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SHORT COMMUNICATIONS

Three-Component Synthesis of 2-Chloropyridine-3,4-dicarbonitriles

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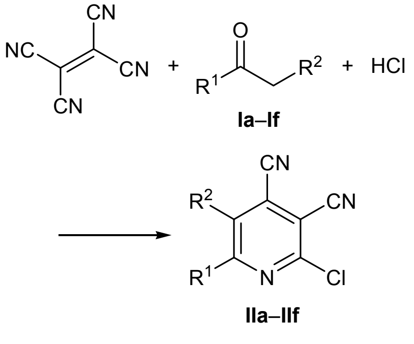
According to published data, tetracyanoethylene reacts with ketones in the presence of a catalytic amount of hydrochloric acid to give 4-oxoalkane-1,1,2,2-tetracarbonitriles [1, 2]. It is also known that concentrated hydrochloric acid reacts with 4-oxoalkane-1,1,2,2-tetracarbonitriles to produce 2-chloropyridine-3,4-dicarbonitriles [3]. These data suggest that 2-chloropyridine-3,4-dicarbonitriles could be prepared via one-pot procedure, i.e., without isolation of 4-oxoalkane-1,1,2,2-tetracarbonitriles, which should make their preparation simpler and less expensive.

In fact, three-component reaction of tetracyanoethylene with the corresponding ketone **Ia**–**If** (aliphatic, aromatic, or heterocyclic) and hydrochloric acid in 1,4-dioxane afforded substituted 2-chloropyridine-3,4-dicarbonitriles **IIa**–**IIf** in 86–97% yield. The structure of compounds **IIa**–**IIf** was confirmed by IR, ^{1}H NMR, and mass spectra.



$R^1 = R^2$ = Me (**a**); R^1 = Me, R^2 = Et (**b**); $R^1R^2 = (CH_2)_4$ (**c**), $(CH_2)_6$ (**d**); R^1 = Ph, R^2 = H (**e**); R^1 = 2-thienyl, R^2 = H (**f**).

Thus we proposed a one-pot procedure for the synthesis of 2-chloropyridine-3,4-dicarbonitriles, which ensured higher yield and shorter reaction time. Compounds **IIb** and **IId**–**IIf** were not reported previously.

2-Chloro-5,6-dimethylpyridine-3,4-dicarbonitrile (IIa). Tetracyanoethylene, 0.64 g (0.005 mol), was added to a solution of 0.45 g (0.006 mol) of butan-2-one in 10 ml of 1,4-dioxane, 5 ml of concentrated hydrochloric acid was then added, and the mixture was stirred for 1–2 h at 60–70°C. When the reaction was complete (TLC), the mixture was diluted with water, and the precipitate was filtered off, washed with water and propan-2-ol, and recrystallized from propan-2-ol. Yield 0.85 g (89%), mp 72–74°C [3]. IR spectrum, ν, cm^{-1}: 2233 (C≡N), 1561, 1535 (C=C). ^{1}H NMR spectrum, δ, ppm: 2.56 s (3H, CH_3), 2.68 s (3H, CH_3). Mass spectrum: *m*/*z* 191 (I_{rel} 57%). Found, %: C 55.98; H 3.15; N 21.58. $C_9H_6ClN_3$. Calculated, %: C 56.41; H 3.16; N 21.93. *M* 191.62.

Compounds **IIb**–**IIf** were synthesized in a similar way.

2-Chloro-5-ethyl-6-methylpyridine-3,4-dicarbonitrile (IIb). Yield 0.95 g (93%), mp 46–48°C. IR spectrum, ν, cm^{-1}: 2234 (C≡N), 1554 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.19 t (3H, CH_3, J = 8 Hz), 2.66 s (3H, CH_3), 2.86 q (2H, CH_2, J = 8 Hz). Mass spectrum: *m*/*z* 205 (I_{rel} 45%). Found, %: C 57.98; H 3.15; N 20.02. $C_{10}H_8ClN_3$. Calculated, %: C 58.41; H 3.92; N 20.43. *M* 205.65.

2-Chloro-5,6,7,8-tetrahydroquinoline-3,4-dicarbonitrile (IIc). Yield 1.05 g (97%), mp 95–96°C [3]. IR spectrum, ν, cm^{-1}: 2222 (C≡N), 1539 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.90 m (4H, CH_2), 2.89 t (2H, CH_2, J = 6 Hz), 3.09 t (2H, CH_2, J = 6 Hz). Mass spectrum: *m*/*z* 217 (I_{rel} 100%). Found, %: C 59.96;

H 3.56; N 20.28. $C_{11}H_8ClN_3$. Calculated, %: C 60.70; H 3.70; N 19.31. *M* 217.66.

2-Chloro-5,6,7,8,9,10-hexahydrocycloocta[*b*]pyridine-3,4-dicarbonitrile (IId). Yield 1.15 g (94%), mp 72–74°C. IR spectrum, ν, cm^{-1}: 2234 (C≡N), 1552, 1538 (C=C). ^1H NMR spectrum, δ, ppm: 1.31 m (4H, CH_2), 1.74 m (4H, CH_2), 3.01 t (2H, CH_2, *J* = 6 Hz), 3.03 t (2H, CH_2, *J* = 6 Hz). Mass spectrum: *m*/*z* 245 (I_{rel} 29%). Found, %: C 62.98; H 4.75; N 17.01. $C_{13}H_{12}ClN_3$. Calculated, %: C 63.55; H 4.92; N 17.10. *M* 245.71.

2-Chloro-6-phenylpyridine-3,4-dicarbonitrile (IIe). Yield 1.04 g (87%), mp 171–172°C. IR spectrum, ν, cm^{-1}: 2232 (C≡N), 1601, 1573, 1526 (C=C), ^1H NMR spectrum, δ, ppm: 7.61 m (3H, H_{arom}), 8.23 t (2H, H_{arom}, *J* = 5 Hz), 8.89 s (1H, CH). Mass spectrum: *m*/*z* 239 (I_{rel} 100%). Found, %: C 65.35; H 2.99; N 17.78. $C_{13}H_6ClN_3$. Calculated, %: C 65.15; H 2.52; N 17.53. *M* 239.66.

2-Chloro-6-(2-thienyl)pyridine-3,4-dicarbonitrile (IIf). Yield 1.06 g (86%), mp 155–156°C. IR spectrum, ν, cm^{-1}: 2234 (C≡N), 1542, 1518 (C=C). ^1H NMR spectrum, δ, ppm: 7.33 t (1H, thiophene, *J* = 4 Hz), 8.03 d (1H, thiophene, *J* = 4 Hz), 8.21 d (1H, thiophene, *J* = 4 Hz), 8.80 s (1H, CH). Mass spectrum: *m*/*z* 245 (I_{rel} 100%). Found, %: C 53.63; H 1.62; N 17.23. $C_{11}H_4ClN_3S$. Calculated, %: C 53.77; H 1.64; N 17.10. *M* 245.69.

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

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