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Oxidative coupling of malononitrile with formation of 1,1,2,3,3-pentacyanopropene salts

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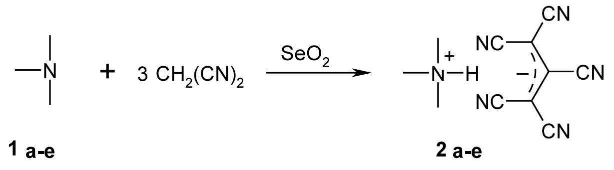
Abstract—A simple and convenient route for the synthesis of 1,1,2,3,3-pentacyanopropene salts is reported. These salts are formed by interaction of malononitrile with SeO_2 in presence of organic *N*-containing bases or pyridinium salts. © 2002 Elsevier Science Ltd. All rights reserved.

1,1,2,3,3-Pentacyanopropene (PCP) is one of the strongest CH-acids known. PCP salts, like other derivatives of superacids, are of importance in electrochemical technologies and in different fields of organic synthesis.[1]

PCP salts have usually been prepared by the reaction of bases with tetracyanoethene (TCNE)[2a–c] or with mixtures of TCNE and malononitrile.[3] These salts are also formed in reactions of hexacyanocyclopropane[4] or carboethoxypentacyanocyclopropane[5] with aliphatic amines and pyridine, and in reactions of aromatic *N*-oxides with TCNE.[6]

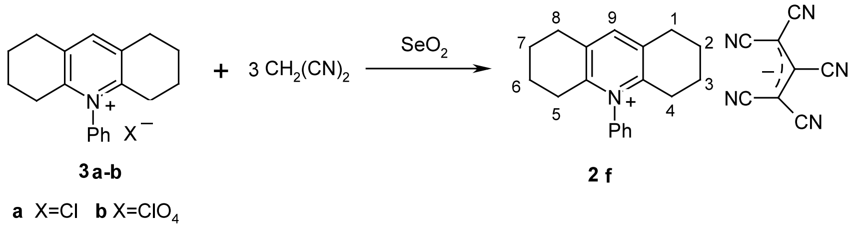


Scheme 1. **a**, triethylamine; **b**, pyridine; **c**, α-picoline; **d**, quinoline; **e**, benzimidazole.

We report a very simple and convenient method to synthesise PCP salts by selenium dioxide-promoted oxidative coupling of malononitrile in the presence of an *N*-containing organic base **1a**–**e** (Scheme 1) or a pyridinium salt **3a**,**b** (Scheme 2).[7] Dimethylsulfoxide is the best solvent for these reactions. The reactions are exothermic and evolution of CO_2 is observed.

The PCP salts **2a**–**e** are identical with authentic samples (IR). The PCP-anion ($m/z=166$) was observed in the mass spectra (APCI, negative mode) of all the salts; the cations of the corresponding bases were observed in the mass spectra of the salts **2d** and **2e** (APCI, positive mode). An X-ray structure analysis of salt **2e** was carried out (Fig. 1).[8] Exchange reactions **2b**→**2a**, **2b**→**2d** and **2b**→**2f** were also carried out.[9]

We hypothesise that the formation of the PCP-anion is the result of oxidative coupling of two malononitrile molecules to give intermediate TCNE,[3] followed by the usual formation of the PCP-anion. The HCN eliminated in this reaction is probably oxidised to CO_2 and



Scheme 2.

Keywords: oxidative coupling; malononitrile; 1,1,2,3,3-pentacyanopropene salts.

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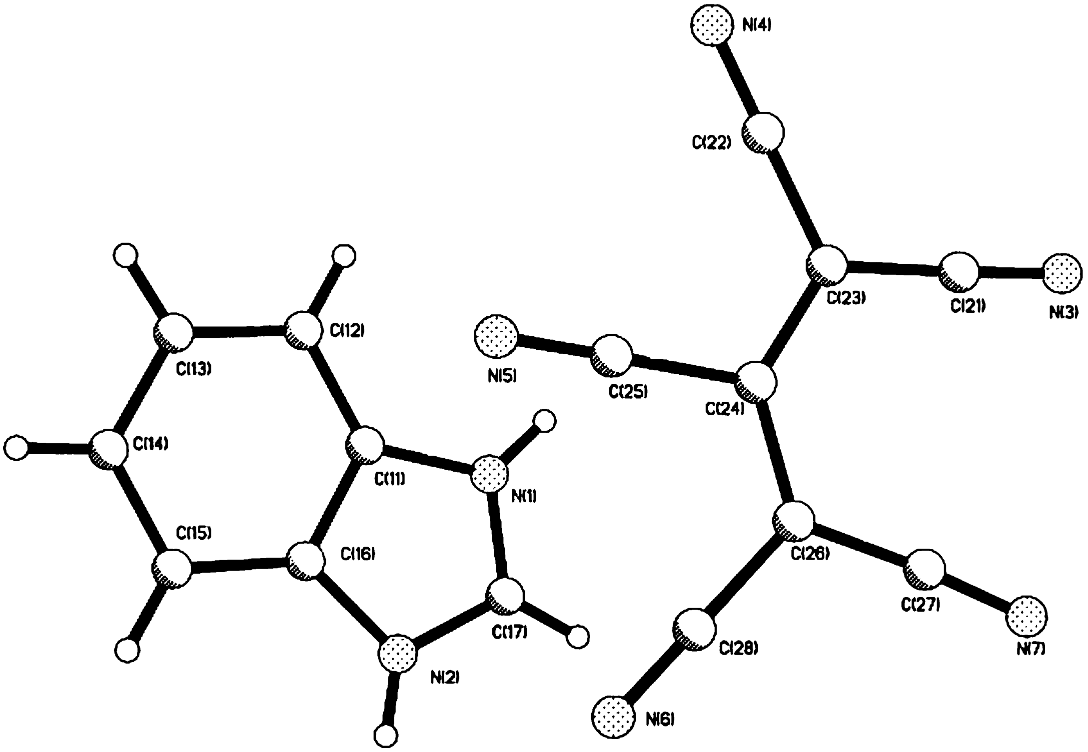

Figure 1. X-Ray structure of compound **2e**.

N_2 (the evolution of HCN from the reaction mixture was not observed).

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7. **Typical experimental procedure for PCP salt formation**:
   (a) The organic base **1** (15 mmol) and malononitrile (0.5 g, 7.5 mmol) were dissolved in DMSO (3 ml), then SeO_2 (1.65 g, 15 mmol) was added with stirring. The mixture became reddish and turbid in 2–10 min, then transparent and intensive gas evolution was observed with the temperature increasing to 50–70°C. The mixture was diluted with water after cooling, the precipitate was filtered and crystallised from water.
   (b) Pyridinium salts **3a**,**b** (3.5 mmol) and malononitrile (0.54 g, 8.2 mmol) were dissolved in 7 ml DMSO, then SeO_2 (0.8 g, 7.2 mmol) was added; the reaction proceeded as above. The filtered precipitate was purified by chromatography on Al_2O_3 (hexane–ethyl acetate 3:1).
   Selected data for compounds **2a**–**f** is listed as follows: yield, %; melting point, °C (literature melting point, °C),[2a] IR spectra, ν, cm^{-1}; mass spectra (chemical ionisation), m/z (PCP anion).
   2a: 70; 142–144 (126–128); 2203 (2211), 1514 (1612); 166.
   2b: 68; 164–165 (167–168); 2202 (2212), 1500 (1623); 166.
   2c: 88; 92–94 (85–87); 2204, 1511; 166.
   2d: 95; 142–144 (165–166); 2203, 1520; 166.
   2e: 93; 228–230; 2204, 1487, 15; 166.
   2f: 50; 112–114; 2199, 1506; 166; ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.00 (s, 1H, H-9), 7.71 (m, 3H, H-Ph), 7.34 (d, $J=2.45$, 1H, H-Ph), 7.30 (d, $J=1.71$, 1H, H-Ph), 3.03 (s, 4H, H-4, 5), 2.5 (s, 4H, H-1, 8), 1.87 (m, 8H, H-2, 3, 6, 7).
8. The deposition number at the Cambridge Crystallographic Data Centre is CCDC 190069.
9. **The exchange reaction of PCP salts**:
   The excess of triethylamine (**2b**→**2a**), quinoline (**2b**→**2d**) or *N*-phenylsymm.octahydroacridinium chloride (**2b**→**2f**) were added to a hot water solution of **2b**. The mixture was heated to boiling, the precipitate was filtered after cooling. The PCP salts **2a** and **2d** were identical with samples obtained from malononitrile and the corresponding bases. The PCP salt **2f** was purified by chromatography on Al_2O_3; it was identical with a sample obtained from malononitrile and pyridinium salts **3a**,**b**.