

Furan derivatives. CVII.

Stereochemistry of substituted β -(2-furyl)vinyl cyanides

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Condensation of substituted 2-furaldehydes with phenylacetonitrile or 4-nitrophenylacetonitrile afforded the respective β -(5-X-2-furyl)- α -(4-Y-phenyl)-vinyl cyanides. $^1\text{H-n.m.r.}$ spectroscopy evidenced these products to be *Z* isomers.

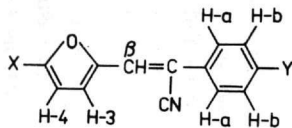
Методом $^1\text{H-ЯМР}$ было найдено, что в результате конденсации замещенных 2-фуральдегидов с фенилацетонитрилом или 4-нитрофенилацетонитрилом образуются соответствующие β -(5-X-2-фурил)- α -(4-Y-фенил)винилцианиды как *Z* изомеры.

The corresponding derivatives of vinyl cyanide, formed on condensation of aromatic aldehydes with derivatives of phenylacetonitrile can exist, as trisubstituted derivatives of ethylene, as *E* or *Z* isomers. Some papers investigating the stereospecific course of this type of condensation [1, 2] concluded that probably only the *Z* isomer was formed. Pfeiffer and co-workers [2] adduced on the basis of reactivity of the nitrile group in addition reactions that condensation of benzaldehyde with phenylacetonitrile furnished a product, which is a *Z* isomer. The corresponding *E* isomer was obtained from the *E* isomer of α -phenylcinnamic acid.

Our preceding paper [3] dealt with the synthesis of β -(5-X-2-furyl)- α -(4-Y-phenyl)vinyl cyanides from substituted 2-furaldehydes and derivatives of phenylacetonitrile; their i.r. and u.v. spectra let us assume these compounds to be *Z* isomers.

This paper was aimed to determine the spatial arrangement of substituents on the double bond of β -(5-X-2-furyl)- α -phenylvinyl cyanides (I—V) and β -(5-X-2-furyl)- α -(4-nitrophenyl)vinyl cyanides (VI—X) by means of $^1\text{H-n.m.r.}$ spectroscopy. The spectra showed (Table 1) that condensation products were formed by one isomer only. The unequivocal assignment of configuration on the

Table 1

¹H-n.m.r. data^a of β-(5-X-2-furyl)-α-phenylvinyl cyanides and β-(5-X-2-furyl)-α-(4-nitrophenyl)vinyl cyanides

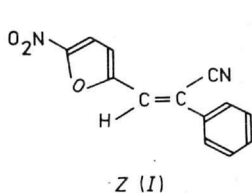
X	Compound	Y	Isomer	H-β	H-3	H-4	J _{3,4}	H-a	H-b	J _{a,b}
	<i>I</i>									
NO ₂		H	<i>Z</i>	7.99 s	7.38 d	7.70 d	4.0	(7.38—7.93) m ^c		—
	<i>II</i>									
NO ₂		H	<i>E</i>	7.74 s	6.85 d	7.73 d	4.0	7.67 b s ^c		—
	<i>III</i>									
I		H	<i>Z</i>	7.80 s	7.09 d	6.96 d	3.5	(7.32—7.78) m ^c		—
	<i>IV</i>									
Br		H	<i>Z</i>	7.84 s	7.14 d	6.87 d	3.6	(7.33—7.80) m ^c		—
	<i>V^b</i>									
H		H	<i>Z</i>	7.88 s	7.17 dd	6.75 dd	3.6	(7.33—7.83) m ^c		—
	<i>VI</i>									
NO ₂		NO ₂	<i>Z</i>	8.31 s	7.86 d	8.72 d	4.0	8.06 d	8.35 d	9.0
	<i>VII</i>									
I		NO ₂	<i>Z</i>	8.26 s	7.16 d	7.03 d	3.7	7.97 d	8.30 d	9.0

Table 1 (Continued)

X	Compound	Y	Isomer	H- β	H-3	H-4	$J_{3,4}$	H-a	H-b	$J_{a,b}$
	VIII									
Br		NO ₂	Z	8.09 s	7.22 d	6.93 d	3.6	8.00 d	8.32 d	9.0
	IX ^d									
H		NO ₂	Z	8.13 s	7.28 dd	6.81 dd	3.6	7.96 d	8.30 d	9.0
	X ^e									
H		NO ₂	E	7.58 s	6.85 dd	6.58 dd	3.5	7.77 d	8.29 d	9.0

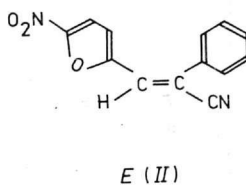
a) Chemical shifts δ (p.p.m.), J (Hz); b) H-5 8.01 (dd), $J_{4,5} = 1.7$, $J_{3,5} < 1$; c) H aromatic; d) H-5 8.11 (dd), $J_{4,5} = 1.6$, $J_{3,5} < 1$; e) H-5 7.68 (dd), $J_{4,5} = 1.7$, $J_{3,5} < 1$.

basis of calculated values of chemical shift of the olefinic proton H- β using additive increments was unreal, since values for heteroaromatic substituents are unknown and also no planar molecule is involved in all cases. To determine configuration of substances under study, β -(5-nitro-2-furyl)- α -phenylvinyl cyanide (*II*) was prepared according to [3]. The u.v. spectra of *I* and *II* indicate the respective *Z* and *E* isomers



$$\lambda_{\max} = 380 \text{ nm}$$

$$\log \epsilon = 4.59$$



$$\lambda_{\max} = 365 \text{ nm}$$

$$\log \epsilon = 4.28$$

As follows from u.v. spectral characteristics of these substances, *I* lies in a plane. On the other hand, due to the bulky phenyl and furyl groups in *cis* position in compound *II*, a twisting out from the plane of double bond took place, this being manifested by a shift of the main absorption band of compound *II* towards lower wavelength. The assignment of substances *I* and *II* as *Z* and *E* isomers was substantiated by ¹H-n.m.r. spectroscopy on the basis of differences in chemical shifts of proton signals H- β , H-3 and aromatic ones (Table 1). The signal of the olefinic proton H- β of *Z* isomer is by 0.25 p.p.m. downfield shifted when compared with that of *E* isomer. Proton H- β of the *Z* isomer is shielded by the benzene ring in α position in the double bond plane. Due to steric hindrance a torsion of the plane of the system takes place, proton H-3 of the furan ring comes above the benzene ring; consequently, a shielding becomes effective and signal of the H-3 proton of *E* isomer is by 0.53 p.p.m. upfield shifted. Differentiation between *E* and *Z* isomers is evident through a characteristic pattern of aromatic protons: aromatic protons of *E* isomer, where the benzene ring is out of the double bond plane, reveal a broad singlet, whereas those of *Z* isomer a diagnostic multiplet. Chemical shift of H-4 proton of the particular compounds is influenced only by the substituent at the furan ring. Comparison of signals of aromatic protons and chemical shifts of H- β and H-3 of compounds *III*, *IV*, and *V* with those of compounds *I* and *II* proves that the former are *Z* isomers.

To assign structure to compounds *VI*–*IX*, substance *IX* was isomerized. The mixture of isomers thus obtained (*IX* and *X*) was subjected to ¹H-n.m.r. measurement. Similarly as with substances *I* and *II*, chemical shifts of protons H- β and H-3 were crucial. Chemical shifts of aromatic protons H-a of *Z* isomers are of

almost the same value. The position of H- α protons of *E* isomer (substance *X*) is by 0.19 p.p.m. upfield shifted as a consequence of the anisotropic effect of double bond. Comparison of chemical shifts of these protons of substances *IX* and *X* and *VI*—*VIII* showed substances *VI*—*IX* to be *Z* isomers.

Values of chemical shift of the H-3 proton allow to propose conformation of the furylethylene system. The observed signal of H-3 proton of the furan ring of *E* isomer was upfield shifted when compared with that of *Z* isomer; this indicates that the former are *s-cis* conformers. The same results were obtained from other stereochemical investigations of further furylethylene derivatives [4, 5].

Experimental

β -(5-*X*-2-Furyl)- α -(4-*Y*-phenyl)vinyl cyanides were synthesized according to [3, 6—8]. Substance *II* was prepared according to Pfeiffer's method [2] reported in [3].

¹H-n.m.r. spectra were recorded with a Tesla BS 487 C spectrometer operating at 80 MHz in hexadeuteriodimethylsulfoxide with tetramethylsilane as an internal reference substance; Indor technique was used for assignment of signals.

Isomerization of β -(2-furyl)- α -(4-nitrophenyl)vinyl cyanide (IX)

A solution of *IX* (0.5 g) in ethanol (250 ml) was irradiated by a mid-pressure mercury UVS/375 W lamp for 12 h in a photochemical apparatus passed with bulb nitrogen. The mixture of isomers (*IX*, *X*), obtained after removal of the solvent under diminished pressure, was identified by ¹H-n.m.r. spectroscopy.

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