TRANSMISSION OF POLAR EFFECTS ACROSS THE CH=CH LINK IN STYRYLFURAN SYSTEM*

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Received September 8th, 1980

Transmission of polar substituent effect through the vinylidene grouping in 5-(4-X-styryl)-2-furaldehydes (X = H, Cl, Br, $COOCH_3$, CN and NO_2) was studied by polarographic reduction of the aldehyde group as well as by kinetics of their condensation with malononitrile. The obtained transmission coefficients π' were compared with the corresponding values for systems, containing other links between the benzene and furan nuclei. Thermodynamic parameters of the condensation with malononitrile were determined. The transmission of polar effects is discussed also from the point of view of ^{1}H-NMR spectra.

As shown previously, the furan nucleus transmits well electronic substituent effects to the reaction center[1-4]. It is known[1] that the reaction constant ϱ (1,4) for dissociation of 5-substituted 2-furancarboxylic acids is larger than that for the corresponding aromatic analogue. Also in arylfuran derivatives transmission across the aromatic and furan ring was observed[2] (transmission coefficient $\pi'(\text{Fu}) = 0{\cdot}46$). We investigated the transmission of substituent effect to the reaction center (a CHO or COOH group) in systems containing an atom or group linking together benzene and furan nuclei, such as in 5-benzoyl-[3], 5-phenylthio-[4], 5-phenylsulfonyl-[5] and 5-phenoxy--2-furan derivatives[5,6].

The aim of the present communication is to investigate the transmission of polar substituent effects through a system in which the benzene and furan nuclei are joined by a vinylidene grouping and to compare the transmission ability of the —CH=CH— group with other linking atoms or groups. We studied polarographic reduction of the aldehyde group and determined the $E_{1/2}$ values for 5-(4-X-styryl)-2-furaldehydes (Table I, *1–6*). Rate constants of condensation of these aldehydes with malononitrile (Table II) at three different temperatures were also determined.

The polarographic behaviour of compounds *1–6* (Table I) is similar to that of their analogues studied so far[5,7]. According to the results obtained, the mechanism of reduction of the aldehyde group is the same as that found for 5-aryl-2-furaldehydes[8]. However, the recently studied derivatives exhibited two cathodic waves in

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* Part CLXI in the series Furan Derivatives; Part CLX: This Journal *46*, 2724 (1981).

the alkaline region, even at very high pH values (12·2). The difference in $E_{1/2}$ values (300 mV) shows that the vinylidene grouping is preserved and is not reduced in aqueous–ethanolic Britton–Robinson buffers used as reaction medium.

TABLE I

Half-wave potentials, $-E_{1/2}$ (V), and limiting currents, i_d/c (μA mmol^{-1} l), of 5-(4-X-styryl)-2-furaldehydes at pH 12·2

N°	X	Wave I	Wave II
1	H	1·249	1·532
		2·7	2·9
2	Cl	1·222	1·525
		2·5	2·9
3	Br	1·225	1·518
		2·3	2·7
4	CH_3COO	1·201	1·491
		2·2	1·8
5	CN	1·186	1·458
		2·2	2·4
6	NO_2	1·278	1·582
		2·5	2·6

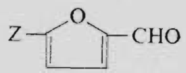
TABLE II

Rate constants, k_2 (l mol^{-1} s^{-1}), and thermodynamic parameters of condensation of compounds *1*—*6* with malononitrile in methanol at 18°, 25°C and 35°C (±0·2°C)

No	k_2 (18°)	k_2 (25°)	k_2 (35°)	$E_a{}^a$	ΔH^a	$-\Delta S^*_{25°}{}^a$
1	0·93 ± 0·02	1·43 ± 0·03	2·85 ± 0·02	50·44	47·98	218·42
2	1·01 ± 0·03	1·88 ± 0·01	4·75 ± 0·01	69·80	67·40	215·15
3	1·15 ± 0·01	1·98 ± 0·02	4·55 ± 0·03	61·84	59·38	214·41
4	—	—	—	—	—	—
5	1·86 ± 0·01	3·08 ± 0·02	11·5 ± 0·05	82·30	79·84	204·31
6	2·06 ± 0·01	3·10 ± 0·02	19·1 ± 0·04	100·40	97·94	156·91
7^b	0·912 ± 0·02	1·34 ± 0·02	2·00 ± 0·01	35·33	32·87	226·42

^{a} E_a in kJ mol^{-1}; ΔH^* in kJ mol^{-1}; ΔS^* in *J* grad^{-1} mol^{-1}; ^{b} X = CH_3.

Reaction constants ϱ were calculated from linear plots of the $E_{1/2}$ values and Hammett σ constants. The value $\varrho_I = 0{\cdot}094 \pm 0{\cdot}003$ ($q = -1{\cdot}246$, $r = 0{\cdot}997$, $s = 0{\cdot}002$) for the first cathodic wave indicates a smaller retarding effect of the CH=CH group in comparison with the hitherto studied systems[5,7]. The transmission coefficient π' was calculated from the equation $\pi' = \varrho/\varrho_0$, where ϱ_0 relates to the benzaldehyde series ($\varrho_0 = 0{\cdot}298$). The value of π' ($0{\cdot}32$) is higher than values found for systems containing an oxygen or sulfur atom as the link. We thus obtain the following order of systems with decreasing transmission effect:



Z	aryl >	aryl-CH=CH >	aryl-S ≧	aryl-O >	aryl-SO$_2$
ϱ	0·179	0·094	0·086	0·084	0·065
π'	0·60	0·32	0·29	0·281	0·21

These results agree well with those obtained with systems containing similar linking groups[9]. For the nitro derivatives we used the σ value of an NHOH group ($-0{\cdot}34$) (ref.[10]) because the NO$_2$ group is reduced preferentially with 4 electrons to give the aminohydroxy derivative before the reduction of the aldehyde group takes place.

The reaction constant ϱ_{II} for the second wave was higher ($\varrho_{II} = 0{\cdot}118 \pm 0{\cdot}010$, $q = -1{\cdot}542 \pm 0{\cdot}005$; $r = 0{\cdot}985$, $s = 0{\cdot}008$) and was not used for calculation of the transmission coefficient π' because of possible effects of the radical system on the reaction course.

It is known that 5-substituted 2-furaldehydes are condensed with malononitrile in alkaline media. We used also this reaction for study of substituent effect, transmitted through the vinylidene group in substituted 5-styryl-2-furaldehydes. The reaction was followed spectrophotometrically at the absorption maximum of the arising condensation product, using an excess of the methylene component (pseudomonomolecular reaction). At the end of the reaction the UV spectrum of the mixture was compared with that of the corresponding substituted 2-cyano-3-(5-styryl-2-furyl)-acrylonitrile. In all cases the spectra were identical with the course of the UV curves in the kinetic measurements. The rate constants k_{obs} were calculated according to a first order reaction equation; division of k_{obs} values by concentration of the methylene component gave the k_2 values.

The observed reaction rate depends on the magnitude of electron deficiency at the aldehyde carbon atom, affected by substituents in *para* position of the styrene moiety. The value of ϱ, calculated from the linear plot of log k_2 against σ, was used in calculation of the transmission coefficient $\pi' = \varrho/\varrho_0$. We determined the value of ϱ_0 ($0{\cdot}752 \pm 0{\cdot}027$) for a series of substituted benzaldehydes (values of k_2 are given in Table III). The thus calculated value of π' is higher than that obtained from the polarographic reduction; this can be ascribed to a different solvation of the studied system in a different solvent system, which is in accord with the previous results[11].

Transmission of the substituent effect across various links (—O—, —S—, —CH==CH—) was studied also by following the ^{1}H-NMR chemical shifts of aldehyde protons (Table IV). The substituents had only a small effect on the aldehyde and olefinic proton shifts. The greatest effect was found for the furan proton H_4: in this position both the link as well as the substituent, attached to the aromatic nucleus affect the electron density and the proton signal shift. We found a linear correlation between the H_4 chemical shifts and the Hammett σ constants. The ϱ constants (Table IV) for 5-phenylthio- and 5-phenoxy-2-furaldehydes are higher as compared with those for 5-styryl derivatives. This fact is probably connected with an interaction of the sulfur and oxygen lone *p*-electrons with the H_4 proton of the furan ring.

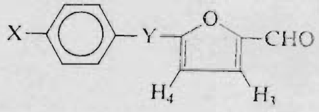
TABLE III

Rate constants, k_2 (l mol^{-1} s^{-1}), of condensation of 4-X-benzaldehydes with malononitrile in methanol at 25° ± 0·2°C

X	k_2	X	k_2
H	7·01 ± 0·02	CH_3CONH	6·90 ± 0·03
Br	10·60 ± 0·025	CH_3O	6·51 ± 0·025
I	13·76 ± 0·014	$(CH_3)_2N$	1·95 ± 0·015
NO_2	28·80 ± 0·08		

TABLE IV

Reaction constants (ϱ) and changes in chemical shifts ($\Delta\delta_{ppm}$) of the H_4 protons for aldehydes of the formula



Y	$\Delta\delta_{ppm}$ [a]	ϱ	r	ref.
S	0·61	0·554	0·99	14
O	0·48	0·438	0·99	12
CH=CH	0·20	0·223	0·90	13

[a] Difference between chemical shifts for derivatives with substituents of the highest electron donating and accepting effect.

EXPERIMENTAL

The ^{1}H-NMR spectra were measured at 25°C on a Tesla BS 487 C (80 MHz) spectrometer in deuteriochloroform with tetramethylsilane as internal standard. The assignment of signals was performed by the INDOR technique.

Preparation of the employed 5-(4-X-styryl)-2-furaldehydes is described elsewhere[13]. Kinetic measurements were carried out according to reference[12] and the polarographic study was performed as described by us previously[5].

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Translated by M. Tichý.