

5-TRICYANOVINYL-2-FURYLATION OF AROMATIC DERIVATIVES

Dušan BERKEŠ and Jaroslav KOVÁČ

*Department of Organic Chemistry, Faculty of Chemical Technology,
Slovak Institute of Technology, 812 37 Bratislava*

Received June 24th, 1985

A new method for heteroarylation of aromatic derivatives has been developed. The highly reactive 2-bromo-5-tricyanovinylfuran acts in the presence of AlCl_3 under conditions of Friedel-Crafts reaction as an electrophilic furylation reagent to give 5-aryl-2-tricyanovinylfurans with selected benzene and naphthalene derivatives.

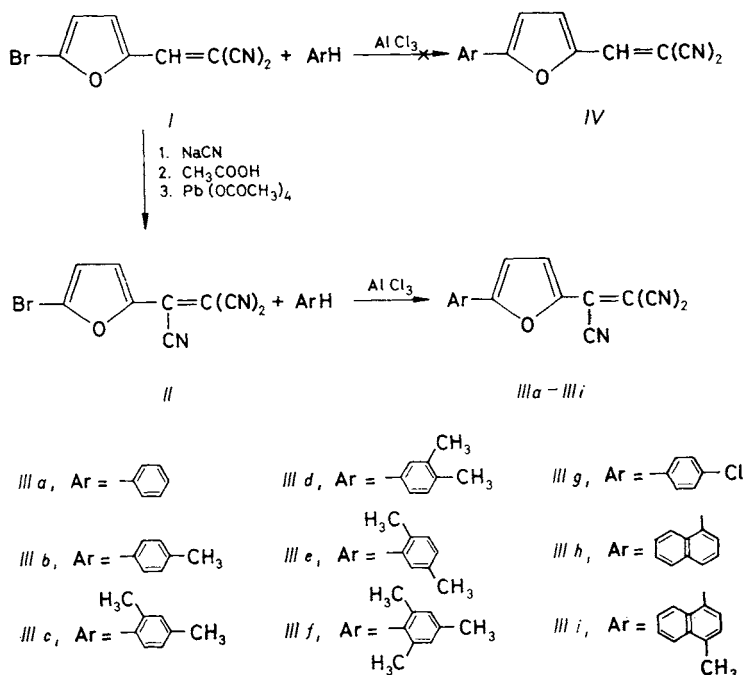
Heteroarylations of aromatic derivatives under conditions of the Friedel-Crafts reaction were carried out with a series of halogenated six-membered nitrogen-containing heterocycles¹⁻³, and recently, they have been utilized for thienylations with chloro derivatives of thiophene proceeding *via* protonization of the thiophene ring^{4,5}. The reactivity of activated halogen derivatives of furan in the presence of strong Lewis acids was investigated with 2-bromo-5-tricyanovinylfuran (*II*) in reactions with selected aromatic hydrocarbons in the presence of AlCl_3 . The starting derivative *II* was synthesized from the available 5-bromofurfurylidene malonodinitrile (*I*) by addition of hydrogen cyanide and dehydrogenation of the tricyanoethyl derivative with lead (*IV*) acetate⁶ in 65% yield in one-pot procedure. An enhancement of the strong $-M$ effect⁷ of tricyanovinyl group [$\sigma_p(-\text{C}(\text{CN})=\text{C}(\text{CN})_2) = 1.70$] by the formation of a complex with AlCl_3 made it possible to prepare 5-aryl-2-tricyanovinylfurans *IIIa-IIIi* (Scheme 1) in good yields; the less activated bromofuran derivative *I* [$\sigma_p(-\text{CH}=\text{C}(\text{CN})_2) = 1.20$] does not produce the arylation product *IV* under the same conditions. The influence of the amount of AlCl_3 on the reaction course was investigated in the reaction with *para*-xylene (reaction time 30 min at 100°C) by determining the amount of the unreacted *II*.

<i>II</i> to AlCl_3 ratio	1 : 1.5	1 : 2.5	1 : 3.5
% of unreacted <i>II</i>	42	6	0

The consumption of equivalent AlCl_3 amounts is due, similarly as with Friedel-Crafts acylations, to a higher stability of the AlCl_3 complex with the product than with the starting material.

The reaction course depends on the reactivity of the aromatic derivative and is accompanied by noticeable changes in colour varying from red of the complex

of reagent *II* with AlCl_3 to blue and green of the complex of product with AlCl_3 . Whereas the reactive naphthalenes react at room temperature in dichloroethane, the methylbenzenes and benzene require $80-100^\circ\text{C}$ in the excess of the aromatic; the little reactive chlorobenzene afforded a low yield even at an extended 5 h-reflux in chlorobenzene itself.



SCHEME 1

Structure of the prepared derivatives was deduced from elemental analyses data, IR and UV (Table I) and ^1H NMR spectra (Table II). The obtained data evidenced the specific furylation to the free *para*-position, or to the site with the greatest electron density, this being in line with the electrophilic character of the attacking particle. This reaction constitutes the first example for an electrophilic furylation of aromatic derivatives under conditions of Friedel-Crafts reaction.

EXPERIMENTAL

The melting points were measured with a Kofler micro hot-stage, the IR spectra of compounds in KBr were run on a Specord IR-71, the UV spectra of methanolic or acetone solutions on a Specord UV-VIS (Zeiss, Jena) spectrophotometers, the ^1H NMR spectra of hexadeuterioacetone solutions were recorded with a Jeol FX-100 instrument operating at 100 MHz, the

internal reference being tetramethylsilane. 5-Bromofurfurylidemalononitrile (*I*) was obtained by condensation of 5-bromofuraldehyde with malonodinitrile according to⁸ in 89% yield.

2-Bromo-5-tricyanovinylfuran (*II*)

Sodium cyanide (1.0 g, 20.4 mmol) dissolved in water (2 ml) was added to a stirred solution of *I* (4.46 g, 20 mmol) in dimethylformamide (25 ml) acidified with hydrochloric acid at 0–5°C; finally acetic acid (50 ml) and lead(IV) acetate (9.0 g, 20.3 mmol) in small portions were added during 5 min. The mixture was stirred for 10 min, poured into ice-cold water (400 ml), the precipitated product was filtered off, dried and crystallized from toluene–heptane 1 : 1. Yield 3.2 g (65%), m.p. 160–162°C. For C₉H₂BrN₃O (248.0) calculated: 43.60% C, 0.81% H, 32.3% Br, 16.94% N; found: 43.71% C, 0.83% H, 32.1% Br, 16.94% N. IR spectrum (ν , cm⁻¹): 2 210 (C≡N), 1 563 (C=C). UV spectrum (λ_{\max} , nm; log ϵ , m² mol⁻¹): 400; 3.2. ¹H NMR spectrum (δ , ppm): 7.16 (1 H, d, $J_{3,4}$ = 3.91 Hz, H₃), 7.76 (1 H, d, $J_{3,4}$ = 3.91 Hz, H₄).

TABLE I

Some physicochemical properties of 5-aryl-2-tricyanovinylfurans *IIIa–IIIi*

Compound	Formula (<i>M_r</i>)	M.p., °C (Yield, %)	Calculated/found			$\tilde{\nu}(\text{C}\equiv\text{N})$ cm ⁻¹	λ_{\max} , nm (log ϵ)
			% C	% H	% N		
<i>IIIa</i>	C ₁₅ H ₇ N ₃ O (245.2)	195–197 (55.6)	73.46	2.88	17.13	2 220	467 (3.23)
			73.31	2.97	17.05		
<i>IIIb</i>	C ₁₆ H ₉ N ₃ O (259.3)	193–195 (69.5)	74.12	3.50	16.21	2 216	479 (3.50)
			74.00	3.70	16.05		
<i>IIIc</i>	C ₁₇ H ₁₁ N ₃ O (273.3)	176–178 (80.5)	74.71	4.06	15.38	2 209	475, 417 (3.18; 3.15)
			74.91	4.08	15.28		
<i>III d</i>	C ₁₇ H ₁₁ N ₃ O (273.3)	223–224 (71.5)	74.71	4.06	15.38	2 200	486 (3.16)
			74.87	4.05	15.18		
<i>III e</i>	C ₁₇ H ₁₁ N ₃ O (273.3)	232–234 (69.6)	74.71	4.06	15.38	2 201	468 ^b (3.39)
			74.79	4.07	15.30		
<i>III f</i>	C ₁₈ H ₁₃ N ₃ O (287.3)	115–117 (60.7)	75.25	4.56	14.63	2 220	422, 364 (3.02; 3.02)
			74.97	4.53	14.54		
<i>III g</i>	C ₁₅ H ₆ ClN ₃ O (279.8)	230–231 (33.2)	64.42	2.16	15.02 ^a	2 211	461 ^b (3.48)
			64.21	2.20	14.92		
<i>III h</i>	C ₁₉ H ₉ N ₃ O (295.3)	229–231 (47.5)	77.28	3.07	14.23	2 224	486 ^b (3.34)
			77.28	3.09	14.19		
<i>III i</i>	C ₂₀ H ₁₁ N ₃ O (309.3)	242–244 (64.7)	77.66	3.58	13.58	2 196	495 ^b (3.18)
			77.53	3.52	13.42		

^a % Cl calculated: 12.68; found: 12.75; ^b in acetone solution.

5-Aryl-2-tricyanovinylfurans *IIIa*–*IIIg*

Aluminium chloride (technical grade, 0.5 g, 3.75 mmol) was added to a stirred solution of *II* (0.25 g, 1 mmol) in the respective benzene derivative (15 ml). The mixture was heated at 80 to 100°C till a darkblue complex was formed (5–25 min, compound *IIIg* requires a 5 h-boiling in chlorobenzene), cooled to an ambient temperature and hydrolyzed in ice-cold water (70 ml). The product was extracted with ethyl acetate, the solvent was evaporated and the residue crystallized from toluene–heptane 1 : 1.

5-Naphthyl-2-tricyanovinylfurans *IIIh*–*IIIi*

Aluminium chloride (technical grade, 0.5 g, 3.75 mmol) was added to a stirred solution of *II* (0.25 g, 1 mmol) in dichloroethane (20 ml). After 10 min of stirring at room temperature the

TABLE II

¹H NMR spectra (δ scale, ppm) of 5-aryl-2-tricyanovinylfurans *IIIa*–*IIIi*

Compound	H ₃ (d)	H ₄ (d) ^a	CH ₃ (s)	Others
<i>IIIa</i>	7.84	7.56	—	7.98–8.09 (m, H ₂ H ₆) 7.53–7.62 (m, H ₃ H ₄ H ₅)
<i>IIIb</i>	7.81	7.49	2.42	7.92 (d, H ₂ H ₆ , $J = 8.2$ Hz) 7.39 (d, H ₃ H ₅ , $J = 8.2$ Hz)
<i>IIIc</i>	7.86	7.32	2.38 2.60	7.91 (d, H ₆ , $J_{5,6} = 9.0$ Hz) 7.23 (d, H ₅ , $J_{5,6} = 9.0$ Hz) 7.26 (s, H ₃)
<i>III d</i>	7.81	7.49	2.35 (6 H)	7.34 (d, H ₅ , $J_{5,6} = 8.3$ Hz) 7.77 (dd, H ₆ , $J_{5,6} = 2.0$ Hz) 7.80 (s, H ₂)
<i>IIIe</i>	7.88	7.36	2.36 2.59	7.87 (s, H ₆) 7.29–7.31 (m, H ₃ H ₄)
<i>III f</i>	7.89	7.13	2.30 (3 H) 2.32 (6 H)	7.02 (s, H ₃ H ₅)
<i>IIIg</i>	7.84	7.58	—	7.62 (d, H ₃ H ₅ , $J = 8.5$ Hz) 8.02 (d, H ₂ H ₆ , $J = 8.5$ Hz)
<i>IIIh</i>	7.97	7.63	—	8.53–8.63 (m, H ₈) 8.03–8.21 (m, H ₂ H ₃ H ₅) 7.61–7.76 (m, H ₄ H ₆ H ₇)
<i>IIIi</i>	7.94	7.58	2.79	8.20–8.60 (m, H ₅ H ₈) 7.60–7.78 (m, H ₆ H ₇) 8.16 (d, H ₂ , $J_{2,3} = 7.3$ Hz) 7.56 (d, H ₃ , $J_{2,3} = 7.3$ Hz)

^a $J_{3,4} = 4.0$ Hz.

naphthalene derivative (2 mmol) was added in one run, the mixture was stirred for 3–5 h and worked up as in the preceding procedure.

REFERENCES

1. Thomas C. A.: *Anhydrous Aluminium Chloride in Organic Chemistry*, p. 148. Amer. Chem. Soc., Monograph Series, Reinhold, New York 1941.
2. Horikoshi Y., Ohto Y., Sekiguchi S., Matsui K.: *Nippon Kagaku Kaishi* **3**, 530 (1974); *Chem. Abstr.* **81**, 152177 (1974).
3. Pogosyan G. M., Zaplishnyi V. N., Avanesyan E. S.: *Arm. Khim. Zh.* **31**, 634 (1978); *Chem. Abstr.* **90**, 87407 (1979).
4. Sone T., Kawasaki H., Nagasawa S., Takahashi N., Tate K., Sato K.: *Chem. Lett.* **1981**, 399.
5. Yokoyama Y., Yamashita Y., Takahashi K., Sone T.: *Bull. Chem. Soc. Jap.* **56**, 2208 (1983).
6. Sausen G. N., Engelhardt V. A., Middleton W. J.: *J. Amer. Chem. Soc.* **80**, 2815 (1958).
7. Sheppard W. A., Henderson R. M.: *J. Amer. Chem. Soc.* **89**, 4446 (1967).
8. Ilavský D.: *Thesis*. Slovak Institute of Technology, Bratislava 1982.

Translated by Z. Votický.