NEW REACTION OF MALONONITRILE AND ARYLIDENE- AND 1-ARYLETHYLIDENEMALONONITRILES

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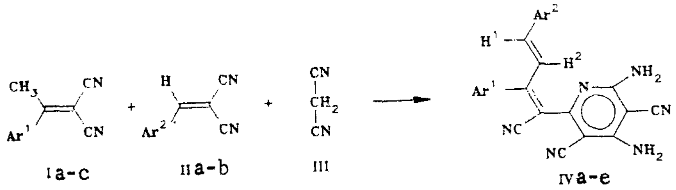
The dimerization of 1-arylethylidenemalononitriles I [1] and their cross-dimerization with arylidenemalononitriles II [2], as well as an example of the dimerization of isopropylidenemalononitrile in the presence of malononitrile (III) with the formation of 1-amino-3-dicyanomethyl-3,5,5-trimethyl-1-cyclohexene-2,6,6-tricarbonitrile [3], have been previously described. However, as a result of the cross-dimerization of nitriles Ia-c and IIa, b in the presence of malononitrile (III), instead of the expected 1-amino-3-dicyanomethyl-3,5-diaryl-1-cyclohexene-2,6,6-tricarbonitriles, we obtained the previously unknown 2,4-diamino-3,5-dicyano-6-(2,4-diaryl-1-cyano-1,3-butadienyl)pyridines IVa-e.



I a Ar^1=C$_6$H$_5$, b Ar^1=4-(C$_6$H$_5$)C$_6$H$_4$, c Ar^1=4-CH$_3$C$_6$H$_4$; II a Ar^2=C$_6$H$_5$, b Ar^2=4-FC$_6$H$_4$; IV a, e Ar^1=C$_6$H$_5$, b, d Ar^1=4-CH$_3$C$_6$H$_5$, c Ar^1=4-(C$_6$H$_5$)C$_6$H$_4$; a, c, d Ar^2=C$_6$H$_5$, b, e Ar^2=4-FC$_6$H$_4$

Mixtures of I-III (0.01 mole each) and several drops of 2 N KOH in ethanol were maintained at 30-40°C for 10-15 min, after which they were heated to the boiling point. The 2,4-diamino-3,5-dicyano-6-(2,4-diaryl-1-cyano-1,3-butadienyl)pyridines IVa-e that crystallized out from the stirred reaction mixtures were removed by filtration after cooling of the reaction mixtures.

Pyridine IVa. This compound was obtained in 50% yield and had mp 261-263°C (from acetonitrile). PMR spectrum (D$_3$-acetonitrile): 6.17 (4H, broad s, 2 NH$_2$), 6.57 (1H, d, J = 15.8 Hz, 1-H), 7.17 (1H, d, J = 15.8 Hz, 2-H), and 7.2-7.7 ppm (10H, m, aromatic protons).

Pyridine IVb. This compound was obtained in 46% yield and had mp 284-286°C (sublimed). PMR spectrum (d$_6$-acetone): 2.35 (3H, s, CH$_3$), 6.63 (1H, d, J = 15.8 Hz, 1-H), 6.90 and 6.97 (2H each, broad s, NH$_2$), 7.27 (1H, d, J = 15.8 Hz, 2-H), and 7.10-7.55 ppm (8H, m, aromatic protons).

Pyridine IVc. This compound was obtained in 43% yield and had mp 278-280°C (from dioxane hexane). PMR spectrum (D$_6$-acetone): 6.75 (1H, d, J = 15.8 Hz, 1-H), 6.92 and 7.00 (2H each, broad s, NH$_2$), 7.35 (1H, d, J = 15.8 Hz, 2-H), and 7.30-8.0 ppm (14H, m, aromatic protons).

Pyridine IVd. This compound was obtained in 50% yield and had mp 271-273°C (from dioxane hexane). PMR spectrum (D$_6$-acetone): 2.47 (3H, s, CH$_3$), 6.63 (1H, d, J = 15.8 Hz, 1-H), 6.90 and 6.98 (2H each, broad s, NH$_2$), 7.30 (1H, d, J = 15.8 Hz, 2-H), and 7.30-7.45 ppm (9H, m, aromatic protons).

Pyridine IVe. This compound was obtained in 62% yield and had mp 266-267°C (from acetonitrile). PMR spectrum (D$_6$-acetone): 6.63 (1H, d, J = 15.8 Hz, 1-H), 6.90 and 6.97 (2H each, broad s, NH$_2$), 7.33 (1H, d, J = 15.8 Hz, 2-H), and 7.10-7.63 ppm (9H, m, aromatic protons).

The results of elementary analysis of pyridines IVa-e were close to the calculated values. Intense peaks of the corresponding molecular ions were observed in the mass spectra of

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these compounds. The structure of pyridine IVa was proved unambiguously by x-ray diffraction analysis. The mechanism of this reaction and the spectral properties of the synthesized compounds IV will be described in special communications.

LITERATURE CITED

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