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Aromatic Ring Opening of Pyridinium Salts using Carbanions formed from Malononitrile and Ethyl Cyanoacetate

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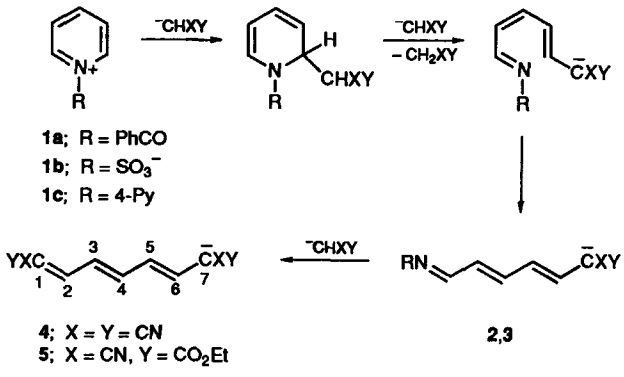
Carbanions formed from malononitrile and ethyl cyanoacetate have been found to react with pyridinium salts *via* ring-opening to form 1,1,7,7-tetrasubstituted hepta-1,3,5-trienes.

The interaction of activated pyridinium salts with nucleophiles, leading to conjugated polyene structures, is of continuing interest.[1,2] Nevertheless, it is not clear which factors determine the occurrence of aromatic ring opening rather than the formation of 1,2- and/or 1,4-dihydropyridines,[3,4] chinone-like structures,[5,6] substituted pyridines[7] or nucleophilic attack on an exocyclic group.[8]

We have studied the interaction of activated pyridinium salts **1a–c** with sodio derivatives of malononitrile and ethyl cyanoacetate, in order to obtain compounds **2–5**. Compounds **4** and **5** have previously been obtained in good yields, starting from glutaconaldehyde and its derivatives.[9] We propose the aromatic ring opening of the pyridinium salt, when treated with carbanions of malononitrile and ethyl cyanoacetate as a method for the synthesis of the title compounds. It should be noted that the alternative synthetic approach to **4** or **5** involves gradual construction of the hepta-1,3,5-triene system from aliphatic components using the Wittig or Reformatsky reactions.[10]



Scheme 1

Carbanions of malononitrile and ethyl cyanoacetate were found to react smoothly with **1a–c** in EtOH or *N*,*N*-dimethylformanide (DMF), to give compounds **4** and **5** in good yields (Scheme 1, Table 1).†‡

Table 1

Salt	Heptatriene yield (%)	
1	**4**	**5**
a	55	51
b	61	68
c	69	70

Sodio derivatives of acetylacetone, ethyl malonate, ethyl nitroacetate and nitromethane react with **1a, b** by another possible mechanism: nucleophilic attack at the exocyclic group of the ring and an investigation of the chemistry of **1c** is now in progress. No products of types **2** or **3** were detected. We have shown that pyridinium salts **1a–c** readily undergo aromatic ring opening by carbanions formed from malononitrile and ethyl cyanoacetate. The resulting 1,1,7,7-tetrasubstituted hepta-1,3,5-triene systems are of great interest for the synthesis of heteroaromatic compounds,[11] for use as laser dyes and as potential anti-ulcer agents.

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† *Characterisation data* for tetrabutylammonium 1,1,7,7-tetracyanohepta-1,3,5-trien-1-ide **4**: UV (CH_2Cl_2) λ_{max}/nm 555, ϵ 91 000; ^{1}H NMR ($CDCl_3$) δ 7.03 (H^2, H^6, d, *J* 13 Hz), 6.93 (H^4, t, *J* 13 Hz), 6.03 (H^3, H^5, t, *J* 13 Hz), 1.05–3.14 (Bu_4N^+), ^{13}C NMR ($CDCl_3$) δ 155.61 (C^2, C^6, dd), 153.68 (C^4, dt), 120.16 (CN, d), 117.96 (CN, d), 112.33 (C^3, C^5, dd), 55.62 (C^1, C^7, d), 13.53–58.90 (Bu_4N^+); IR (CH_2Cl_2) ν/cm^{-1} 908, 1000, 1152, 1184, 1312, 1484, 1560, 2192, 2880, 2968, 3012, 3384.

For 1,7-bis(ethoxycarbonyl)-1,7-dicyanonona-2,4,6-trien-1-ide **5**: UV (CH_2Cl_2) λ_{max}/nm 562, ϵ 93 000; ^{1}H NMR ($CDCl_3$) δ 7.55 (H^2, H^6, d, *J* 13 Hz), 7.06 (H^4, t, *J* 13 Hz), 6.02 (H^3, H^5, t, *J* 13 Hz), 4.13 (2×OCH_2, q, *J* 8 Hz), 1.26 (2Me, t, *J* 8 Hz), 0.98–3.13 (Bu_4N^+); ^{13}C NMR ($CDCl_3$) δ 162.96 (CO, s), 155.24 (C^4, dt), 153.30 (C^2, C^6, dd), 113.11 (2CN, s), 111.94 (C^3, C^5, dt), 79.58 (C^1, C^7, d), 59.74 (2×OCH_2, t), 13.89 (2Me, q), 13.48–58.87 (Bu_4N^+); IR (CH_2Cl_2)ν/cm^{-1} 874, 1006, 1080, 1134, 1198, 1280, 1330, 1368, 1388, 1482, 1562, 1668, 1750, 2188, 2892, 2968, 3008, 3404.

‡ A typical experimental procedure for preparation of **4** and **5** was as follows: 0.025 mol pyridinium salt **1a–c** was added gradually to a stirred solution of sodium dicyanomethanide or sodium cyanoethoxycarbonylmethanide in 50 ml absolute EtOH at 70 °C. The mixture was allowed to stand for 1 h, and then cooled to room temperature and stirred for 1 h. A solution of 0.02 mol Bu_4NBr in 15 ml H_2O was added to the resulting deep red, viscous mixture; the mixture was extracted with 3×30 ml CH_2Cl_2, dried over $MgSO_4$ and the solvent was evaporated. The deep violet oil was purified by column chromatography [silica gel, 2×50 cm $CHCl_3$–acetone (12:1)]. Yields of **4**: 55% (from **1a**), 61% (from **1b**), 69% (from **1c**); **5**: 51% (from **1a**), 68% (from **1b**), 70% (from **1c**).

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