Electrocatalytic Transformation of 1,1,2,2-Tetracyanocyclopropanes into Bicyclic Pyrrolines

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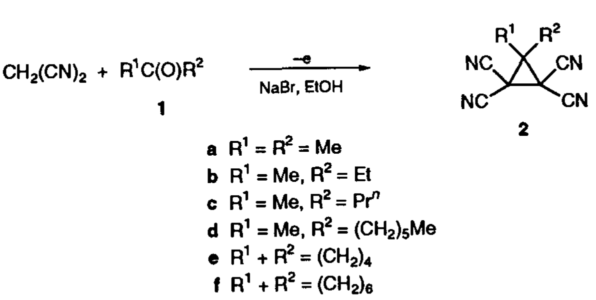
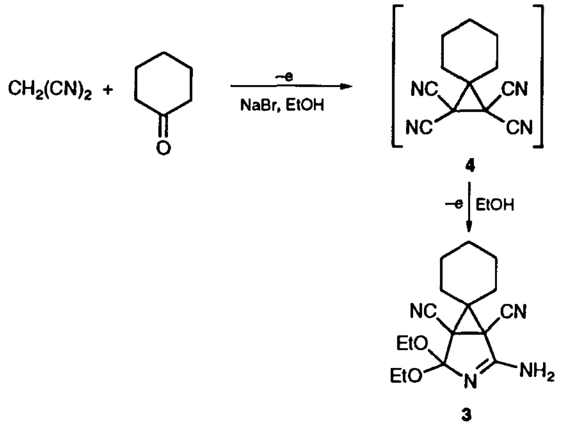
Electrolysis of 1,1,2,2-tetracyanocyclopropanes in alcohols in undivided cells leads to 2-amino-4,4-dialkoxy-1,5-dicyano-3-azabicyclo[3.1.0]hex-2-enes after 0.05–0.20 F mol^{-1} of electricity has been passed.

In the course of our studies on the synthetic utility of alkali metal halides as mediators in electrooxidation of organic compounds[1–3] we have found an electrochemical transformation of malononitrile and ketones **1a–f** into 3,3-disubstituted-1,1,2,2-tetracyanocyclopropanes **2a–f** in 60–80% yields:[4]

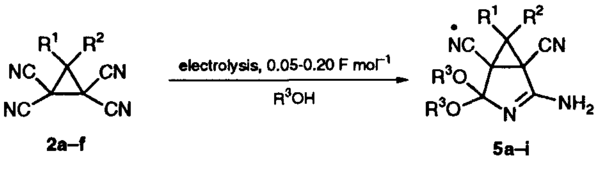


Meanwhile, under the conditions used[4] the reaction of malononitrile and cyclohexanone has surprisingly led to the 2-amino-1,5-dicyano-4,4-diethoxy-6,6-pentamethylene-3-azabicyclo[3.1.0]hex-2-ene **3** in 62% yield:



1,1,2,2-Tetracyanospiro[2.5]octane **4** initially formed from cyclohexanone and malonodinitrile reacts further under electrolytic conditions with ethanol and is transformed into **3**.

Recently we have found that electrocatalytic alcoholysis resulting in the formation of substituted pyrrolines is a general reaction for 1,1,2,2-tetracyanocyclopropanes (Table 1).



Ion R^{3}O$^-$ generated at the cathode reacts with **2a–f** forming **5a–i**; complete conversion of **2a–f** was achieved when only 0.05–0.20 F mol^{-1} of electricity had been passed (current yield 500–2000%).

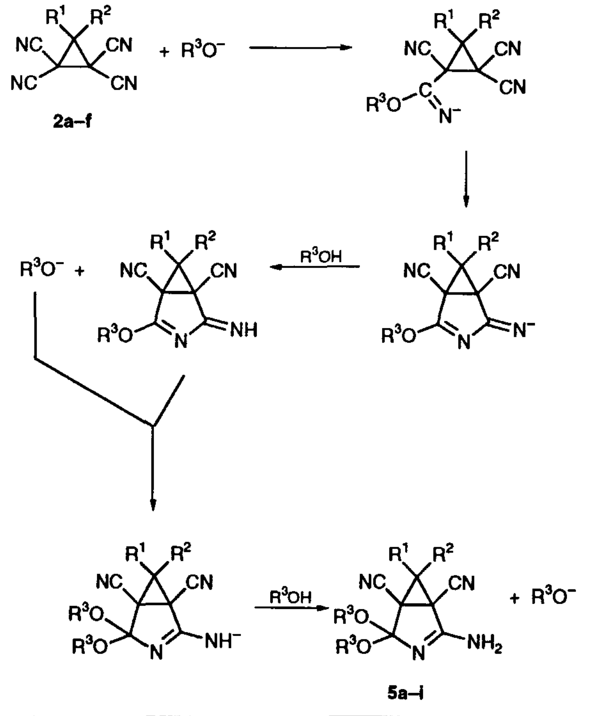
Table 1 Electrocatalytic transformation of 1,1,2,2-tetracyanocyclopropanes into 2-amino-4,4-dialkoxy-1,5-dicyano-3-azabicyclo[3.1.0]hex-2-enes[a]

Substrate	R^1	R^2	R^3	Electricity passed F mol^{-1}	Product† yield (%)	M.p./°C (decomp.)
2a	Me	Me	Me	0.2	**5a**, 94	170
2a	Me	Me	Et	0.2	**5b**, 95	130
2b	Et	Me	Me	0.05	**5c**, 93	153
2b	Et	Me	Et	0.2	**5d**, 85	134
2c	Pr	H	Me	0.2	**5e**, 80	187
2d	Pr	Me	Me	0.2	**5f**, 71	127
2d	Pr	Me	Et	0.2	**5g**, 56	112
2e	Ph	H	Et	0.1	**5h**, 81	247
2f	-(CH$_2$)$_4$-		Me	0.1	**5i**, 95	138

[a] 6 mmol **2a–f**, 8 mmol NaBr or NaOAc in 20 ml ROH, Fe-cathode, Pt- or C-anode, current density 110 mA cm^{-2}, temperature 20 °C, reaction time 2–4 min.

A suggested reaction mechanism involves the following:

cathode: 2R^{3}OH + 2e → 2R^{3}O$^-$ + H$_2$



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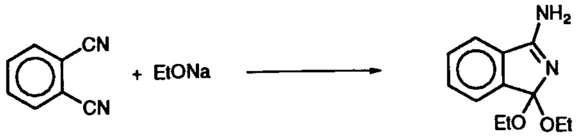
† All new compounds were characterised by ^{1}H and ^{13}C NMR spectroscopy and had satisfactory elemental analyses.

Spectral data for **5a**: ^{1}H NMR ([^{2}H$_6$]DMSO): δ 1.27 (s, 3H, CH$_3$), 1.57 (s 3H, CH$_3$), 3.25 (s, 3H, CH$_3$O), 3.26 (s, 3H, CH$_3$O), 7.29 (s, 2H, NH$_2$). ^{13}C NMR ([^{2}H$_6$]DMSO): δ 15.3 (q), 21.5 (q), 39.2 (s), 40.2 (s), 40.5 (s), 48.8 (t), 51.3 (t), 113.3 (s), 114.7 (s), 117.1 (s), 157.3 (s).

Formation of **5a–i** as a result of the realization of the electrocatalytic mechanism shown in Scheme 1 takes place by the successive addition of two R^3OH molecules to **2a–f**, initiated by R^3O^- ion, and regeneration in the final stage of R^3O^-.

Compounds **5a,b** and **5e,f** were crystallized directly from the reaction mixture. In the other experiments solvent was removed, the residue was extracted with ethyl acetate, washed with water, dried with Na_2SO_4, then solvent was removed once more and, after extraction of the residue with ether, pure pyrrolines were obtained.

The only analogue of the reaction known to us is the interaction between phthalonitrile and EtONa:[5]



The molecular structures of 2-amino-1,5-dicyano-4,4-dimethoxy-6,6-dimethyl-3-azabicyclo[3.1.0]hex-2-ene (**5a**) and 2-amino-1,5-dicyano-4,4-diethoxy-6-phenyl-3-azabicyclo[3.1.0]hex-2-ene (**5h**) were unequivocally established by a monocrystal X-ray diffraction study‡ (Figs. 1 and 2).

In molecules **5a** and **5b** both C≡N groups (and in **5h** also the Ph-group) have a *cis*-orientation relative to the cyclopropane ring (CPR). The pyrroline cycle (PYC) has an almost planar conformation with a slight envelope-like distortion: the C(4) atom is displaced out of the mean (within ±0.018 Å in the molcule **5a** and ±0.006 Å in the molecule **5h**) plane of the rest of the bicycle atoms by 0.094 and 0.111 Å in **5a** and **5h**, respectively. The dihedral angle between the CPR and the mean PYC plane is 71.8° in the molecule **5a** and 67.7° in the molecule **5h**. Bond lengths in both CPR and PYC in molecules **5a** and **5h** are quite similar, the only exception being the C(5)–C(6) bond which is noticeably shorter in **5a** [1.495(5) Å] than in **5h** [1.533(4) Å]. A detailed discussion on molecular geometry **5a,h** and other cyclopropane derivatives, studied by us recently (*cf.*, refs. 6 and 7), will be published elsewhere.

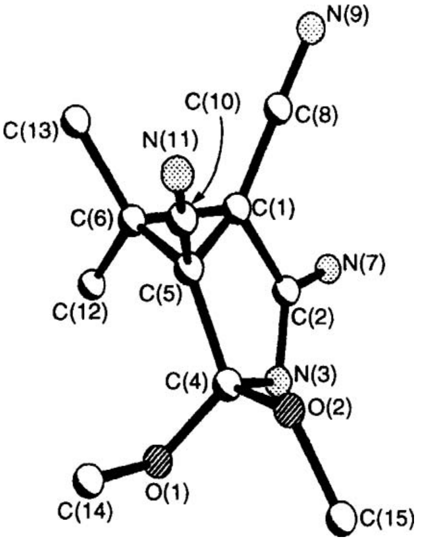


Fig. 1 Molecular structure of **5a**. The main bond lengths (Å) and angles (°): C(1)–C(6) 1.528(4), C(1)–C(5) 1.527(4), C(5)–C(6) 1.533(4), C(1)–C(2) 1.512(4), C(2)–N(3) 1.285(4), N(3)–C(4) 1.436(3), C(4)–C(5) 1.549(4), C(1)–C(8) 1.432(4), C(8)–N(9) 1.131(5), C(5)–C(10) 1.443(4), C(10)–N(11) 1.130(4), C(2)–N(7) 1.327(4), C(6)C(1)C(5) 60.2(2), C(1)C(5)C(6) 59.9(2), C(5)C(6)C(1) 59.8(2), C(1)C(8)N(9) 179.5(4), C(5)C(10)N(11) 178.9(4).

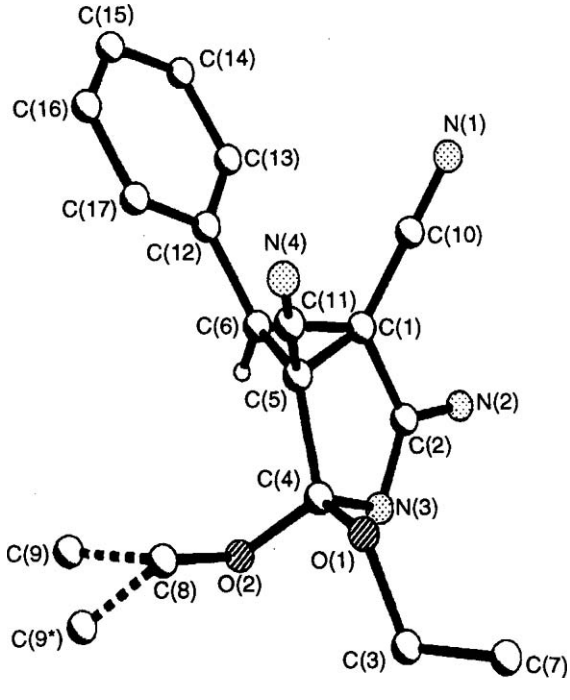


Fig. 2 Molecular structure of **5h**. Two positions of the disordered Me group are shown by dashed lines. The main bond lengths (Å) and angles (°) are averaged over two independent molecules (**5h** and **5h′**): C(1)–C(6) 1.529(6), C(1)–C(5) 1.534(5), C(5)–C(6) 1.495(5), C(1)–C(2) 1.504(5), C(2)–N(3) 1.296(4), N(3)–C(4) 1.440(5), C(4)–C(5) 1.557(4), C(1)–C(10) 1.435(5), C(10)–N(1) 1.131(6), C(5)–C(11) 1.444(5), C(11)–N(4) 1.134(6), C(2)–N(2) 1.318(6), C(6)C(1)C(5) 58.4(2), C(1)C(5)C(6) 60.6(3), C(5)C(6)C(1) 60.9(3), C(1)C(10)N(1) 179.7(5).

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‡ Crystal data for **5a**: $C_{11}H_{14}N_4O_2$, $M = 234.2$, monoclinic, space group $P2_1/c$ $a = 11.980(2)$ Å, $b = 8.216(3)$ Å, $c = 12.842(4)$ Å, $\beta = 98.40(2)°$, $Z = 4$, $V = 1250(1)$ Å^3, $D_c = 1.244$ g cm^{-3}. Intensities of 1844 reflections with $I \geqslant 3.5\sigma(I)$ were measured at +23 °C with a Siemens P3/PC difractometer (λMo$K\alpha = 0.71073$ Å graphite monochromator, $\theta < 30°$, $\theta/\theta 2$ scan).

Crystal data for **5h**: $C_{17}H_{18}N_4O_2$, $M = 310.4$, triclinic, space group $P\bar{1}$, $a = 10.233(2)$ Å, $b = 11.695(2)$ Å, $c = 16.061(3)$ Å, $\alpha = 69.68(2)°$, $\beta = 73.21(2)°$, $\gamma = 86.97(2)°$ $Z = 4$: $V = 1723.2(6)$ Å^3, $D_c = 1.196$ g cm^{-3}, (two crystallographically independent molecules **5h** and **5h′** with almost identical geometry). Intensities of 4266 reflections with $I \geqslant 3.5\sigma(I)$ were measured as indicated for **5a**. Both structures were solved by direct methods and refined in full-matrix anisotropic approximation for non-hydrogen atoms. In the molecule of **5h** the Me group of one of the Et groups is disordered over two positions C(9) and C(9*) with populations of 0.65 and 0.35, respectively. In the molecule **5h′** one of two Et groups is disordered over two positions with equal populations. Most of the hydrogen atoms were localized in the difference Fourier map: the H-atoms of the disordered groups were placed in calculated positions. In the final least-squares cycles the former H atoms were refined isotropically and disordered group hydrogens were treated in a riding-model approximation. The final discrepancy factors are $R = 0.050$, $R_w = 0.053$ for **5a**, $R = 0.076$, $R_w = 0.080$ for **5h**. 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.

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