

NITRILE SPLITTING IN 2-AMINO- 1-(ARYLMETHYLENEAMINO)- 5-ARYL-3,4-DICYANOPYRROLES

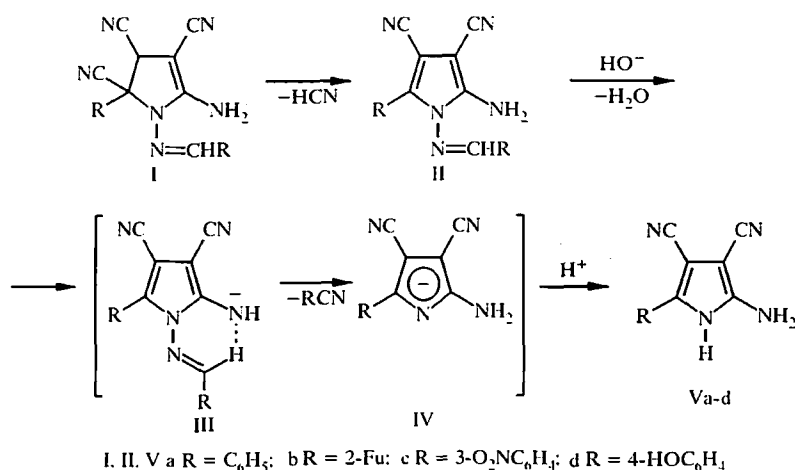
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Nitrile splitting of the N-N bond with formation of 2-amino-5-aryl-3,4-dicyanopyrroles and the corresponding benzonitrile occurs when 2-amino-5-aryl-1-(arylmethyleneamino)-3,4-dicyanopyrroles are boiled in DMSO in the presence of alkali.

Azomethine compounds react with 1,1,2,2-tetracyanoethane forming N-substituted derivatives of pyrroles [1, 2]. Yet the synthesis of N-unsubstituted compounds by this method is not possible because of instability of the corresponding imines. However these compounds are of interest for further use, since there is the possibility of obtaining of glycosides and condensed systems with pyrrolopyrimidine structures from them.

Pyrroles undergo nitrile splitting at the N-N bond under the influence of alkali [5]. The presence of analogous structural unit in 2-amino-1-(arylmethyleneamino)-5-aryl-3,4-dicyanopyrroles II, synthesized by the interaction of 1,1,2,2-tetracyanoethane with aldehyde azines [2], suggests the possibility of such a splitting and its use for the synthesis of NH-pyrroles. This suggestion is based on mass spectrometric data for these pyrroles in which the main fragmentation pathway is scission of the N-N bond [4].

The starting aryl-substituted pyrrolines I for the study of aminonitrile splitting were synthesized by the reaction of 1,1,2,2-tetracyanoethane with azines of aromatic aldehydes by a known method [2]. They were converted into the pyrroles II by boiling in DMF. The aromatic derivatives II were more stable than the alkyl derivatives, and remained unchanged on prolonged boiling in such a high-boiling solvent as DMSO, however they were completely converted into 2-amino-5-aryl-3,4-dicyanopyrroles Va-d by boiling in the presence of alkali for 1-2 h.



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Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 12, pp. 1627-1629, December, 1999. Original article submitted August 3, 1998.

TABLE 1. Characteristics of Compounds Ic,d, IIc,d, and Va-d

Compound	Empirical formula	Found, % Calculated, %			mp, °C	IR spectra, cm ⁻¹	Yield, %
		C	H	N			
Ic	C ₂₀ H ₁₂ N ₄ O ₄	<u>56.15</u> 56.08	<u>2.89</u> 2.82	<u>26.07</u> 26.16	165-167 dec.	3440-3220, 1640 (NH ₂), 2205, 2265 (C≡N), 1615 (C=N)	96
Id	C ₂₀ H ₁₂ N ₄ O ₂	<u>64.95</u> 64.86	<u>3.87</u> 3.81	<u>22.53</u> 22.69	154-156 dec.	3450-3190, 1650 (NH ₂), 2260, 2270 (C≡N), 1615 (C=N)	40
IIc	C ₁₉ H ₁₁ N ₄ O ₄	<u>56.97</u> 56.86	<u>2.84</u> 2.76	<u>24.29</u> 24.43	224-225	3330-3140, 1650 (NH ₂), 2200, 2230 (C≡N), 1615 (C=N)	72
IIId	C ₁₉ H ₁₁ N ₄ O ₂	<u>66.59</u> 66.47	<u>3.88</u> 3.82	<u>20.25</u> 20.40	246-247	3470-3260, 1630 (NH ₂), 2205, 2235 (C≡N), 1605 (C=N)	55
Va	C ₁₂ H ₈ N ₄	<u>69.29</u> 69.22	<u>3.92</u> 3.87	<u>26.79</u> 26.91	276-277	3455-3240, 1630 (NH ₂), 2230 (C≡N), 3200 (N-H)	56
Vb	C ₁₀ H ₆ N ₄ O	<u>60.73</u> 60.61	<u>3.12</u> 3.05	<u>28.15</u> 28.27	255-256	3450-3245, 1630 (NH ₂), 2230 (C≡N), 3200 (N-H)	65
Vc	C ₁₂ H ₇ N ₄ O ₂	<u>56.99</u> 56.92	<u>2.85</u> 2.79	<u>27.54</u> 27.66	287-288	3450-3230, 1625 (NH ₂), 2225 (C≡N), 3200 (N-H)	60
Vd	C ₁₂ H ₈ N ₄ O	<u>64.37</u> 64.28	<u>3.51</u> 3.60	<u>24.87</u> 24.99	289-290	3450-3240, 1635 (NH ₂), 2230 (C≡N), 3200 (N-H)	52

A proton is probably removed under the influence of alkali to give N-anion III which is converted into pyrrole V by splitting of the N-N bond and transfer of a proton with the intermediate formation of anion IV.

The presence of an electron-acceptor group in the aromatic substituent would stabilize the anion III considerably and facilitate the acceleration of the reaction: splitting of pyrroles II occurs practically twice as fast, but the impossibility of such splitting in 1,2-di(benzylideneamino)-3,4-dicyano-5-phenylpyrrole under analogous conditions confirms that the proton is removed from the amino group. Benzonitrile liberated during formation of pyrrole Va was identified chromatographically in the distillate after removal of part of the solvent from the reaction mixture.

The IR spectra of compounds V (Table 1) contain broad stretching vibration bands of the pyrrole NH at 3200 cm⁻¹ but no absorption band for the C=N bond at 1605-1615 cm⁻¹ occurs. However the structure of pyrroles V was confirmed by independent synthesis of compound Va prepared by hydrolysis of 2-(N-benzylideneamino)-5-phenyl-3,4-dicyanopyrrole [5]. Samples synthesized by the two different methods have identical IR spectra and no depression of the melting point was observed with a mixture of the two.

Thus heating of 2-amino-1-(arylmethyleneamino)-5-aryl-3,4-dicyanopyrroles in DMSO in the presence of alkali results in nitrile splitting with formation of N-unsubstituted 2-amino-5-aryl-3,4-dicyanopyrroles.

EXPERIMENTAL

The course of reactions and the purity of synthesized products were monitored by TLC on Silufol UV-254 plates with detection in UV light or iodine vapor. IR spectra of nujol mulls were recorded with a UR-20 spectrometer. Chromatography was carried out with an LKhM-8MD apparatus, with a thermal conductivity detector, 3000 × 3 mm column filled with 5% of silicone XE-60 on Chromaton N-AW-DMCS, column temperature 120°C, and helium as carrier gas (40 ml/min).

2-Pyrrolines I and Pyrroles II were prepared by a known method [2]. The characteristics of the synthesized compounds Ic,d, IIc,d are cited in Table I.

2-Amino-5-aryl-3,4-dicyanopyrroles (Va-d). Mixture of compound II (1 mmol) and sodium hydroxide (0.01 g, 0.25 mmol) in DMSO (5-8 ml) was boiled for 1-2 h. After the reaction mixture had been acidified with an excess of acetic acid, the diluted solution was saturated with sodium chloride. The precipitate was filtered off, washed with water and isopropanol and recrystallized from isopropanol.

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