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METHOD FOR THE SYNTHESIS OF 2-(2-FURYL)ACRYLONITRILES

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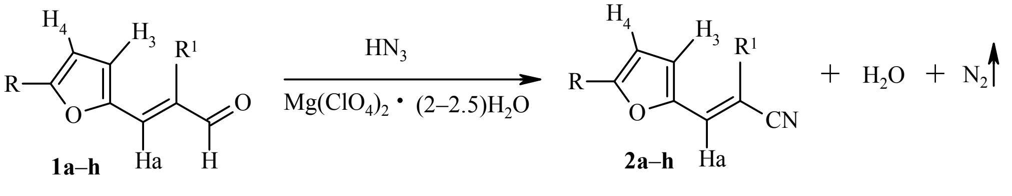
A new method was developed for the production of 2-(2-furyl)acrylonitriles on the basis of the Schmidt reaction.

Keywords: hydrazoic acid, magnesium perchlorate, 1,4-dioxanium perchlorate, furancarbaldehyde, 2-(2-furyl)acrylonitrile, perchloric acid.

The method that we developed for the single-stage synthesis of 5-substituted 2-cyanofurans from furfurals by the Schmidt reaction, which requires a catalytic system containing 72% perchloric acid and anhydrous magnesium perchlorate [1, 2], proved unsuitable for the synthesis of furylacrylonitriles from furylacroleins **1a-h** on account of resinification of the reaction mixture.

During study of the prospects of using perchloric acid in organic synthesis [3] it was shown that it was capable of forming with 1,4-dioxane the stable complex 1,4-dioxanium perchlorate, which forms colorless hygroscopic crystals with the composition 1,4-dioxane·$HClO_4$, melting at 80°C and having high solubility in most solvents. It was mentioned in the review [4] that the 1,4-dioxanium cation has lower electrophilicity than the hydrated proton of perchloric acid. In view of this the catalytic system containing 1,4-dioxanium perchlorate and anhydrous magnesium perchlorate was used as catalyst in the reaction of furylacroleins with hydrazoic acid. This made it possible to obtain the required products **2a-h** with yields of 75-95% [5, 6].

It was found, however, that the single-stage method that we developed for the production of 2-(2-furyl)acrylonitriles, which requires the use of benzene solutions of hydrazoic acid, anhydrous magnesium perchlorate, and 1,4-dioxanium perchlorate [5, 6], can be simplified significantly by not using the difficultly obtainable anhydrous magnesium perchlorate [7] and the 1,4-dioxanium perchlorate that requires previous preparation. The yields of the required products **2a-h** are increased by 7-10%, and the controllability of the reaction is improved (securing uniform release of gaseous nitrogen). Benzene is replaced by chloroform indifferent to hydrazoic acid, and the easily obtainable industrial product anhydrone (hydrated magnesium perchlorate $Mg(ClO_4)_2 \cdot (2\text{-}2.5)H_2O$), which has not only strong dehydrating capability but also the typical characteristics of "soft" Lewis acids [3, 4, 7], is used as catalyst.



1a–h **2a–h**

a R, R^1 = H, H; **b** H, CH_3; **c** CH_3, H; **d** CH_3, CH_3; **e** C_6H_5, H; **f** C_6H_5, CH_3; **g** 2,4,6-$Cl_3C_6H_2$, H; **h** NO_2, H

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TABLE 1. Spectral Characteristics of the Furylacrylonitriles **2a-h**

Com-pound	UV spectrum, λ_{max}, nm (log ε)	IR spectrum, cm^{-1}		^{1}H NMR spectrum							
				δ, ppm					SSCC, Hz		other SSCC, Hz
		ν_{CN}	$\nu_{C=C}$	H-3	H-4	H_R	H_a	$H_{R'}$	J_{34}	$J_{aR'}$	
2a	300 (4.32)	2220	1620, 968	6.53 (d)	6.38 (q)	7.40 (d)	7.01 (d)	5.60 (d)	3.6	17.0	J_{H4R} = 1.8 J_{H4Ha} = 1.0
2b	303 (4.43)	2220	1620, 971	6.70 (d)	6.43 (dd)	7.45 (d)	6.47 (d)	2.01 (s)	3.6	2.0	J_{H4R} = 1.9 J_{H4Ha} = 1.0
2c	312 (4.40)	2210	1625, 969	6.40 (d)	6.00 (dd)	2.28 (d)	6.90 (d)	5.45 (d)	3.6	17.0	J_{H4Ha} = 1.0
2d	305 (4.48)	2200	1620, 968	6.35 (d)	6.00 (dd)	2.27 (s)	6.61 (dd)	2.01 (s)	3.6	1.8	J_{H4Ha} = 1.0
2e	237 (4.50) 353 (4.74)	2220	1620, 970	7.16 (d)	7.55 (d)	6.58-7.61 (m)	6.98 (d)	5.68 (d)	4.0	16.5	J_{H4Ha} = 0.9
2f	230 (4.46) 351 (4.80)	2200	1610, 967	6.81 (d)	7.36 (d)	6.96-7.71 (m)	7.33 (d)	2.28 (s)	4.0	1.4	J_{H4Ha} = 1.0
2g	209 (4.31) 318 (4.41)	2220	1620, 969	6.68 (d)	6.62 (d)	7.30 (s)	7.06 (s)	5.72 (d)	2.0	17.0	J_{H4Ha} = 1.0
2h	344 (4.34)	2227	1620, 970	6.72 (d)	7.25 (d)	—	7.07 (d)	6.02 (d)	4.0	16.0	J_{H4Ha} = 0.9

TABLE 2. Characteristics of the Furylacrylonitriles **2a-h**

Compound	Empirical formula	Found, % / Calculated, % C	H	N	bp, °C (mm Hg), mp, °C	d_4^{20}	n_D^{20}	Yield, %
2a	C_7H_5NO	71.29 70.58	4.14 4.20	11.73 11.76	34	—	—	84
2b	C_8H_7NO	71.15 72.18	5.48 5.26	10.70 10.52	95 (5)	1.1898	1.6036	92
2c	C_8H_7NO	72.16 72.18	5.64 5.26	10.73 10.52	94 (5)	1.1732	1.5665	92
2d	C_9H_9NO	73.98 73.46	6.36 6.12	9.60 9.52	112 (5)	1.1611	1.5710	82
2e	$C_{13}H_9NO$	80.36 80.00	4.80 4.61	7.71 7.71	71	—	—	95
2f	$C_{14}H_{11}NO$	81.00 80.38	5.38 5.26	6.71 6.69	138	—	—	92
2g	$C_{13}H_6Cl_3NO$	51.69 52.00	1.90 2.00	4.67 4.66	180	—	—	93
2h	$C_7H_4N_2O_3$	51.19 51.21	2.40 2.43	16.54 16.56	112	—	—	95

The spectral and physicochemical characteristics of compounds **2a-h** are given in Tables 1 and 2.

EXPERIMENTAL

The ^1H NMR spectra were recorded on a Tesla BS-467 spectrometer (60 MHz) in CCl_4 at 25°C with TMS as internal standard. The IR spectra were recorded on a UR-20 spectrophotometer in thin films (compounds **2b-c**) and in vaseline oil (compounds **2a**,**d-h**). The electronic spectra were recorded in ethanol on a Specord UV-Vis instrument. The solutions of hydrazoic acid in chloroform were prepared by the method in [8]. The anhydrone of pure grade was produced at the Altaikhimprom plant.

(*E*)-2-(2-Furyl)-1-ethenyl Cyanide (2a), (*E*)- 2-(2-Furyl)-1-methyl-1-ethenyl Cyanide (2b), (*E*)-2-(5-Methylfur-2-yl)-1-ethenyl Cyanide (2c), (*E*)-2-(1-Methylfur-2-yl)-1-ethenyl Cyanide (2d), (*E*)-2-(5-Phenylfur-2-yl)-1-ethenyl Cyanide (2e), (*E*)-1-Methyl-2-(5-phenylfur-2-yl)-1-ethenyl Cyanide (2f), (*E*)-2-[5-(2,4,6-Trichlorophenyl)fur-2-yl]-1-ethenyl Cyanide (2g), and (*E*)-2-(5-Nitrofur-2-yl)-1-ethenyl Cyanide (2h) (General Procedure). In a three-necked flask fitted with a magnetic stirrer and a reflux condenser we placed the initial furylacrolein (0.1 mol), a solution of hydrazoic acid in chloroform (0.11 mol), and anhydrone (25.0 g, 0.1 mol). Gaseous nitrogen began to be released after 5-10 min. The reaction mixture was kept at 30°C for 40 min and then at 45-50°C for 30 min, after which the solution was boiled for 1 h with stirring. The reaction mass was cooled to room temperature, water was added, and the organic layer was separated. It was washed twice with water, dried with anhydrous sodium sulfate, and evaporated at reduced pressure. The residue was distilled under vacuum, and compounds **2e-h** were recrystallized from ethanol.

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