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SHORT COMMUNICATIONS

Reaction of 4-Aryl-4-oxobutane-1,1,2,2-tetracarbonitriles with Hydrochloric Acid

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We previously reported that tetracyanoalkanones react with hydrohalic acids to give alkyl-substituted 2-halopyridine-3,4-dicarbonitriles [1] or 2-halo-6-hydroxy-1,4,5,6-tetrahydropyridine-3,4,4-tricarbonitriles [2]. In the present communication we describe a novel path of this reaction, which is possible only with aryl-substituted tetracyanoalkanones. 4-Aryl-4-oxobutane-1,1,2,2-tetracarbonitriles **Ia**–**Ic** were found to react with hydrochloric acid to produce either 6-aryl-2-chloropyridine-3,4-dicarbonitriles **IIa**–**IIc** or 3a-(2-aryl-2-oxoethyl)perhydropyrrolo[3,4-*c*]pyrrole-1,3,4,6-tetraones **IIIa**–**IIIc**.

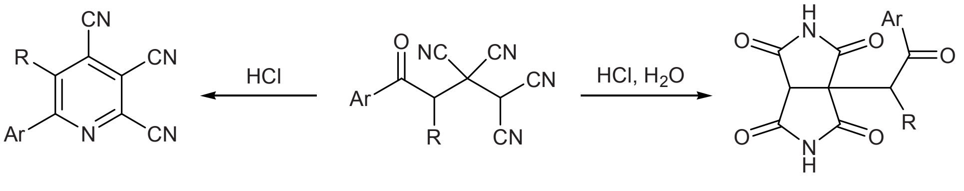
No data were reported previously on the effect of water on reactions of tetracyanoalkanones with hydrogen halides. According to our results, this factor is very important in the reactions with aryl-substituted tetracyanoalkanones: pyridines **IIa**–**IIc** are formed in anhydrous medium, whereas diimides **IIIa**–**IIIc** are obtained in the presence of water. The structure of compounds **IIa**–**IIc** and **IIIa**–**IIIc** was confirmed by the IR, ^{1}H NMR, and mass spectra.

2-Chloro-6-(4-methoxyphenyl)pyridine-3,4-dicarbonitrile (IIa). Acetyl chloride, 1.5–2 ml, was added to a suspension of 0.56 g (2 mmol) of 4-(4-methoxyphenyl)-4-oxobutane-1,1,2,2-tetracarbonitrile (**Ia**) in propan-2-ol. After some time, the precipitate was filtered off and washed with water and propan-2-ol. Yield 0.41 g (76%), mp 133–134°C. IR spectrum: ν 2228 cm^{-1} (C≡N). ^{1}H NMR spectrum, δ, ppm: 3.87 s (3H, OCH_3), 7.14 d and 8.21 d (2H each, C_6H_4, $J = 9$ Hz), 8.79 s (1H, 5-H). Mass spectrum: *m*/*z* 269 (I_{rel} 100%). Found, %: C 62.75; H 2.79; N 14.89. $C_{14}H_8ClN_3O$. Calculated, %: C 62.35; H 2.99; N 15.58.

Compounds **IIb** and **IIc** were synthesized in a similar way.

2-Chloro-6-(3,4-dimethoxyphenyl)pyridine-3,4-dicarbonitrile (IIb). Yield 0.47 g (78%), mp 139–140°C. IR spectrum: ν 2221 cm^{-1} (C≡N). ^{1}H NMR spectrum, δ, ppm: 3.87 s and 3.88 s (3H each, OCH_3), 7.17 d (1H, H_{arom}, $J = 9$ Hz), 7.74 s (1H, H_{arom}, $J = 9$ Hz), 7.89 d (1H, H_{arom}, $J = 9$ Hz), 8.86 s (1H, 5-H). Mass spectrum: *m*/*z* 299 (I_{rel} 100%). Found, %: C 59.75; H 3.45; N 13.42. $C_{15}H_{10}ClN_3O_2$. Calculated, %: C 60.11; H 3.36; N 14.02.

2-Chloro-6-(4-methoxyphenyl)-5-methylpyridine-3,4-dicarbonitrile (IIc). Yield 0.40 g (75%), mp 141–142°C. IR spectrum: ν 2228 cm^{-1} (C≡N). ^{1}H NMR spectrum, δ, ppm: 2.59 s (3H, CH_3), 3.87 s (3H, OCH_3), 7.11 d and 7.65 d (2H each, C_6H_4, $J = 9$ Hz). Mass spectrum: *m*/*z* 283 (I_{rel} 100%). Found, %:



IIa–IIc **Ia–Ic** **IIIa–IIIc**

R = H, Ar = 4-$MeOC_6H_4$ (**a**), 3,4-$(MeO)_2C_6H_3$ (**b**); R = Me, Ar = 4-$MeOC_6H_4$ (**c**).

C 63.78; H 3.55; N 14.81. $C_{15}H_{10}ClN_3O$. Calculated, %: 63.50; H 3.75; N 15.01.

3a-[2-(4-Methoxyphenyl)-2-oxoethyl]perhydropyrrolo[3,4-*c*]pyrrole-1,3,4,6-tetraone (IIIa). Concentrated hydrochloric acid, 10 ml, was added under stirring to a suspension of 0.56 g (2 mmol) of compound **Ia** in propan-2-ol. After 2–3 h, the precipitate was filtered off and washed with water and propan-2-ol. Yield 0.52 g (81%), mp 286–288°C (decomp.). IR spectrum, ν, cm^{-1}: 3309, 3184 (NH); 1670–1750 (C=O). ^1H NMR spectrum, δ, ppm: 3.85 s (3H, OCH_3), 3.91 s (2H, CH_2), 3.93 s (1H, CH), 7.05 d and 7.94 d (2H each, C_6H_4, J = 9 Hz), 11.82 s (2H, NH). Mass spectrum: m/z 316 (I_{rel} 2%). Found, %: C 56.06; H 3.49; N 8.98. $C_{15}H_{12}N_2O_6$. Calculated, %: C 56.96; H 3.82; N 8.86.

Compounds **IIIb** and **IIIc** were synthesized in a similar way.

3a-[2-(3,4-Dimethoxyphenyl)-2-oxoethyl]perhydropyrrolo[3,4-*c*]pyrrole-1,3,4,6-tetraone (IIIb). Yield 0.53 g (76%), mp 231–232°C (decomp.). IR spectrum, ν, cm^{-1}: 3308, 3175 (NH); 1669–1747 (C=O). ^1H NMR spectrum, δ, ppm: 3.81 s and 3.85 s (3H each, OCH_3), 3.93 s (2H, CH_2), 3.94 s (1H, CH), 7.07 d (1H, H_{arom}, J = 8 Hz), 7.42 s (1H, H_{arom}), 7.65 d (1H, H_{arom}, J = 8 Hz), 11.81 s (2H, NH). Mass spectrum: m/z 346 (I_{rel} 4%). Found, %: C 56.15; H 4.12; N 8.34. $C_{16}H_{14}N_2O_7$. Calculated, %: C 55.49; H 4.07; N 8.09.

3a-[2-(4-Methoxyphenyl)-1-methyl-2-oxoethyl]perhydropyrrolo[3,4-*c*]pyrrole-1,3,4,6-tetraone (IIIc). Yield 0.47 g (75%), mp 275–277°C (decomp.). IR spectrum, ν, cm^{-1}: 1667–1751 (C=O), 3225 (NH). ^1H NMR spectrum, δ, ppm: 1.21 d (3H, CH_3, J = 7 Hz), 3.86 s (3H, OCH_3), 4.37 s (1H, 6a-H), 4.45 q (1H, C**H**CH_3, J = 7 Hz), 7.07 d and 7.97 d (2H each, C_6H_4, J = 9 Hz), 11.73 s and 12.00 s (1H each, NH). Mass spectrum: m/z 330 (I_{rel} 2%). Found, %: C 61.29; H 4.67; N 9.34. $C_{16}H_{14}N_2O_6$. Calculated, %: C 58.18; H 4.27; N 8.48.

The IR spectra were recorded from samples dispersed in mineral oil on an FSM-1202 spectrometer with Fourier transform. The ^1H NMR spectra were measured on a Bruker DRX-500 instrument at 500.13 MHz using DMSO-d_6 as solvent and tetramethylsilane as internal reference. The mass spectra (electron impact, 70 eV) were obtained on a Finnigan MAT Incos-50 spectrometer. The purity of the products was checked by TLC on Silufol UV-254 plates; spots were visualized under UV light, by treatment with iodine vapor, or by thermal treatment.

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