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SYNTHESIS AND THREE-DIMENSIONAL STRUCTURES OF 2-(2-FURYL)-ACRYLONITRILES

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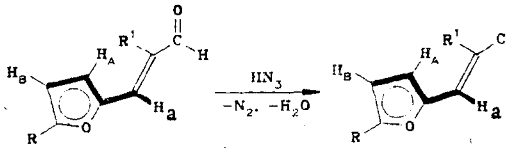
543.422.254.6

Conditions for carrying out the Schmidt reaction that make it possible to obtain β-(2-furyl)acrylonitriles in high yields were found. It was shown by PMR and IR spectroscopy that the furylacrylonitriles obtained have an E-s-cis configuration.

In a previous communication [1] we described the conditions for the synthesis of 2-cyanofurans from the corresponding 2-formylfurans via the Schmidt reaction. These conditions were found to be unsuitable for the synthesis of furylacrylonitriles IIa-h from furylacroleins Ia-h because of pronounced resinification of the reaction mixtures. One can, however, avoid resinification if dioxonium perchlorate is introduced into the reaction mixture instead of $HClO_4$.



Ia-h IIa-h

$R = H, CH_3, C_6H_5, 2,4,6-C_6H_2Cl_3, NO_2; R^1 = H, CH_3$

According to PMR data, starting furylacroleins I have an E configuration [2, 3]. We were interested in the peculiarities of the three-dimensional structures of the resulting nitriles IIa-h (Table 1).

The H_aR^1 spin-spin coupling constants (SSCC), which are 15.0-17.0 Hz (when $R^1 = H$) and 1.4-2.0 Hz (when $R^1 = CH_3$) (Table 2), constitute evidence for a trans orientation of these groups relative to the exocyclic double bond in IIa-h. Their IR spectra contain an absorp-

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TABLE 1. Characteristics of β-(2-Furyl)acrylonitriles IIa-h

Compound	bp (mm) [mp], °C	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	N		C	H	N	
IIa	[34]	71,2	4,4	11,8	C_7H_5NO	70,6	4,2	11,8	75
IIb[a]	95 (5)	72,85	5,5	10,7	C_8H_7NO	72,2	5,3	10,5	84
IIc[b]	94 (5)	72,8	5,6	10,7	C_8H_7NO	72,2	5,3	10,5	74
IId[c]	112 (5)	73.9	6,4	9,6	C_9H_9NO	73,5	6,1	9,5	78
IIe	[71]	80,6	4,8	7,7	$C_{13}H_9NO$	80,0	6,1	7,7	86
IIf	[138]	81,0	5,4	6,7	$C_{14}H_{11}NO$	80,4	5,3	6,7	85
IIg	[180]	51,7	1,9	4,7	$C_{13}H_6ClNO$	52,0	2,0	4,6	88
IIh	[112]	51,2	2,4	16,5	$C_7H_4N_2O_3$	51,2	2,4	16,6	95

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[a] Data: d_4^{20} 1.1898 and n_D^{20} 1.6036. [b] Data: d_{20}^4 1.1734 and n_D^{20} 1.5665. [c] Data: d_{20}^4 1.1611 and n_D^{20} 1.5710.

TABLE 2. Spectral Characteristics of the β-(2-Furyl)acrylonitriles

Compound	R*	UV spectrum (ethanol), λ_{max}, nm (log ε)	IR spectrum, cm^{-1}		PMR spectrum, ppm					SSCC, Hz		
			CN	C=C	H_A	H_B	R	CH_a	R^1	$J_{H_AH_B}$	$J_{H_aR^1}$	others
IIa	H	300 (4,32)	2220	1620, 968	6,53	6,38	7,40	7,01	5,60	3,6	17,0	$J_{H_BR}=1,8$ $J_{H_BH_a}=1,0$
IIb	H	303 (4,43)	2220	1620, 971	6,70	6,43	7,45	6,47	2,01	3,6	2,0	$J_{H_BR}=1,9$ $J_{H_BH_a}=1,0$
IIc	CH_3	312 (4,40)	2210	1625, 969	6,40	6,00	2,28	6,90	5,45	3,6	17,0	$J_{H_BH_a}=1,0$
IId	CH_3	305 (4,48)	2200	1620, 968	6,35	6,00	2,27	6,61	2,01	3,6	1,8	$J_{H_BH_a}=1,0$
IIe	C_6H_5	237 (4,50)	2200	1620, 970	7,16	7,55	6,58, 7,28, 7,61	6,98	5,68	4,0	16,5	$J_{H_BH_a}=0,9$
IIf	C_6H_5	230 (4,46), 351 (4,80)	2200	1610, 967	6,81	7,36	6,96, 7,33, 7,71	7,33	2,28	4,0	1,4	$J_{H_BH_a}=1,0$
IIg	$C_6H_2Cl_3$-2,4,6	209 (4,31), 318 (4,41)	2220	1620	6,68	6,62	7,30	7,06	5,72	2,0	17,0	$J_{H_BH_a}=1,0$
IIh	NO_2	344 (4,34)	2227	1620, 970	6,72	7,25	—	7,07	6,02	4,0	16,0	$J_{H_BH_a}=0,9$

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*For IIa, c, e, g, h, R^1 = H; R^1 = CH_3 for IIb, d, f.

tion band of CH deformation vibrations of the trans form of the exocyclic double bond (967-970 cm^{-1}).

A constant of ultra long-range spin-spin coupling between the H_B and H_a protons ($J_{H_aH_B} \approx$ 1.0 Hz) is observed in the PMR spectra for the entire series of furylacrylonitriles II. The intensity of this coupling constitutes evidence [4, 5] for a W-shaped orientation of the bonds between the H_B and H_a atoms. An s-cis configuration of the furan ring and the exocyclic double bond corresponds to this coupling [6, 7].

Of the other properties of the furylacrylonitrile system let us note the significant effect of substituents on the positions of the chemical shifts in the PMR spectra. Methyl groups (substituent R^1) in the side chain of II have a large shielding effect on the H_a proton. Donors in the 5 position of the furan ring shield the H_B and R^1 = H protons to the greatest degree. A phenyl substituent in the 5 position of the furan ring has a stronger deshielding effect on the furan ring than a nitro group (Table 1, IIe, h). The 2,4,6-trichlorophenyl ring shields the furylacrylic system to a considerably lesser extent (Table 1, IIe, g) than the phenyl ring, apparently because of "twisting away" of the trichlorophenyl ring from the plane of the furan ring. This is also confirmed by the hypsochromic shift of the long-wave absorption band in the electronic spectrum of IIg as compared with the absorption band of phenyl derivatives IIe, f. Other characteristics that confirm the structure of II are presented in Tables 1 and 2.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in CCl_4 were recorded with a Tesla BS-467 spectrometer (60 MHz) at 25°C with hexamethyldisiloxane (HMDS) as the internal standard.

The IR spectra of thin films (IIb-d) and mineral oil suspensions were recorded with a UR-20 spectrometer. The electronic spectra of solutions in ethanol were recorded with a Specord UV-vis spectrophotometer. Benzene solutions of hydrazoic acid were prepared by the method in [8].

2-(2-Furyl)acrylonitriles IIa-h. A 6.7 g (0.03 mole) sample of anhydrous magnesium perchlorate was added to 0.1 mole of the corresponding furylacrolein and 0.11 mole of a benzene solution of hydrazoic acid, after which 0.01 mole of dioxonium perchlorate [5 ml of 1,4-dioxane and 0.01 mole (1.4 ml) of 72% $HClO_4$ at 35°C (ice bath)] was added dropwise with stirring. The rate of dropwise addition was monitored with respect to the stream of evolved nitrogen, which should be rapid but not too vigorous. When nitrogen evolution ceased (after 1-1.5 h), the mixture was treated with water, and the benzene layer was separated, washed with water, and dried with Na_2SO_4. The benzene was removed by distillation at reduced pressure, and the residue was distilled in vacuo. Compounds IIe-h were recrystallized from ethanol.

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CONFORMATIONS OF ISOMERIC 2,3,4-TRISUBSTITUTED TETRAHYDROTHIOPHENES

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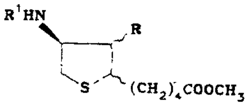
541.621.2

The conformations of a number of isomeric 2,3,4-trisubstituted tetrahydrothiophenes were determined by means of angular and temperature dependences of the vicinal proton-proton spin-spin coupling constants (SSCC).

It has previously been shown that differences in the ^{13}C chemical shifts (CS) of isomeric 2,3,4-trisubstituted tetrahydrothiophenes can be used to determine the structures of the individual isomers and to analyze a mixture of isomers [1]. In the present research we studied the conformations of isomeric 2,3,4-trisubstituted tetrahydrothiophenes I-IV.



I R=OH, $R^1=COC_6H_5$; II R=OH, $R^1=CONH_2$; III R=OH, $R^1=H\cdot HCl$; IV R=$NHCONH_2$, $R^1=CONH_2$; **a** 4-*r*, 3-*t*, 2-*t*; b 4-*r*, 3-*t*, 2-*c*; c 4-*r*, 3-*c*, 2-*c*; d 4-*r*, 3-*c*, 2-*t*

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*Deceased.

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