(\text{NO}_2)$	1542 cm^{-1} ;	$\tilde{\nu}_{\text{s}}(\text{NO}_2)$	1355 cm^{-1} .

The frequencies of the nitro groups of 3-substituted derivatives are, as expected, at higher values of $\tilde{\nu}_{\text{max}}$ compared to those of 4-substituted derivatives. Higher values of $\tilde{\nu}(\text{NO}_2)$ of 2-nitrosubstituted derivatives compared to 4-nitro compounds are due to the nonpolar arrangement of the molecule. A detailed discussion of these aspects has already been reported [9, 24–27].

In the spectra of *VIII* and *XVI* there are intense absorption bands of the methoxy group at 1272 and 1263 cm^{-1} , respectively, characteristic of the stretching vibrations of C–O bonds, where C is the carbon atom of the benzene ring. The band at 1185 cm^{-1} corresponds to the vibrations of $\text{H}_3\text{C–O}$ [27].

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