Russian Journal of Organic Chemistry, Vol. 37, No. 9, 2001, pp. 1310–1312. Translated from Zhurnal Organicheskoi Khimii, Vol. 37, No. 9, 2001, pp. 1376–1378.
Original Russian Text Copyright © 2001 by Pavlov.

Synthesis of 2-Cyano-1-(4-nitrophenyl)pyrrole and Its 5-Bromo- and 4,5-Dibromo Derivatives

P. A. Pavlov

Kuban' State University, ul. Stavropol'skaya 149, Krasnodar, 350040 Russia

Received July 4, 2000

Abstract—1-(4-Nitrophenyl)pyrrole-2-carbaldehyde and its 5-bromo- and 4,5-dibromo derivatives react with hydrazoic acid in chloroform in the presence of $Mg(ClO_4)_2 \cdot 2.5H_2O$ (Schmidt reaction) to form the corresponding pyrrole-2-carbonitriles.

The Schmidt reaction [1] is superior to the other methods of preparation of nitriles, for it includes only one step and utilizes readily accessible initial compounds (aldehydes). Moreover, this procedure ensures simple isolation of the target products (nitriles) and regeneration of the reaction medium.

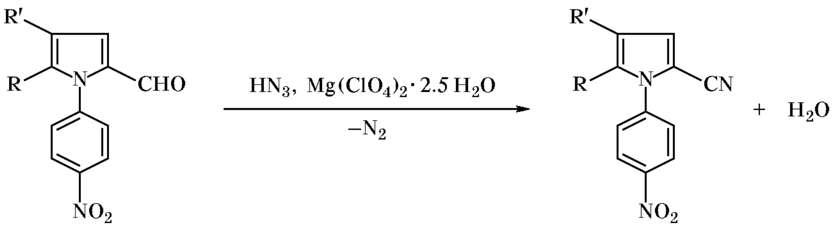
The results of our previous studies on the transformation of aldehydes into nitriles via the Schmidt reaction involving perchloric acid and its derivatives as catalyst [2–6] allowed us to synthesize some nitriles of the pyrrole series from the corresponding aldehydes. As starting compounds we used 1-(4-nitrophenyl)pyrrole-2-carbaldehyde and its 5-bromo- and 4,5-dibromo derivatives which were prepared by the procedure reported in [7]. The most appropriate solvent was found to be chloroform which is usually used in the classical Schmidt reaction. Chloroform is inert toward HN_3 and well dissolve the pyrroles under study. As catalyst we used hydrated magnesium perchlorate $Mg(ClO_4)_2 \cdot 2.5H_2O$.

The structure of products **I**–**III** (Scheme 1) was confirmed by elemental analysis (Table 1) and IR, UV, and ^{1}H NMR spectroscopy (Table 2). Cyanopyrroles **I**–**III** are colorless (**I**) or slightly yellowish (**II**, **III**) crystalline substances with sharp melting points. They are readily soluble in most organic solvents at room temperature, sparingly soluble in alcohol and benzene, and insoluble in water and aliphatic hydrocarbons.

In the IR spectra of **I**–**III** stretching vibrations of the cyano group give a strong absorption band in the region 2220–2225 cm^{-1}. Three bands at 1550–1520, 1350–1320, and 860 ± 5 cm^{-1} belong to the nitro group vibrations [8]. Out-of-plane bending vibrations of the pyrrolic C–H bonds appear at 735 ± 15 cm^{-1}. Aromatic C=C bonds give rise to absorption at 1605 ± 5 cm^{-1}, and the band at 765 ± 10 cm^{-1} corresponds to out-of-plane bending vibrations of C–H bonds in the *para*-substituted benzene ring [9].

The UV spectra of compounds **I** and **II** are characterized by the presence of two absorption maxima (Table 2). Introduction of the second bromine atom into the pyrrole ring (compound **III**) leads to disappearance of the short-wave maximum. These data are

Scheme 1.



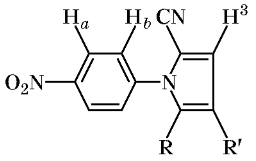
I–III

I, R = R′ = H; **II**, R = Br, R′ = H; **III**, R = R′ = Br.

Table 1. Yields, melting points, and elemental analyses of 2-cyano-1-(nitrophenyl)pyrroles **I**–**III**

Comp. no.	Yield, %	mp, °C	Found, %				Formula	Calculated, %			
			C	H	Br	N		C	H	Br	N
I	97	95	61.64	3.20	–	19.68	$C_{11}H_7N_3O_2$	61.91	3.28	–	19.71
II	98	128	45.16	1.98	27.28	14.30	$C_{11}H_6BrN_3O_2$	45.20	2.05	27.39	14.38
III	98	214	35.49	1.22	43.05	11.30	$C_{11}H_5Br_2N_3O_2$	35.57	1.34	43.12	11.32

Table 2. IR, UV, and ^{1}H NMR spectra of compounds **I**–**III**



Comp. no.	IR spectrum, ν, cm^{-1}		UV spectrum, λ_{max}, nm (log ε)	^{1}H NMR spectrum, δ, ppm
	CN	NO$_2$		
I	2225	1550, 1350, 1320	222 (3.51), 281 (4.23)	6.43 d.d (1H, 4-H, $^3J_{4,5}$ = 3.0, $^3J_{4,3}$ = 4.0 Hz), 7.15 d.d (1H, 3-H, $^4J_{3,5}$ = 1.75, $^3J_{3,4}$ = 4.0 Hz), 7.48 d.d (1H, 5-H, $^3J_{5,4}$ = 3.0, $^4J_{5,3}$ = 1.75 Hz), 7.85 d (2H, H$_b$, ^3J = 10.0 Hz), 8.32 d (2H, H$_a$, ^3J = 10.0 Hz)
II	2210	1545, 1350, 1320	218 (3.43), 255 (4.21)	6.53 d (1H, 4-H, ^3J = 3.5 Hz), 7.13 d (1H, 3-H, ^3J = 3.5 Hz), 7.78 d (2H, H$_b$, J = 9 Hz), 8.47 d (2H, H$_a$, J = 9 Hz)
III	2200	1520, 1350, 1320	257 (4.09)	7.16 s (1H, 3-H), 7.73 d (2H, H$_b$, J = 10 Hz), 8.43 d (2H, H$_a$, J = 10 Hz)

typical of such pyrrole derivatives [10, 11]. The ^{1}H NMR spectra of compounds **I**–**III** contain signals from aromatic protons as two doublets at δ 7.7–7.9 and 8.3–8.5 ppm with a coupling constant of 9–10 Hz. The signals from the *ortho*-protons (with respect to the nitro group) are located in a weaker field than those from the *meta*-protons [8]. Signals from the pyrrole ring protons are observed in the region δ 6.4–7.5 ppm (Table 2).

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer in mineral oil. The ^{1}H NMR spectra were obtained on a Tesla BS-487 instrument (80 MHz) in DMSO-d_6 using *t*-BuOH as internal reference. The UV spectra were measured on a Specord UV-Vis spectrophotometer in ethanol. The purity of the products was checked by TLC on Silufol UV-254 plates using ethanol–toluene (3 : 20) as eluent; spots were visualized by treatment with iodine vapor. Solutions of hydrazoic acid in chloroform were prepared by the procedure reported in [1].

1-(4-Nitrophenyl)-2-pyrrolecarbonitrile (I). A three-necked flask equipped with a mechanical stirrer and reflux condenser was charged with 21.6 g (0.1 mol) of 1-(4-nitrophenyl)pyrrole-2-carbaldehyde, a solution of 0.11 mol of hydrazoic acid in chloroform, and 25 g (0.1 mol) of $Mg(ClO_4)_2 \cdot 2.5H_2O$. After ~5 min, nitrogen began to evolve, and the mixture warmed up to 30–35°C. It was kept for 2 h at that temperature (until nitrogen no longer evolved) and was refluxed for 1 h. The mixture was then cooled to room temperature, treated with water, and filtered. The organic layer was washed with two portions of water, treated with charcoal (to decolorize), and filtered. The solvent was evaporated under reduced pressure to obtain 20.5 g (97%) of compound **I** with mp 95°C. Compounds **II** and **III** were synthesized in a similar way.

REFERENCES

1. Wolf, H.W., *Organic Reactions*, Adams, R., Ed., New York: Wiley, 1946, vol. 3. Translated under the title *Organicheskie reaktsii*, Moscow: Inostrannaya Literatura, 1951, vol. 3, p. 291.
2. Pavlov, P.A. and Kul'nevich, V.G., USSR Inventor's Certificate no. 1130566, 1983; *Byull. Izobret.*, 1984, no. 47.
3. Pavlov, P.A., *Khimiya i tekhnologiya furanovykh soedinenii. Mezhvuzovskii sbornik* (Chemistry and Technology of Furan Compounds. Interinstitution Collection), Krasnodar: Politekh. Inst., 1983, pp. 33–37.
4. Pavlov, P.A. and Kul'nevich, V.G., USSR Inventor's Certificate no. 1398353, 1986; *Byull. Izobret.*, 1987, no. 38.
5. Pavlov, P.A. and Kulnevich, V.G., Abstracts of Papers, *Int. Symp. of Furan Chemistry*, Riga, 1988, p. 79.
6. Pavlov, P.A. and Kul'nevich, V.G., *Khim. Geterotsikl. Soedin.*, 1986, no. 2, p. 181.
7. Baum, E., Belen'kii, L.I., and Kul'nevich, V.G., *Khim. Geterotsikl. Soedin.*, 1982, no. 5, pp. 662–665.
8. *The Chemistry of the Nitro and Nitroso Groups*, Feuer, H., Ed., New York: Wiley, 1969, part 1. Translated under the title *Khimiya nitro- i nitrozogrupp*, Moscow: Mir, 1972, vol. 1.
9. Silverstein, R.M., Bassler, G.C., and Morrill, T.C., *Spectrometric Identification of Organic Compounds*, New York: Wiley, 1974, 3rd ed. Translated under the title *Spektrometricheskaya identifikatsiya organicheskikh soedinenii*, Moscow: Mir, 1977.
10. Baum, E., *Cand. Sci. (Chem.) Dissertation*, Krasnodar, 1981.
11. Kul'nevich, V.G., Baum, E., and Goldovskaya, T.E., *Khim. Geterotsikl. Soedin.*, 1982, no. 4, pp. 495–498.