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NOTE

Synthesis of Aryl(benzyl)-(Z)-N-[2-Amino-1,2-dicyanovinyl]-formamidines

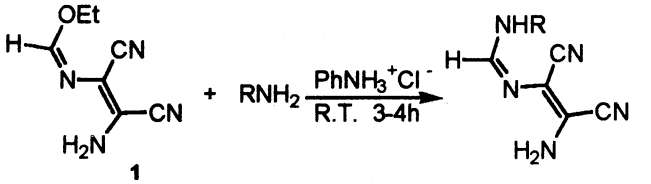
ASIEH YAHYAZADEH* and BABAK POURROSTAM
Department of Chemistry, University of Guilan, P.O. Box 1914, Rasht, Iran
E-mail: yahyazadeh@guilan.ac.ir

Starting from readily available ethyl(Z)-N-(2-amino-1,2-dicyanovinyl)formimidate **1**, the N-aryl (or benzyl)-N′-(2-amino-1,2-dicyanovinyl)formamidines **2** can be prepared in good yields by reaction with aromatic amines at room temperature in the presence of a catalytic amount of aniline hydrochloride.

Key Words: Diaminomaleonitrile, Formimidate, Formamidine.

Amidines are an important class of compounds which have proved to be intermediates in a number of biological processes[1–4]. The chemistry and preparation of amidines have been reviewed by Shriner and Neumann[5]. Synthesis and characterization of several alkyl, aryl amidine and also the amidrazone have been reported previously[6, 7]. Various aryl and benzyl amidines of type **2a–c** by the reaction of imidate **1** with aromatic amines have been prepared in the present communication.

In order to synthesize the required amidines **2a–c,** the following method, which involves treatment of imidate **1** with the appropriate arylamine, were used **(Scheme-1)**. Ethyl(Z)-N-(2-amino-1,2-dicyanovinyl)formimidate **1** was prepared according to a reported procedure by treatment of equimolar quantities of triethylorthoformate and diaminomaleonitrile in refluxing dioxane[2, 8–10].

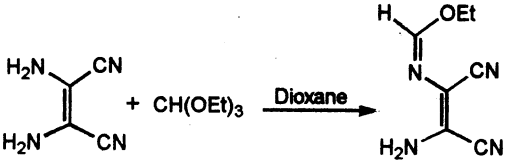


a R=3,4-$(CH_3)_2$-C_6H_3-
b R=3,4-$(OCH_3)_2$-C_6H_3-
c R=C_6H_5-CH_2-

Scheme-1

Having obtained the imidate **1** in good yield it was then treated with arylamine in a 1 : 1 molar ratio in ethanol in the presence of a catalytic amount of aniline hydrochloride. The reaction mixture was stirred under an inert atmosphere at room temperature with the exclusion of light. A homogeneous solution was obtained

and within 10 min, a white solid precipitated out. The product was filtered off after 3–4 h. It was washed with diethyl ether and was found to be pure by TLC, ^{1}H NMR and IR spectroscopy.



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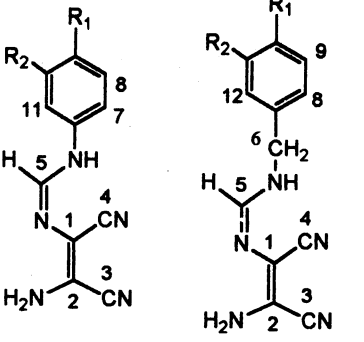
The ^{1}H NMR spectra of compounds **2a, 2b** and **2c** in [$^2H_6$]dimethyl sulfoxide ([$^2H_6$]DMSO) had some interesting features. The HC=N proton was a multiplate, at δ 7.12–7.70 ppm and showed coupling with protons H7 and H11 aromatic ring. NH proton appeared as a broad singlet at 8.17–9.94 ppm and was confirmed by D_2O exchange. The infrared spectrum of amidine **2a–c** showed two strong absorption bands in the region 2235–2105 cm^{-1} characteristic of CN stretching vibrations, together with an NH and a C=N stretching vibration at 3450–3100 and 1645–1630 cm^{-1} respectively.



2a: $R_1 = R_2 = CH_3$ **2c**: $R_1 = R_2 = H$

2b: $R_1 = R_2 = OCH_3$

The ^{1}H NMR spectra were recorded on Hitachi-Perkin-Elmer R24B (60 MHz) or Bruker XL 500 (500 MHz) instruments and IR spectra on a Shimadzu IR-470 spectrophotometer. The melting points were measured on an electrothermal digital melting point apparatus and are uncorrected.

General Procedure for the Preparation of the N-aryl-N′-[2-amino-1,2-dicyanovinyl]formamidines (2a–c): The aromatic amines (1.01 g, 6.07 mmol) were added to a suspension of **1** (1.00 g, 6.09 mmol) in dry ethanol or ethyl acetate, which contained aniline hydrochloride (0.02%). The mixtures were stirred at room temperature until TLC (9 : 1 chloroform/ethanol eluant) showed that all the formimidates had disappeared (usually 3 to 4 h) and the amidines were isolated by filtration. In most cases the products were pale green to white. The precipitates were washed with dry diethyl ether and were dried under vacuum to give the analytically pure products **2a–c.**

(3,4-Dimethylphenyl)-(Z)-N-[2-amino-1,2-dicyanovinyl]formamidine (2a, $C_{13}H_{13}N_5$): m.p. 124–126°C (decomp.), yield 87%; δ_H (300 MHz, d_6-DMSO) 2.15 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 6.31 (br s, 2H, NH_2), 6.65 (d, 1H, $^3J_{8,7}$ 8.0 Hz), 7.12–7.18 (complex m, 3H, H7, H11 and H5), 9.94 (br s, 1H, NH) ppm; ν_{max} (Nujol mull) 3450 s, 3320 s, 3240 s (NH str.), 2235 s (CN str.), 2190 s (CN str.), 1645 m (C=N str.), 1590 m (NH bend), 1570 s, 1510 s, 1300 s, 1250 w, 1225 s, 1160 s, 1140 s, 1135 s, 1020 s, 960 s, 935 s, 820 s, 790 s, 760 s cm^{-1}.

(3,4-Dimethoxyphenyl)-(Z)-N-[2-amino-1,2-dicyanovinyl]formamidine (2b, $C_{15}H_{19}N_5O_2$): m.p. 137–139°C (decomp.), yield 92%; δ_H (300 MHz, d_6-DMSO) 3.65 (s, 6H, 2 x OCH_3), 6.15 (br s, 2H, NH_2), 6.73 (d, 1H, $^3J_{8,7}$ 8.5 Hz, H8), 7.45–7.70 (br complex m, 3H, H7, H11 and H5), 9.75 (br s, < 1H, NH) ppm; ν_{max} (Nujol mull) 3450 s, 3325 s, 3100 s (N—H str.) 2210 s (CN str.), 2105 s (CN str.), 1630 s (C=N str.), 1600 m (NH bend), 1580 s, 1510 s, 1375 s, 1255 m, 1230 s, 1165 s, 1145 s, 1130 s, 960 w, 870 s cm^{-1}.

Benzyl-(Z)-N-[2-amino-1,2-dicyanovinyl]formamidine (2c, $C_{11}H_{11}N_5$): m.p. 90–92°C (decomp.), yield 89%; δ_H (300 MHz, d_6-DMSO) 4.58 (d, 2H, $J_{6,NH}$ 6Hz, CH_2), 6.12 (s, 2H, NH_2), 7.21–7.33 (m, 5H, Ph), 7.75 (d, 1H, $J_{5,NH}$ 6Hz, H5), 8.17 (br s, 1H, NH) ppm; ν_{max} (Nujol mull) 3350 s, 3260 s, 3105 s (N—H str.), 2215 s (CN str.), 2110 s (CN str.), 1640 s (C=N str.), 1610 m (NH bend), 1570 s, 1500 s, 1370 s, 1250 m, 1200 s, 1160 s, 1145 s, 1130 s, 965 w, 860 s cm^{-1}.

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