ISSN 1070-4280, Russian Journal of Organic Chemistry, 2011, Vol. 47, No. 3, pp. 405–407. © Pleiades Publishing, Ltd., 2011. Original Russian Text © S.V. Karpov, Ya.S. Kayukov, I.N. Bardasov, O.V. Kayukova, O.V. Ershov, O.E. Nasakin, 2011, published in Zhurnal Organicheskoi Khimii, 2011, Vol. 47, No. 3, pp. 412–414.

2-Acyl(aroyl)-1,1,3,3-tetracyanopropenides: I. Synthesis of 2-[5-Amino-2-aryl-2-chloro-4-cyanofuran-3(2*H*)-ylidene]propanedinitriles by Reaction of Potassium 2-Aroyl-1,1,3,3-tetracyanopropenides with Concentrated Hydrochloric Acid

S. V. Karpov, Ya. S. Kayukov, I. N. Bardasov, O. V. Kayukova, O. V. Ershov, and O. E. Nasakin

I.N. Ul'yanov Chuvash State University, Moskovskii pr. 15, Cheboksary, 428015 Russia e-mail: serg31.chem@mail.ru

Received January 26, 2010

Abstract—Potassium 2-aroyl-1,1,3,3-tetracyanopropenides reacted with concentrated hydrochloric acid to give the corresponding 2-[5-amino-2-aryl-2-chloro-4-cyanofuran-3(2*H*)-ylidene]propanedinitriles.

DOI: 10.1134/S1070428011030134

Polycyano-substituted propenides are known as precursors of six-membered heterocycles [1–4]. A convenient procedure for the synthesis of polycyanopropenides is based on opening of the three-membered ring in polycyanocyclopropanes [5]. We previously described the synthesis of 2-aroyl-1,1,3,3-tetracyanopropenides II via reaction of tetracyanocyclopropyl ketones I with bases. Compounds II attract interest taking into account that the presence of an aroyl group in the 2-position makes it possible to convert them into five-membered heterocycles [5]. We have improved the procedures for the synthesis, isolation, and purification of potassium 2-aroyl-1,1,3,3-tetracyanopropenides **II**, so that the latter have become accessible reagents for further studies.

The present communication opens a series of publications on reactions of propenides **II** with nucleophiles under various conditions. Here, we report on the reaction of propenides **IIa–IId** with hydrochloric acid as acid catalyst and source of nucleophilic chloride ions. Propenides **II** may be regarded as conjugate anions of strong acids; therefore, their protonation is possible only by the action of strong mineral acids. Proton addition to anions **II** having delocalized negative charge could give rise to tautomeric structures, nitrile and ketene imine, where nucleophilic attack is



 $R = Ph(a), 4-BrC_6H_4(b), 4-MeOC_6H_4(c), 3-O_2NC_6H_4(d).$





likely to be directed at the cyano groups with subsequent closure of pyridine ring (structure IV). Alternative protonation at the carbonyl oxygen atom should yield zwitterionic species **A** which should undergo nucleophilic attack at the carbonyl carbon atom, favoring formation of five-membered heteroring (Scheme 1).

We found that treatment of compounds **IIa–IId** with concentrated hydrochloric acid leads to the formation of 2-[5-amino-2-aryl-2-chloro-4-cyano-furan-3(2*H*)-ylidene]propanedinitriles **IIIa–IIId** in 68–72% yield (Scheme 1). A probable reaction mechanism involves initial addition of proton to the carbonyl oxygen atom with formation of zwitterion **A** which undergoes nucleophilic attack by chloride ion to give chlorohydrin **B**. Next follows heterocyclization to afford intermediate furan derivative **C**, and protonation of the latter in the presence of concentrated hydrochloric acid yields final compounds **III** (Scheme 2).

The structure of compounds IIIa-IIId was determined on the basis of their ¹H and ¹³C NMR, IR, and mass spectra. Unlike alternative pyridine structure IV, compounds **IIIa–IIId** displayed in the ¹H NMR spectra a downfield signal at δ 10.5–11.0 ppm from protons in the amino group [5]; the corresponding signal of α -aminopyridines is located at δ 6–8 ppm. According to the ¹³C NMR data, molecule IIIa contains three cyano groups (δ_C 110.47, 112.44, 113.13 ppm) [6] rather than two in compounds like IV. In addition, a signal at $\delta_{\rm C}$ 70 ppm was present in the ¹³C NMR spectrum of IIIa due to the central carbon atom in the dicyanomethylidene fragment. The IR spectra of IIIa-**IIId** did not contradict the assumed structure: the double carbon-carbon bond gave rise to absorption band at $1665 - 1685 \text{ cm}^{-1}$.

Relatively few furan derivatives with analogous substituents have been reported. At present, substituted 2,2-dichloro-5-aminodihydrofurans are available via reaction of oxalyl chloride with *N*,*N*-dialkyl(aryl)acet-amides [7], methyl 3-(dimethylamino)propynoate [8], or *N*,*N*-diisopropylcubanecarboxamide [9]. Speziale et al. [10] described the synthesis of 5,5-dichloro-2-[methyl(phenyl)amino]-4-oxotetrahydrofuran-3-carbo-

nitrile by reaction of oxalyl chloride with *N*-methyl-*N*-phenylcyanoacetamide.

Thus we have proposed a novel synthetic approach to functionally substituted furan derivatives on the basis of the reaction of potassium 2-aroyl-1,1,3,3-tetracyanopropenides **II** with concentrated hydrochloric acid; the proposed procedure is advantageous due to accessibility of the initial reactants and high yield.

EXPERIMENTAL

The progress of reactions and the purity of products were monitored by thin-layer chromatography on Silufol UV-254 plates; spots were detected by UV irradiation, treatment with iodine vapor, or thermal treatment. The IR spectra were recorded from samples dispersed in mineral oil on an FSM-1202 spectrometer with Fourier transform. The ¹H and ¹³C NMR spectra were measured on a Bruker DRX-500 spectrometer at 500.13 (¹H) and 126.13 MHz (¹³C) using DMSO-*d*₆ as solvent and tetramethylsilane as internal reference. The mass spectra (electron impact, 70 eV) were obtained on a Shimadzu GCMS-QP2010S DI instrument.

Potassium 2-benzoyl-1,1,3,3-tetracyanoprop-2en-1-ide (IIa). Substituted cyclopropane Ia, 2.46 g (0.01 mol), was dissolved in 10 ml of acetonitrile, and 1.0 g (0.01 mol) of potassium acetate and 0.5 ml of water were added under stirring. The mixture was stirred for 30 min at room temperature (TLC), the solvent was distilled off under reduced pressure, the residue was ground with 20 ml of benzene, and the precipitate was filtered off, washed with benzene, dried in air, and recrystallized from 5 ml of a 0.05 M aqueous solution of KCl. Yield 2.3 g (81%), bright yellow needles, mp. 228–229°C (decomp.). IR spectrum, v, cm⁻¹: 2205 (C=N), 1655 (C=O).

Compounds **IIb–IId** were synthesized in a similar way from substituted cyclopropanes **Ib–Id**.

Potassium 2-(4-bromobenzoyl)-1,1,3,3-tetracyanoprop-2-en-1-ide (IIb). Yield 62%, mp 221–222°C (decomp.). IR spectrum, v, cm^{-1} : 2205 (C=N), 1681 (C=O). Potassium 1,1,3,3-tetracyano-2-(4-methoxybenzoyl)prop-2-en-1-ide (IIc). Yield 55%, mp 223–224°C (decomp.). IR spectrum, v, cm⁻¹: 2200 (C=N), 1664 (C=O).

Potassium 1,1,3,3-tetracyano-2-(3-nitrobenzoyl)prop-2-en-1-ide (IId). Yield 72%, mp 213–214°C (decomp.). IR spectrum, v, cm⁻¹: 2230 (C=N), 1656 (C=O).

2-[5-Amino-2-chloro-4-cyano-2-phenylfuran-3(2H)-ylidene|propanedinitrile (IIIa). A solution of 2.84 g (0.01 mol) of propenide **IIa** in 10 ml of 30% hydrochloric acid was stirred for 15 min at 80°C. The precipitate was filtered off, washed with water, and recrystallized from isopropyl alcohol-5% sulfuric acid (1:1). Yield 2.04 g (72%), mp 150–151°C (decomp.). IR spectrum, v, cm⁻¹: 3250, 3110 (NH₂); 2215 (C=N); 1696 (C=C). ¹H NMR spectrum, δ, ppm: 7.53–7.62 m (3H, H_{arom}), 7.68 d (2H, H_{arom}, ${}^{3}J = 6.6$ Hz), 10.72 s (2H, NH₂). ¹³C NMR spectrum, δ_{C} , ppm: 55.67 (C⁴), $69.59 [C(CN)_2], 105.34 (C^2), 110.47 (CN), 112.94,$ 113.13 [C(CN)₂], 126.87, 128.94, 131.38, 132.46 (C_{arom}) , 168.09 (C^3) , 170.36 (C^5) . Mass spectrum, m/z(Irel, %): 282 (55), 283 (10), 284 (15). Found, %: C 59.75; H 2.52; N 18.83. C₁₄H₇ClN₄O. Calculated, %: C 59.48; H 2.50; N 19.82. M 282.68.

Compounds **IIIb–IIId** were synthesized in a similar way.

2-[5-Amino-2-(4-bromophenyl)-2-chloro-4cyanofuran-3(2H)-ylidene]propanedinitrile (IIIb). Yield 69%, mp 135–136°C (decomp.). IR spectrum, v, cm⁻¹: 3253, 3102 (NH₂); 2219 (C=N); 1685 (C=C). ¹H NMR spectrum, δ , ppm: 7.66 d (2H, H_{arom}, ³*J* = 8.7 Hz), 7.76 d (2H, H_{arom}, ³*J* = 8.7 Hz), 10.75 s (2H, NH₂). Mass spectrum, *m*/*z* (*I*_{rel}, %): 362 (10), 363 (3), 361 (1). Found, %: C 46.57; H 1.62; N 15.43. C₁₄H₆BrClN₄O. Calculated, %: C 46.50; H 1.67; N 15.49. *M* 361.58.

2-[5-Amino-2-chloro-4-cyano-2-(4-methoxyphenyl)furan-3(2*H***)-ylidene]propanedinitrile (IIIc). Yield 72%, mp 141–142°C (decomp.). IR spectrum, v, cm⁻¹: 3255, 3102 (NH₂); 2217 (C≡N); 1694 (C=C). ¹H NMR spectrum, δ, ppm: 7.05–7.08 m (2H, H_{arom}), 7.58–7.61 m (2H, H_{arom}), 10.70 s (2H, NH₂). Mass spectrum, m/z (I_{rel}, %): 312 (10), 314 (3). Found, %:** C 57.65; H 2.93; N 17.88. C₁₅H₉ClN₄O₂. Calculated, %: C 57.61; H 2.90; N 17.92. *M* 312.71

2-[5-Amino-2-chloro-4-cyano-2-(3-nitrophenyl)furan-3(2*H***)-ylidene]propanedinitrile (IIId). Yield 68%, mp 146–147°C (decomp.). IR spectrum, v, cm⁻¹: 3253, 3102 (NH₂); 2217 (C=N); 1691 (C=C). ¹H NMR spectrum, \delta, ppm: 7.87 t (1H, H_{arom}, ³***J* **= 8.1 Hz), 8.18 d.d (1H, H_{arom}, ³***J* **= 7.8, ⁴***J* **= 1.4 Hz), 8.46 d.d (1H, H_{arom}, ³***J* **= 8.1, ⁴***J* **= 1.8 Hz), 8.51 t (1H, H_{arom}, ⁴***J* **= 2 Hz), 10.89 s (2H, NH₂). Mass spectrum,** *m/z* **(***I***_{rel}, %): 327 (10), 329 (3). Found, %: C 51.37; H 1.92; N 21.33. C₁₄H₆ClN₅O₃. Calculated, %: C 51.31; H 1.85; N 21.37.** *M* **327.68.**

This study was performed under financial support by the Federal Special-Purpose Program "Scientific and Scientific–Pedagogical Staff of Innovation Russia" (state contract no. 16.740.11.0335).

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