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Electrochemical Cyclotrimerization of Cyanoacetic Ester into *trans*-1,2,3-Tricyanocyclopropane-1,2,3-tricarboxylate

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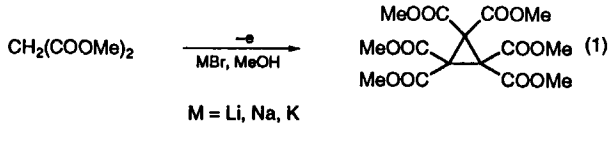
Electrolysis of cyanoacetic ester in the presence of NaBr in acetone or acetonitrile in the undivided cell leads to *trans*-1,2,3-tricyanocyclopropane-1,2,3-tricarboxylate.

Earlier we found that electrolysis of dimethyl malonate in the presence of bromides in methanol in the undivided cell at 50 °C results in the formation of cyclopropanehexacarboxylate in 50–60% yield,[1] reaction (1).



(1)

Recently we have found that reactions of this type are more general for C–H acids. Thus, cyanoacetic ester **1** under electrolysis in acetone or acetonitrile (but not in alcohols), in the presence of mediators–sodium iodides or bromides–in the undivided cell at 0–30 °C is stereoselectively transformed into *trans*-1,2,3-tricyanocyclopropane-1,2,3-tricarboxylate **2** (Table 1), reaction (2).

Table 1 Electrochemical cyclotrimerization of cyanoacetic ester in the presence of halides[a]

Electrolyte	Solvent	Temperature /°C	Electricity passed /F mol^{-1}	Conversion of **1** (%)	Yield of **2** (%)[b]
NaI	Acetone	0	1.2	46	80
NaI	Acetone	20	1.2	58	87
NaI	MeCN	20	1.2	47	68
LiBr	Acetone	20	1.2	59	62
NaI	Acetone	20	2.0	80	80(64)[c]
NaI	Acetone	20	2.8	91	75(68)[c]

[a] 30 mmol of **1**, 8 mmol of electrolyte in 20 ml of solvent, Pt- or C-anode, Fe-cathode, current density 110 mA cm^{-1}. [b] Based on **1** converted. [c] Yield of **2** based on **1** taken is given in parentheses.

The yield of cyclic ester **2** depends on the type of mediator. The maximum yield was achieved using NaI as mediator and electrolyte.

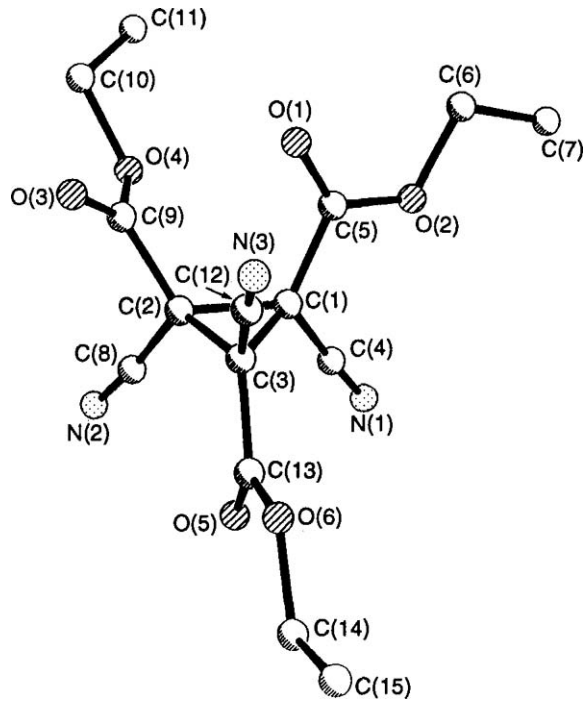
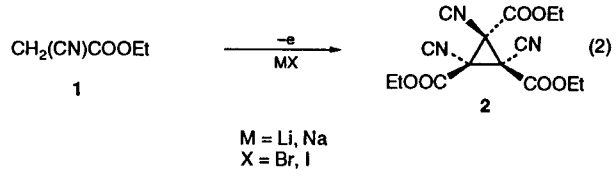


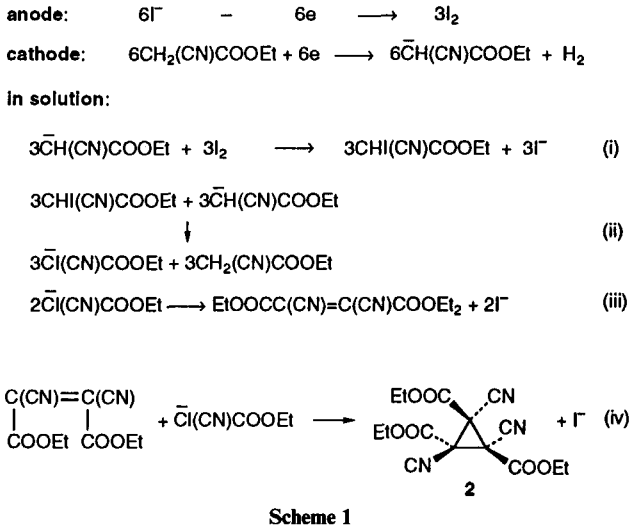
Fig. 1 Molecular structure of **2**. The main bond lengths (Å) and angles (°): C(1)–C(2) 1.529(4), C(1)–C(3) 1.564(4), C(2)–C(3) 1.515(4), C(3)C(1)C(2) 58.7(2), C(1)C(2)C(3) 61.8(2), C(2)C(3)C(1) 59.5(2).



The reaction is greatly sensitive to solvent. Electrolysis of cyanoacetic ester in ethanol in the presence of NaI results in low conversion of **1** and formation of a linear oligomeric mixture without any cyclic ester **2**. Using acetonitrile instead of acetone leads to decreasing yield of cyclic ester **2**.

Dimer EtOOCCH(CN)–CH(CN)COOEt and dehydrodimer EtOOCC(CN)=C(CN)COOEt were not found in the reaction mixture even under conditions in which a low conversion of cyanoacetic ester **1** was achieved.

The suggested reaction mechanism is given in Scheme 1.



Scheme 1

We suppose that stage (iv) is one of the quickest in the whole process. As a result even at low conversion of cyanoacetic ester **1** only cyclic ester **2** was found in the reaction mixture.

The structure of the *trans*-1,2,3-tricyanocyclopropane-1,2,3-tricarboxylate **2** was established by NMR spectroscopy and a single-crystal X-ray diffraction study (Fig. 1).†

In the molecule of **2** two ethoxycarbonyl groups are arranged on one side and one ethoxycarbonyl group on the opposite side of the cyclopropane ring (CPR) plane.

Two *cis*-arranged ethoxycarbonyl groups have a different orientation relative to CPR: the ethoxycarbonyl group at C(1) is *cis*-orientated and the one at C(2) is in an orthogonal orientation. The third *trans*-arranged ethoxycarbonyl group at C(3) the same as at C(1), is also *cis*-orientated.

Two *cis*-orientated (relative to CPR) ethoxycarbonyl groups are probably conjugated with CPR electrons.[2]

The result of the absence of conjugation with the orthogonal ethoxycarbonyl group at C(2) is a difference in bond lengths in CPR of molecule **2**. Bond C(1)–C(3) opposite to the non-conjugated ethoxycarbonyl group at C(2) is essentially longer [1.564(4) Å] compared to two others [1.529(4) Å for C(1)–C(2) and 1.515(4) Å for C(2)–C(3)]. The latter two bonds are similar in length to those in hexamethoxycarbonylcyclopropane in which all methoxycarbonyl groups are *cis-gauche*-orientated relative to CPR [1.505–1.516(5) Å][3], in hexacyanocyclopropane [1.530(6) Å][4] and in unsubstituted cyclopropane [1.510 Å][5].

References

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† *Spectral data for* **2**: ^{1}H NMR ($CDCl_3$): δ 1.40 (t, 6H, 2Me), 1.45 (t, 3H, Me), 4.45 (q, 4H, $2OCH_2$), 4.53 (q, 2H, OCH_2). ^{13}C NMR ($CDCl_3$): δ 13.5 (q), 13.6 (q), 24.7 (s), 66.2 (t), 66.5 (t), 107.9 (s), 108.6 (s), 157.2 (s), 157.6 (s).

Crystal data for **2**: $C_{15}H_{15}N_3O_6$, $M=333.3$, monoclinic, space group, $P2_1/c$ $a=9.062(2)$ Å, $b=21.515(7)$ Å, $c=8.212(3)$ Å, $\beta=92.25(2)°$, $Z=4$: $V=1600.0(9)$ Å^3, $D_c=1.384$ g cm^{-3}. Intensities of 2166 reflections with $I \geqslant 2\sigma(I)$ were measured at −116 °C with a Siemens P3/PC difractometer [λ(MoKα) = 0.71073 Å, graphite monochromator $\Theta/\Theta 2$ scan, $\Theta < 30°$]. The structure was solved by direct methods and refined in full-matrix anisotropic approximation for non-hydrogen atoms. A difference Fourier synthesis clearly revealed all H atoms which were refined isotropically in the final least-squares cycles. The final discrepancy factors are $R=0.048$, $R_w=0.050$. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, *Mendeleev Commun.*, 1993, Issue 1.