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# Pyridinium bromide as a new mediator for electrochemical transformations involving CH-acids

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All melting points were measured with a Gallenkamp melting point apparatus and are uncorrected. $^{1}H$ and $^{13}C$ NMR were recorded with a Bruker AM300 at ambient temperature in DMSO-$d_6$ or $CDCl_3$ solutions with working frequency of 300.13 MHz. Chemical shifts values are given in δ scale relative to $Me_4Si$. IR spectra were recorded with a Bruker ALPHA-T FT-IR spectrometer in KBr pellets. Mass-spectra (EI = 70 eV) were recorded with a Finnigan MAT INCOS 50 spectrometer. High-resolution mass spectrometry (HRMS) (electrospray ionization, ESI) was measured on a Bruker micrOTOF II instrument; external or internal calibration was done with an Electrospray Calibrant Solution (Fluka).
Alkylidenemalononitriles **1** were synthesized by the condensation of the corresponding carbonyls and malononitrile *via* the Knoevenagel condensation.[S1,S2]

**General procedure.** An undivided cell was equipped with a graphite anode (area 5 $cm^2$) and Fe cathode (area 5 $cm^2$) and connected to a DC regulated power supply. The cell was charged with the corresponding alkylidenemalononitrile **1** (10 mmol), C-H acid **2** (10 mmol), PyHBr (7.5 mmol), and acetonitrile (20 ml). The mixture was electrolyzed (2.2 F $mol^{-1}$) using constant current conditions (50 mA $cm^{-2}$) at 20 °C under magnetic stirring (TLC control). When the reaction was complete, the solvent was removed under reduced pressure. The residue was treated with water, and the product was extracted with dichloromethane (3 × 20 ml), the extract was dried over $Na_2SO_4$, and concentrated in vacuum. The residue was purified by crystallization from methanol to afford the desired cyclopropane **3**.

**3-Phenyl-1,1,2,2-tetracyanocyclopropane (3a)**
White solid. Yield 1.57 g (72%); mp 226-228 °C (lit.[S3] mp 227-230 °C). $^{1}H$ NMR (DMSO-$d_6$) δ: 5.10 (1H, s, CH), 7.48-7.80 (5H, m, Ar).

**3-(4-Methylphenyl)-1,1,2,2-tetracyanocyclopropane (3b)**
White solid. Yield 1.53 g (66%); mp 226-227 °C (lit.[S3] mp 227-230 °C). $^{1}H$ NMR (DMSO-$d_6$) δ: 2.31 (3H, s, $CH_3$), 5.20 (1H, s, CH), 7.28 (2H, d, *J* = 8.0 Hz, Ar), 7.65 (2H, d, *J* = 8.0 Hz, Ar).

**3-(4-Chlorophenyl)-1,1,2,2-tetracyanocyclopropane (3c)**
White solid. Yield 1.61 g (64%); mp 248-251 °C (lit.[S3] mp 250-251 °C). $^{1}H$ NMR (DMSO-$d_6$) δ: 5.28 (1H, s, CH), 7.59 (2H, d, *J* = 8.5 Hz, Ar), 7.88 (2H, d, *J* = 8.5 Hz, Ar).

**3-(3-Bromophenyl)-1,1,2,2-tetracyanocyclopropane (3d)**
White solid. Yield 1.72 g (58%); mp 187-189 °C (lit.[S4] mp 186-187 °C). $^{1}H$ NMR (DMSO-$d_6$) δ: 5.31 (1H, s, CH), 7.44 (1H, t, *J* = 8.5 Hz, Ar), 7.68 (1H, d, *J* = 8.5 Hz, Ar), 7.87(1H, d, *J* = 8.5 Hz, Ar), 8.22 (1H, s, Ar).

**3-(4-Nitrophenyl)-1,1,2,2-tetracyanocyclopropane (3e)**

White solid. Yield 1.26 g (48%); mp 232-234 °C (lit. [S3] mp 232-235 °C). $^1$H NMR (DMSO-*d*$_6$) δ: 5.52 (1H, s, CH), 8.20 (2H, d, *J* = 8.8 Hz, Ar), 8.35 (2H, d, *J* = 8.8 Hz, Ar).

**1,1,2,2-Tetracyanospiro[2.5]octane (3f)**

White solid. Yield 1.26 g (60%); mp 176-178 °C (lit. [S5] mp 177-179 °C). $^1$H NMR (DMSO-*d*$_6$) δ: 1.45-1.55 (2H, m, $CH_2$), 1.60-1.75 (4H, m, $2CH_2$), 1.80-1.95 (4H, m, $2CH_2$).

**Dimethyl 2,2-dicyano-3-phenylcyclopropane-1,1-dicarboxylate (3g)**

White solid. Yield 1.90 g (67%); mp 126-128 °C. (lit. [S6] mp 126-128 °C). $^1$H NMR (DMSO-*d*$_6$) δ: 3.75 (s, 3H, OMe), 3.92 (s, 3H, OMe), 4.41 (s, 1H, CH), 7.35-7.50 (m, 5H, Ph).

**Dimethyl 2,2-dicyano-3-(4-methylphenyl)cyclopropane-1,1-dicarboxylate (3h)**

White solid. Yield 1.87 g (63%); mp 137-139 °C. (lit. [S6] mp 137-139 °C). $^1$H NMR ($CDCl_3$) δ: 2.39 (s, 3H, $CH_3$), 3.79 (s, 3H, OMe), 3.96 (s, 1H, CH), 3.98 (s, 3H, OMe), 7.18-7.30 (m, 4H, Ar).

**Dimethyl 2,2-dicyano-3-(3-methoxylphenyl)cyclopropane-1,1-dicarboxylate (3i)**

White solid. Yield 2.10 g (67%); mp 92-94 °C (methanol). $^1$H NMR ($CDCl_3$) δ: 3.78 (s, 3H, OMe), 3.80 (s, 3H, OMe), 3.92 (s, 1H, CH), 3.95 (s, 3H, OMe), 6.92-7.02 (m, 2H, Ar), 7.24-7.40 (m, 2H, Ar). $^{13}$C NMR (75.47 MHz, $CDCl_3$) δ: 16.6, 40.6, 46.6, 53.9, 54.8, 56.0, 110.1, 111.8, 112.4, 113.9, 119.1, 124.6, 146.2, 151.1, 161.9, 163.4. IR, νmax/cm$^{-1}$: 2252, 1748, 1732, 1438, 1272. MS (EI), m/z (%): 344 $[M]^+$ (5), 313 (17), 285 (27), 225 (16), 200 (13), 181 (15), 156 (11), 140 (13), 114 (10), 59 (100). HRMS m/z (ESI) calcd for $C_{16}H_{14}N_2O_5$ $(M+H)^+$ 315.0980, found 315.0976.

**Dimethyl 2,2-dicyano-3-(3-bromophenyl)cyclopropane-1,1-dicarboxylate (3j)**

White solid. Yield 2.32 g (64%); mp 110-111 °C (lit. [S2] mp 110-111 °C). $^1$H NMR ($CDCl_3$) δ: 3.80 (s, 3H, CH3O), 3.95 (s, 1H, CH), 3.97 (s, 3H, $CH_3O$), 7.26-7.35 (m, 2H, Ar), 7.50-7.55 (m, 2H, Ar).

**Dimethyl 2,2-dicyano-3-(3-nitrophenyl)cyclopropane-1,1-dicarboxylate (3k)**

White solid. Yield 1.44 g (44%); mp 113-115 °C (methanol). $^1$H NMR ($CDCl_3$) δ: 3.85 (s, 3H, OMe), 4.03 (s, 3H, OMe), 4.07 (s, 1H, CH), 7.55-7.65 (m, 1H, Ar), 7.70-7.84 (m, 1H, Ar), 8.18-8.32 (m, 2H, Ar). $^{13}$C NMR (75.47 MHz, $CDCl_3$) δ: 16.5, 40.0, 46.2, 54.5, 55.2, 109.8, 111.4, 123.6, 123.9, 130.3, 131.6, 134.8, 149.3, 162.3, 163.8. IR, νmax/cm$^{-1}$: 2256, 1748, 1524, 1438, 1266. MS (EI), m/z (%): 329 $[M]^+$ (4), 298 (11), 270 (57), 239 (16), 200 (11), 173 (15), 153 (11), 140 (13), 114 (12), 59 (100). HRMS m/z (ESI) calcd for $C_{15}H_{11}N_3O_6$ $(M+H)^+$ 330.0726, found 330.0732.

**Dimethyl 2,2-dicyano-3-(4-nitrophenyl)cyclopropane-1,1-dicarboxylate (3l)**

White solid. Yield 1.25 g (38%); mp 140-142 °C. (lit. [S6] mp 140-142 °C). $^1$H NMR ($CDCl_3$) δ: 3.85 (s, 3H, OMe), 4.02 (s, 3H, OMe), 4.05 (s, 1H, CH), 7.62 (2H, d, *J* = 8.0 Hz, Ar), 8.30 (2H, d, *J* = 8.0 Hz, Ar).

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