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A method for the synthesis of stable aryldiazonium salts possessing a 1,1,2,3,3-pentacyanopropenide anion

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ABSTRACT

A method for the synthesis of stable aryldiazonium salts possessing an organic 1,1,2,3,3-pentacyanopropenide anion is reported.

Aryldiazonium salts have very useful applications in organic synthesis as well as in industry, in the synthesis of azo dyes.[1] Aryldiazonium salt formation followed by azocoupling is applied as a sensitive reaction to nitrite anion (Greass reagent). These salts may be used as surface initiators of polymerization[2] and as light-sensitive materials[3] and most are known to have a low level of stability. Their stability depends on the aromatic ring substituents and the nature of the anion. Tetrafluoroborates,[4] tosylates,[5] and disulfonimides[6] are the most stable salts. The presence of inorganic anions in these substances decreases or makes dissolution of these salts impossible in many organic solvents.

Of the organic anions which can stabilise aryldiazonium cations it is necessary to note the 1,1,2,3,3-pentacyanopropenide anion. 1,1,2,3,3-Pentacyanopropene itself is a strong CH-acid, its strength being comparable to 12 M sulfuric acid ($pK_a < -8.5$).[7] Earlier several aryldiazonium salts with this anion were produced.[8] However, they were obtained via an exchange reaction in a diphasic system of solvents: water–ethyl acetate, from commercially accessible tetrafluoroborates. The tetramethylammonium 1,1,2,3,3-pentacyanopropenide that is used as a reagent in this patent was also produced of tetracyanoethylene. We found that the malononitrile autocoupling reaction[9] in the presence of SeO_2 made this anion available.

Herein, a method for obtaining a number of aryldiazonium salts of 1,1,2,3,3-pentacyanopropene **1–10** was developed via the exchange reaction of pyridinium 1,1,2,3,3-pentacyanopropenide with aryldiazonium chlorides in aqueous medium (Scheme 1).[10] Aryldiazonium salts in the form of chlorides were produced directly before the exchange reaction with the appropriate primary arylamines without isolation.[11] After the pyridinium 1,1,2,3,3-pentacyanopropenide has been added as a hot solution to the reaction mixture, the precipitation of the aryldiazonium 1,1,2,3,3-pentacyanopropenides was observed. The presence of 1,1,2,3,3-pentacyanopropenide anion in salts **1–10** was confirmed by IR-spectra—intensive absorption band in the field of 2200 cm^{-1} and by ^{13}C NMR spectra - signals of cyano group 114.2, 114.9, 117.3 and carbon atoms at 58.0 (C-1′, 3′), 135.9 (C-2′). These are present in the spectra of pyridinium 1,1,2,3,3-pentacyanopropenide.

The resulting aryldiazonium 1,1,2,3,3-pentacyanopropenides[12] **1–10** were sufficiently stable and could be isolated. However, they can decay spontaneously and be polluted by admixtures, which is accelerated by heating and sunlight. Depending on the presence of substituents, the shelf-lives of these aryldiazonium salts can vary from days to several weeks and more. Salts with electron-acceptor substituents on the aromatic rings, **7** and **9**, were much more stable than salts with donor substituents, **2** and **3**, or without **1**. The latter representatives showed appreciable signs of decomposition within several hours after isolation, while salts **7** and **9** showed good stability and could be stored for more than a month below 0 °C. Highly polluted salt could be purified by reprecipitation from acetone by the addition of diethyl ether.

Aryldiazonium 1,1,2,3,3-pentacyanopropenides readily took part in azocoupling with phenol or reaction with *N*,*N*-dimethylaniline with the formation of azocoupling products. Due to the solubility of these salts, this reaction could be carried out in polar

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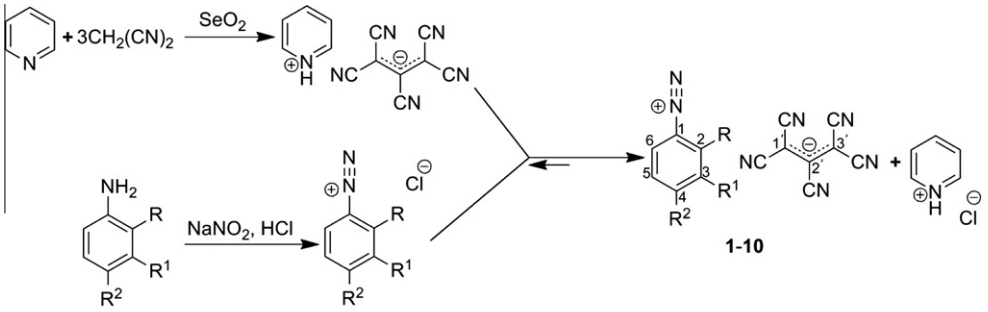

1. R=R^1=R^2=H; **2**. R=R^1=H, R^2=CH_3; **3**. R=R^1=H, R^2=OCH_3; **4**. R=OCH_3, R^1=R^2=H; **5**. R=R^1=H, R^2=OH; **6**. R=R^1=H, R^2=COOH; **7**. R=R^1=H, R^2=NO_2; **8**. R=R^1=H, R^2=$C(O)CH_3$; **9**. R=R^1=H, R^2=SO_2NH_2; **10**. R-R^1=$(CH)_4$, R^2=H.

Scheme 1.

organic solvents, for example, in acetone. It was not necessary to apply any additional activation in the azocoupling with *N*,*N*-dimethylaniline. However, the azocoupling with phenol required the addition of an aqueous solution of alkali. The aryldiazonium 1,1,2,3,3-pentacyanopropenides dissolved in a number of dipolar aprotic solvents, such as dimethylformamide, dimethylsulfoxide, and hexamethylphosphotriamide were observed to decompose with elimination of nitrogen.

In conclusion, we offer a new, simple, and efficient method for the synthesis of aryldiazonium salts possessing a 1,1,2,3,3-pentacyanopropenide anion using aryldiazonium chlorides and pyridinium 1,1,2,3,3-pentacyanopropenide by means of exchange reaction in water solution. The simplicity of the procedure, good yields, and sufficiently stable products are the main advantages of this method.

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12. *General procedure.* **Warning:** some diazonium salts can be explosive! The primary arylamine (2.1 mmol) was dissolved in a mixture of concentrated hydrochloric acid (3 ml) and of water (3 ml) and cooled to 0 °C. A solution 0.145 g (2.1 mmol) of $NaNO_2$ in water (1 ml) was added dropwise with stirring within 1 h. Then, 20 ml of a hot (to 70 °C) aqueous solution of 0.5 g (2 mmol) of pyridinium 1,1,2,3,3-pentacyanopropenide was added to a reaction mixture, without stopping stirring. As a result of the exchange reaction the aryldiazonium 1,1,2,3,3-pentacyanopropenide was precipitated from the solution. This salt was filtered and was washed with water (3 × 5 ml). The salt was dried and purified by reprecipitation from acetone solution (1.0–1.5 ml) by the addition of diethyl ether (10–15 ml) if necessary.
Compound **1**: Yield: 81%, mp ⩾82 °C (dec). IR (KBr): ν_{max} 2286, 2203 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6): δ 8.89 (d, J = 7.9 Hz, 2H), 8.42 (t, J = 7.3 Hz, 1H), 8.13 (t, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, acetone-d_6): δ 120.1 (C-1), 132.8 (C-3, 5), 133.7 (C-2, 6), 142.7 (C-4).
Compound **2**: Yield: 88%, mp ⩾91 °C (dec). IR (KBr): ν_{max} 2264, 2201 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6): δ 2.67 (s, 3H), 7.91 (d, J = 8.5 Hz, 2H), 8.73 (d, J = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, acetone-d_6): δ 23.0 (CH_3), 112.3 (C-1), 133.4 (C-3, 5), 133.7 (C-2, 6), 156.6 (C-4).
Compound **3**: Yield: 81%, mp ⩾107 °C (dec). IR (KBr): ν_{max} 2234, 2203 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6): δ 4.17 (s, 3H), 7.56 (d, J = 9.5 Hz, 2H), 8.79 (d, J = 9.5 Hz, 2H); ^{13}C NMR (100 MHz, acetone-d_6): δ 58.2 (CH_3), 103.5 (C-1), 118.7 (C-3, 5), 137.1 (C-2, 6), 171.0 (C-4).
Compound **4**: Yield: 81%, mp ⩾110 °C (dec). IR (KBr): ν_{max} 2264, 2197 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6): δ 4.35 (s, 3H), 7.55 (t, J = 7.9 Hz, 1H), 7.79 (d, J = 8.9 Hz, 1H), 8.33–838 (m, 1H), 8.65 (dd, J = 8.5, 1.5 Hz, 1H); ^{13}C NMR (100 MHz, acetone-d_6): δ 59.6 (CH_3), 102.5 (C-1), 115.9 (C-3), 124.3 (C-5), 133.2 (C-6), 145.6 (C-4), 164.3 (C-2).
Compound **5**: Yield: 82%, mp ⩾123 °C (dec). IR (KBr): ν_{max} 2241, 2205 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6): δ 4.44 (s, 1H), 7.38 (d, J = 9.4 Hz, 2H), 8.69 (d, J = 9.3 Hz, 2H); ^{13}C NMR (100 MHz, acetone-d_6): δ 101.5 (C-1), 120.1 (C-3, 5), 137.5 (C-2, 6), 170.6 (C-4).
Compound **6**: Yield: 60%, mp ⩾118 °C (dec). IR (KBr): ν_{max} 2289, 2203 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6): δ 8.58 (d, J = 9.0 Hz, 2H), 9.02 (d, J = 9.0 Hz, 2H); ^{13}C NMR (100 MHz, acetone-d_6): δ 115.9 (C-1), 132.7 (C-3), 133.0 (C-5), 134.1 (C-2, 6), 142.4 (C-4), 164.7 (COOH).
Compound **7**: Yield: 84%, mp ⩾119 °C (dec). IR (KBr): ν_{max} 2298, 2209 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6): δ 8.88 (d, J = 9.1 Hz, 2H), 9.25 (d, J = 9.1 Hz, 2H); ^{13}C NMR (100 MHz, acetone-d_6): δ 122.3 (C-1), 127.6 (C-3, 5), 135.8 (C-2, 6), 155.2 (C-4).
Compound **8**: Yield: 81%, mp ⩾99 °C (dec). IR (KBr): ν_{max} 2287, 2201 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6): δ 2.78 (s, 3H), 8.56 (d, J = 9.0 Hz, 2H), 9.04 (d, J = 9.0 Hz, 2H); ^{13}C NMR (100 MHz, acetone-d_6): δ 119.7 (C-1), 131.6 (C-3, 5), 134.4 (C-2, 6), 146.8 (C-4), 196.6 (CO).
Compound **9**: Yield: 79%, mp ⩾120 °C (dec). IR (KBr): ν_{max} 2293, 2207 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6): δ 7.38 (s, 2H), 8.51 (d, J = 8.5 Hz, 2H), 9.11 (d, J = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, acetone-d_6): δ 120.0 (C-1), 130.1 (C-3, 5), 135.2 (C-2, 6), 155.7 (C-4).
Compound **10**: Yield: 90%, mp ⩾100 °C (dec). IR (KBr): ν_{max} 2237, 2205 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6): δ 8.03–8.07 (m, 1H), 8.17 (t, J = 8.1 Hz 1H), 8.18–8.22 (m, 1H), 8.50 (d, J =8.3 Hz, 1H), 8.62 (d, J = 8.5 Hz, 1H), 9.05 (d, J = 8.3 Hz, 1H), 9.39 (dd, J = 7.9, 0.9 Hz, 1H); ^{13}C NMR (100 MHz, acetone-d_6): δ 120.9 (C-1), 122.8 (C-3), 127.6 (C-8), 128.8 (C-9), 131.2 (C-6), 131.8 (C-2), 133.9 (C-7), 134.2 (C-10), 138.6 (C-5), 144.8 (C-4).