PREPARATION AND SPECTRAL PROPERTIES OF SUBSTITUTED 1-(5-ARYL-2-FURYL)-3-PHENYLPROPENONES*

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The preparation of α,β-unsaturated ketones of arylfuran series by condensation of 5-(4-nitrophenyl)-2-acetylfuran and 5-(4-chlorophenyl)-2-acetylfuran with substituted benzaldehydes in ethanol, under catalysis with sodium hydroxide, is described. The exsitence of *s-cis* and *s-trans* conformers has been proved on the basis of a study of $\nu(C{=}O)$ frequencies. A statistically significant linear free-energy relationship between $\nu(C{=}O)$ and σ^+ and σ constants of substituent has been obtained.

In our preceding paper[1] we described the preparation of 1-phenyl-3-(5-aryl-2-furyl)-propenones in which the carbonyl group is separated from the arylfuran skeleton by a double bond. During the study of infrared spectral data of these compounds we observed[2] that they may exist in *s–cis* and *s–trans* conformations. In the same paper[2] we observed a statistically significant linear free-energy relationship between $\nu(C{=}O)$ and σ^+ constants of the substituent and calculated the coefficient of transfer of electronic effects through the furan cycle; it was in good agreement with our preceding data[3,4]. In this paper we describe the preparation of several series of 1-[5--(R[1]-phenyl)-2-furyl]-3-(R[2]-phenyl)propenones in which the carbonyl group is immediately bound to the furan nucleus of the arylfuran skeleton. Our aim was to follow the existence of conformers in the compounds prepared.

Compounds $I-XXV$ were prepared by Claisen–Schmidt condensation of 5-aryl--2-acetylfurans with substituted benzaldehydes. The starting 5-aryl-2-acetylfurans were prepared by a procedure mentioned in paper[5].

The ultraviolet spectra of compounds $I-XXV$ are given in Table I. The absorption band at highest wave-lengths corresponds to the oscillation of electrons over the whole conjugated system.   A distinct bathochromic shift is observed in compounds the substituent R^2 of which possesses distinct electron-donor properties (compounds I and $XIII$).

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The infrared spectra in the $1700-1600 \text{ cm}^{-1}$ region measured in chloroform indicate that compounds $I-XXV$, similarly as 1-phenyl-3(X-furyl)propenones[6-7], exist as equilibrium mixtures of *s-cis* and *s-trans* conformers in view of the simple bond between the C=O and CH=CH groups. This fact is interesting from the point of view of the comparison of compounds $I-XXV$ with 1-phenyl-3-(5-aryl-2-furyl)-propenones described in paper[2], in which we were unable to differentiate the *s-trans* conformer in chloroform. The strong absorption band observed in the spectra of compounds in the $1664-1646 \text{ cm}^{-1}$ region belongs to the C=O stretching vibration of the *s-cis* conformer which, similarly as in the case of 1-phenyl-3-(X-furyl)pro-penones, is represented in the equilibrium mixture in a larger amount than the *s-trans* conformer. The weak absorption peak in the $1645-1633 \text{ cm}^{-1}$ region, which appears in the form of a projection on the preceding peak, is due to the C=O

$$R^1-\underset{}{\bigcirc}-\underset{O}{\bigcirc}-\underset{\underset{O}{\parallel}}{C}-CH=CH-\bigcirc-R^2$$
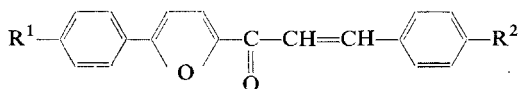
	R^1	R^2		R^1	R^2
I	NO$_2$	4-N(CH$_3$)$_2$	*XIII*	Cl	4-N(CH$_3$)$_2$
II	NO$_2$	4-OCH$_3$	*XIV*	Cl	4-OCH$_3$
III	NO$_2$	4-CH$_3$	*XV*	Cl	2-OCH$_3$
IV	NO$_2$	3-CH$_3$	*XVI*	Cl	4-CH$_4$
V	NO$_2$	4-F	*XVII*	Cl	4-F
VI	NO$_2$	2-F	*XVIII*	Cl	2-F
VII	NO$_2$	H	*XIX*	Cl	H
VIII	NO$_2$	2-Br	*XX*	Cl	3-OCH$_3$
IX	NO$_2$	4-Cl	*XXI*	Cl	2-Br
X	NO$_2$	2-Cl	*XXII*	Cl	4-Cl
XI	NO$_2$	3-NO$_2$	*XXIII*	Cl	2-Cl
XII	NO$_2$	4-NO$_2$	*XXIV*	Cl	4-NO$_2$
			XXV	Cl	2-NO$_2$

stretching band of the *s-trans* conformer. On the spectra of some compounds measured for the sake of comparison in tetrachloromethane a sign of the splitting of the v(C=O) band in the *s-cis* conformer can be observed. This proves a further conformation due to the restricted rotation around the single bond between the car-bonyl group and the furan ring. In the case of the *s-trans* conformer this splitting cannot be differentiated in consequence of the low intensity of the corresponding absorption band of v(C=O). We shall discuss the infrared spectra of these com-pounds, measured in tetrachloromethane, in another paper[8]. In Table I the frequen-cies of C=O vibrations for *s-cis* as well as for *s-trans* conformers of compounds $I-XXV$ are given. The values measured for the *s-trans* conformers should be con-

sidered as approximate in view of the low intensity of the absorption bands. On the other hand the values for *s-cis* conformers may be read with such accuracy as would suffice for their correlation with σ and σ^+ constants of substituents.

Table II gives statistical parameters of linear correlations $v(C=O)$ *vs* σ and $v(C=O)$ *vs* σ^+ for *s-cis* conformers of compounds $I-XXV$. Correlations with σ^+ for compounds $I-XII$ as well as for compounds $XIII-XXV$ are statistically more signi-

TABLE I

Ultraviolet and Infrared Data of Compounds $I-XXV$
λ_{max} in nm, $v(C=O)$ in cm^{-1}.

Com- pound	λ_{max}	$(\log \varepsilon)$	λ_{max}	$(\log \varepsilon)$	λ_{max}	$(\log \varepsilon)$	λ_{max}	$(\log \varepsilon)$	$v(C=O)$	
									s-cis	s-trans
I	472	(4·59)	358	(4·45)	260	(4·00)	204	(4·41)	1 646	1 633
II	387	(4·68)	—	—	243	(4·07)	208	(3·69)	1 657	1 640
III	372	(4·66)	—	—	236	(4·15)	216	(4·25)	1 658	1 640
IV	374	(4·62)	—	—	275	(4·14)	236	(4·47)	1 660	1 641
V	372	(4·64)	310	(4·16)	—	—	216	(4·36)	1 660	1 741
VI	372	(4·48)	312	(4·00)	236	(4·12)	207	(4·48)	1 660	1 641
VII	387	(4·62)	—	—	233	(4·04)	216	(4·07)	1 659	1 641
VIII	372	(4·57)	314	(4·10)	242	(4·12)	207	(4·52)	1 662	1 641
IX	372	(4·56)	323	(4·14)	228	(4·10)	206	(4·18)	1 662	1 641
X	372	(4·60)	312	(4·14)	238	(4·12)	218	(4·30)	1 662	1 642
XI	373	(4·53)	312	(4·12)	239	(4·16)	215	(4·27)	1 663	1 643
XII	373	(4·47)	—	—	217	(4·19)	207	(4·25)	1 664	1 643
XIII	455	(4·60)	347	(4·25)	263	(4·20)	215	(4·00)	1 647	1 635
XIV	377	(4·63)	—	—	245	(4·23)	215	(4·20)	1 655	1 643
XV	379	(4·52)	—	—	261	(4·06)	217	(4·27)	1 656	1 643
XVI	374	(4·56)	—	—	238	(4·09)	215	(4·02)	1 657	1 644
XVII	370	(4·58)	285	(4·07)	229	(4·46)	218	(4·30)	1 659	1 643
XVIII	369	(4·52)	285	(4·07)	228	(4·17)	215	(4·17)	1 659	1 642
XIX	380	(4·63)	272	(4·00)	230	(4·04)	214	(4·07)	1 658	1 644
XX	373	(4·59)	—	—	260	(4·11)	217	(4·38)	1 659	1 643
XXI	370	(4·52)	285	(4·07)	—	—	216	(4·25)	1 659	1 644
XXII	373	(4·62)	283	(4·08)	231	(4·23)	214	(4·17)	1 660	1 643
XXIII	370	(4·35)	285	(3·93)	231	(3·95)	217	(4·08)	1 660	1 643
XXIV	373	(4·49)	309	(4·32)	—	—	217	(4·28)	1 662	1 645
XXV	369	(4·50)	276	(4·25)	227	(4·27)	219	(4·28)	1 662	1 645

TABLE II

Statistical Parameters of Linear Correlations $\nu(C=O)$ *vs* σ and of $\nu(C=O)$ *vs* σ^+ (measured in chloroform) for *s-cis*-Conformers of 1-[5-(4-Nitrophenyl)-2-furyl]-3-(R^2-phenyl)propenones *I—XII* and 1-[5-(4-Chlorophenyl)-2-furyl]-3-(R^2-phenyl)propenones *XIII—XXV*

Compounds	Correlation	n^a	r^b	ϱ^c	$s\varrho^d$	q^e	sq^f	s^g
I—XII	$\nu(C=O)$ *vs* σ	11	0·951	6·57	0·71	1 659·6	0·4	0·7
I—XII	$\nu(C=O)$ *vs* σ^+	11	0·956	5·05	0·60	1 660·5	0·1	0·8
XIII—XXV	$\nu(C=O)$ *vs* σ	12	0·951	5·85	0·60	1 658·0	0·3	0·7
XIII—XXV	$\nu(C=O)$ *vs* σ^+	12	0·968	4·21	0·35	1 658·8	0·0	0·6

[a] Number of compounds used for correlation, [b] correlation coefficient, [c] gradient, [d] standard deviation ϱ, [e] section of the frequency axis, [f] standard deviation q, [g] standard deviation, σ-values of substituents were taken from paper[11] and σ^+ values from paper[12].

TABLE III

1-[5-(4-Nitrophenyl)-2-furyl]-3-(R^2-phenyl)propenones *I—XII* and 1-[5-(4-Chlorophenyl)-2-furyl]-3-(R^2-phenyl)propenones *XIII—XXV*

Com-pound	Formula (m.w.)	Calculated/found				M.p., °C (yield, %)	Solvent
		% C	% H	% N	% Hal		
I	$C_{21}H_{18}N_2O_4$ (362·4)	69·60 69·72	5·00 4·86	7·73 7·68	—	239—240 (90)	ethanol
II	$C_{20}H_{15}NO_5$ (349·3)	68·76 68·74	4·32 4·22	4·01 3·98	—	208—209 (90)	acetic acid
III	$C_{20}H_{15}NO_4$ (333·3)	72·06 72·12	4·53 4·62	4·20 4·28	—	227—228 (90)	ethanol
IV	$C_{20}H_{15}NO_4$ (333·3)	72·06 71·94	4·53 4·50	4·20 4·10	—	199—200 (65)	ethanol
V	$C_{19}H_{12}FNO_4$ (337·3)	67·65 67·45	3·58 3·48	4·15 4·10	—	198—199 (70)	dioxan
VI	$C_{19}H_{12}FNO_4$ (337·3)	67·65 67·62	3·58 3·48	4·15 4·10	—	216—218 (80)	dioxan
VII	$C_{19}H_{13}NO_4$ (319·3)	71·47 71·27	4·10 4·00	4·39 4·29	—	219—220 (90)	ethanol
VIII	$C_{19}H_{12}BrNO_4$ (398·2)	57·31 57·21	3·03 3·03	3·52 3·42	20·06 20·00	215—216 (80)	dioxan
IX	$C_{19}H_{12}ClNO_4$ (353·8)	64·51 64·40	3·42 3·25	3·96 3·90	10·02 10·22	201—202 (85)	dioxan

TABLE III

(*Continued*)

Com-pound	Formula (m.w.)	Calculated/found				M.p., °C (yield, %)	Solvent
		% C	% H	% N	% Hal		
XIX	$C_{19}H_{13}ClO_2$ (308·8)	73·91 73·94	4·24 4·30	—	11·48 11·50	155—156 76	ethanol
XX	$C_{20}H_{15}ClO_3$ (338·8)	70·91 70·78	4·46 4·50	—	10·46 10·50	113 68	50% ethanol
XXI	$C_{19}H_{12}BrClO_2$ (387·7)	58·87 58·90	3·12 3·20	—	—	167—8 78	dioxan
XXII	$C_{19}H_{12}Cl_2O_2$ (343·2)	66·49 66·40	3·52 3·50	—	20·66 20·62	212 78	dioxan
XXIII	$C_{19}H_{12}Cl_2O_2$ (343·2)	66·49 66·50	3·52 3·60	—	20·66 20·70	184 70	dioxan
XXIV	$C_{19}H_{12}ClNO_4$ (353·8)	64·51 64·48	3·42 3·40	3·96 3·90	10·02 10·12	219—221 80	dioxan
XXV	$C_{19}H_{12}ClNO_4$ (353·8)	64·51 64·50	3·42 3·46	3·96 3·98	10·02 10·12	195—197 74	ethanol
X	$C_{19}H_{12}ClNO_4$ (353·8)	64·51 64·51	3·42 3·32	3·96 3·90	10·02 9·90	205—207 (90)	dioxan
XI	$C_{19}H_{12}N_2O_6$ (364·3)	62·64 62·54	3·32 3·22	7·67 7·47	—	216—218 (80)	acetic acid
XII	$C_{19}H_{12}N_2O_6$ (364·3)	62·64 62·44	3·32 3·40	7·67 7·57	—	264—267 (90)	acetic acid
XIII	$C_{21}H_{18}ClNO_2$ (351·8)	71·69 71·70	5·51 5·60	3·98 3·72	10·07 10·00	178—179 (85)	dioxan
XIV	$C_{20}H_{15}ClO_3$ (338·8)	70·91 70·71	4·46 4·50	—	10·46 10·36	181 8	50% ethanol
XV	$C_{20}H_{15}ClO_3$ (338·8)	70·91 70·96	4·46 4·50	—	10·46 10·50	153—154 72	50% ethanol
XVI	$C_{20}H_{15}ClO_2$ (338·8)	74·42 74·48	4·68 4·62	—	10·98 10·96	211·5 75 ·	dioxan
XVII	$C_{19}H_{12}FClO_2$ (326·75)	69·84 69·80	3·70 3·68	—	—	171 76	dioxan
XVIII	$C_{19}H_{12}FClO_2$ (326·75)	69·84 69·90	3·70 3·68	—	—	154 80	dioxan

The purity was controlled by thin-layer chromatography on silica gel (Silufol).

ficant than the correlations with the σ constants; similarly as in the case of other ana-logues of chalcones[2,7] this shows a strong conjugation between the C=O group and the substituted benzene cycle. We did not include into the linear correlations the values v(C=O) for 4-dimethylamino derivatives (compounds *I* and *XIII*) which deviate significantly from the· regression straight lines. In both compounds (*I* and *XIII*) the dimethylamino group shows a stronger electron-donor effect than could be expected on the basis of the regression straight line. Such deviations from Hammett's equation are not rare in the case of strong electron-donating groups and especially of the dimethylamino group.

For the linear correlation the C=O stretching vibration frequencies of *ortho*-substituted derivatives are very suitable; we used for them σ and σ^+ constants for corresponding substituents in the position *para*[9], as also did Boykin and coworkers[7] in the case of substituted chalcones. The gradients of linear correlations ϱ for com-pounds *I — XII* and *XIII — XXV* are approximately equal, but lower in comparison with the gradient of analogous correlations for the series of chalcones[7]. This proves that the strong electron-donating effect of the arylfuran residue decreases the sensi-tivity of the carbonyl group to the effects of substituents on the benzene ring. A similar decrease of the ϱ value of the linear relationship v(C=O) *vs* σ is given in paper[10].

EXPERIMENTAL

Substituted 1-[5-(4-Nitrophenyl)-2-furyl]-3-phenylpropenones (*I— XII*)

A 20% sodium hydroxide solution (0·5 ml) was added at boiling temperature to a mixture of 0·001 mol of 5-(4-nitrophenyl)-2-acetylfuran in 50 ml of ethanol and 0·001 mol of the corresponding substituted benzaldehyde in the necessary amount of ethanol. The mixture was allowed to stand at room temperature for 24 hours, and after cooling the separated solid was filtered off, washed with dilute ethanol and crystallized from a suitable solvent (Table III).

Substituted 1-[5-(4-Chlorophenyl)-2-furyl]-3-phenylpropenones (*XIII— XXV*)

For the preparation of compounds *XIII — XXV* we used a procedure analogous to that employed for the preparation of compounds *I— XII*, with the difference that 30 ml of methanol were used for the dissolution of the starting 5-(4-chlorophenyl)-2-acetylfuran.

Methods

The ultraviolet spectra of compounds *I— XXV* were measured in the 200—480 nm region with a Specord UV VIS (Zeiss, Jena). The measurements were carried out at room temperature in a cell 1 cm thick, in pure dioxan at $3 \cdot 10^{-5}$ M concentration.

The infrared spectra (1 700—1 800 cm^{-1} region) were measured on a Zeiss UR 20 spectro-photometer using chloroform as solvent. Cells 0·1—0·5 cm strong were used. The concentration of the solution was chosen so that the absorption maximum in the 1 700—1 600 cm^{-1} region should be 75 ± 2%. The frequency scale of the spectrophotometer was calibrated using the stan-dard spectrum of polystyrene. The frequencies of the C=O stretching vibrations of *s-cis* con-

formers were read with a ± 0.5 cm^{-1} accuracy and the frequencies of the C=O stretching vibration of the *s-trans* conformers with a ± 3 cm^{-1} accuracy. The spectra of some sufficiently soluble compounds were measured for the sake of comparison under identical conditions in cells $0.5-1$ cm thick also in tetrachloromethane.

The statistical parameters of the linear correlations were calculated on an automatic digital computer Regnezentralen Gier using a standard program.

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