Electronic Supplementary Information

Electrochemical Synthesis of Organochalcogenides in Aqueous Medium

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1. General Remarks
1.1. Materials
Tetrahydrofuran (THF) and ethyl acetate were previously purified in agreement with the literature.1 Tellurium, selenium and sulfur powder (≥99.5%) were purchased from Aldrich and used as received. All other commercially available reagents and solvents were used as received. Reactions were monitored by gas chromatography. The products were characterized by GC/MS and NMR. The isolated product rate, mono- and dichalcogen, was determined by gas chromatography.

1.2. Instrumentation
Controlled-current electrolyses were carried out using Autolab PGSTAT 30 potentiostat/galvanostat or a DC power source, in a two compartment electrochemical cell (Figure 1). Isolated products were determined by GC (Varian CP-3380; Chrompack CP-SPL5CB capillary column 30 m; initial temperature 60 °C then increased to 220°C at 10°C min⁻¹), GC/MS (Agilent 5975C), ¹H NMR (400 MHz) and ¹³C NMR data (100 MHz) were recorded in CDCl₃. The chemical shifts are reported as delta (δ) units in parts per million (ppm) relative to the solvent residual peak as the internal reference. Coupling constants (J) for all spectra are reported in Hertz (Hz). ¹²⁵Te NMR (95 MHz) was obtained using diphenylditellane as external reference (δ 422.0), spectral window equal to 64.4 kHz, acquisition time equal to 0.64 s, 64 repetitions, RF pulse of 45° and line broadening equal to 5.0 Hz.

1.3. Representative Procedure for the Synthesis of dicyclopentyltellane (2j)

Tellurium powder (0.5 mmol, 63.8 mg) and 0.2 mol L\(^{-1}\) NaOH solution (25 mL) were added to the electrochemical cell (Figure 1). A stainless steel grid cathode and anode were used as electrodes with the anodic compartment separated by Nafion®. The system was subjected to constant current (\(I=-70\) mA) electrolysis, under intense argon atmosphere. After the consumption of the Te\(^0\), the solution becomes purple, and then colorless, which determines the end point of the electroreduction.\(^2\) 20 mL of co-solvent (THF) was added and the current maintained till the solution (H\(_2\)O/THF) becomes colorless again. The current was stopped and bromocyclopentane (150 mg, 102 \(\mu\)L, 1.0 mmol) dissolved in THF (5 mL) (deaerated with argon) was added via syringe to the electrochemical cell. The reaction was stirred for 12 hours at room temperature under argon. After this period the reaction was diluted with ethyl acetate (20 mL) and washed with water (2 x 30 mL). The organic layer was separated, dried over Na\(_2\)SO\(_4\) and filtered. The solvent was removed under reduced pressure to yield 96.3 mg (72%) of the title compound without the need of further purification. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.55 (qui, \(J = 6.5\) Hz, 2H); 2.06-1.98 (m, 8H); 1.75-1.57 (m, 8H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 38.0; 25.4; 17.9; \(^{125}\)Te NMR (95 MHz, CDCl\(_3\)). \(\delta\) 211.4. C\(_{10}\)H\(_{18}\)Te: LRMS (EI) \(m/z\) (rel. int.) 268 ([M\(^+\)], 7), 199 (C\(_5\)H\(_{10}\)Te, 7), 41 (C\(_3\)H\(_5\), 28).

$^{125}\text{Te}$ NMR spectrum (95 MHz, CDCl$_3$) of compound 2j

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 2j
1.4 Characterization of products

Dipentyltellane (2a) [71475-88-2] C_{10}H_{22}Te: LRMS (EI) m/z (rel. int.) 272 ([M^+] , 26), 270 ([M^+] - 2, 24), 268 ([M^+] - 4, 16), 202 (C_{5}H_{12}Te^+, 15), 200 ([C_{5}H_{12}Te^+] - 2, 15), 71 (C_{5}H_{11}^+, 99), 43 (C_{3}H_{7}^+, 100). The data match to the previously described compound.  

Dipentylselenide (2b) [14835-67-7] C_{10}H_{22}Se: LRMS (EI) m/z (rel. int.) 222 ([M^+] , 46), 220 ([M^+] - 2, 23), 152 (C_{5}H_{12}Se^+, 55), 71 (C_{5}H_{11}^+, 100), 43 (C_{3}H_{7}^+, 82). The data match to the previously described compound.

Dipentyldiselenide (3b) [52056-07-2] C_{10}H_{22}Se_{2}: LRMS (EI) m/z (rel. int.) 302 ([M^+] , 18), 300 ([M^+] - 2, 17), 232 (C_{5}H_{12}Se_{2}^+, 19), 230 ([C_{5}H_{12}Se_{2}^+] - 2, 17), 71 (C_{5}H_{11}^+, 92), 43 (C_{3}H_{7}^+, 100). The data match to the previously described compound.

Dipentyldisulfide (3c) [112-51-6] C_{10}H_{22}S_{2}: LRMS (EI) m/z (rel. int.) 206 ([M^+] , 67), 136 (C_{5}H_{12}S_{2}^+, 51), 103 (C_{5}H_{11}^+, 86), 71 (C_{5}H_{11}^+, 100), 43 (C_{3}H_{7}^+, 40). The data match to the previously described compound.

Dipentyldisulfide (3c) [112-51-6] C_{10}H_{22}S_{2}: LRMS (EI) m/z (rel. int.) 206 ([M^+] , 67), 136 (C_{5}H_{12}S_{2}^+, 51), 103 (C_{5}H_{11}^+, 86), 71 (C_{5}H_{11}^+, 100), 43 (C_{3}H_{7}^+, 40). The data match to the previously described compound.

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Dihexyltellane (2d) [158734-99-7] C_{12}H_{26}Te, LRMS (El) m/z (rel. int.) 300 ([M⁺], 18), 298 ([M⁺] - 2, 16), 296 ([M⁺] - 4, 10), 216 (C_{6}H_{14}Te⁺, 11), 85 (C_{6}H_{13}⁺, 62), 43 (C_{3}H_{7}⁺, 100). The data match to the previously described compound.  

Dihexylselenide (2e) [7732-99-2] C_{12}H_{26}Se, LRMS (El) m/z (rel. int.) 250 ([M⁺], 60), 248 ([M⁺] - 2, 30), 165 (C_{6}H_{13}Se⁺, 71), 85 (C_{6}H_{13}⁺, 93), 43 (C_{3}H_{7}⁺, 100). The data match to the previously described compound.

Dihexyldiselenide (3e) [52056-08-3] C_{12}H_{26}Se_{2}, LRMS (El) m/z (rel. int.) 330 ([M⁺], 15), 328 ([M⁺] - 2, 13), 245 (C_{6}H_{14}Se_{2}⁺, 16), 85 (C_{6}H_{13}⁺, 66), 43 (C_{3}H_{7}⁺, 100). The data match to the previously described compound.

Dihexylsulfide (2f) [6294-31-1] C_{12}H_{26}S, LRMS (El) m/z (rel. int.) 202 ([M⁺], 35), 117 (C_{6}H_{13}S⁺, 100), 85 (C_{6}H_{13}⁺, 55), 59 (C_{4}H_{9}⁺, 38), 43 (C_{3}H_{7}⁺, 35). The data match to the previously described compound.

Dihexyldisulfide (3f) [10496-15-8] C_{12}H_{26}S_{2}, LRMS (El) m/z (rel. int.) 234 ([M⁺], 56), 150 (C_{6}H_{14}S_{2}⁺, 47), 117 (C_{6}H_{13}S⁺, 21), 85 (C_{6}H_{13}⁺, 53), 43 (C_{3}H_{7}⁺, 100). The data match to the previously described compound.

Dicyclopentylselenide (2k) [136397-83-6] C_{10}H_{18}Se, LRMS (El) m/z (rel. int.) 218 ([M⁺], 13), 149 (C_{5}H_{10}Se⁺, 15), 69 (C_{5}H_{9}⁺, 100), 41 (C_{3}H_{7}⁺, 26). The data match to the previously described compound.

Dicyclopentylselenide (3k) [62212-26-4] C_{10}H_{16}Se_{2}, LRMS (El) m/z (rel. int.) 298 ([M⁺], 10), 296 ([M⁺] - 2, 9), 230 (C_{5}H_{10}Se_{2}⁺, 11), 228 ([C_{5}H_{10}Se_{2}⁺] - 2, 10), 69 (C_{5}H_{9}⁺, 100), 41 (C_{3}H_{7}⁺, 33). The data match to the previously described compound.

Dicyclopentylsulfide (2l) [1126-65-4] C_{10}H_{16}S, LRMS (El) m/z (rel. int.) 170 ([M⁺], 26), 101 (C_{5}H_{9}S⁺, 73), 69 (C_{5}H_{9}⁺, 100), 41 (C_{3}H_{7}⁺, 76). The data match to the previously described compound.

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Dicyclopentyldisulfide (3l) [4485-78-3] \(\text{C}_{10}\text{H}_{18}\text{S}_{2}\), LRMS (EI) \(m/z\) (rel. int.) 202 ([M\(^+\)], 24), 134 (C\(_5\)H\(_{10}\)S\(_2\)\(^+\), 39), 69 (C\(_3\)H\(_9\)\(^+\), 100), 41 (C\(_3\)H\(_5\)\(^+\), 27). The data match to the previously described compound.\(^{15}\)

Dibenzyltellane (2m) [62654-03-9] \(\text{C}_{14}\text{H}_{14}\text{Te}\), LRMS (EI) \(m/z\) (rel. int.) 312 ([M\(^+\)], 5), 310 ([M\(^+\)] - 2, 4), 308 ([M\(^+\)] - 4, 2), 91 (C\(_7\)H\(_7\)\(^+\), 100), 65 (C\(_5\)H\(_5\)\(^+\), 12). The data match to the previously described compound.\(^{16}\)

Dibenzylselenide (2n) [1842-38-2] \(\text{C}_{14}\text{H}_{14}\text{Se}\), LRMS (EI) \(m/z\) (rel. int.) 262 ([M\(^+\)], 19), 260 ([M\(^+\)] - 2, 9), 91 (C\(_7\)H\(_7\)\(^+\), 100), 65 (C\(_5\)H\(_5\)\(^+\), 15). The data match to the previously described compound.\(^{17}\)

Dibenzylsulfide (2o) [538-74-9] \(\text{C}_{14}\text{H}_{14}\text{S}\), LRMS (EI) \(m/z\) (rel. int.) 214 ([M\(^+\)], 41), 123 (C\(_7\)H\(_7\)S\(^+\), 35), 91 (C\(_7\)H\(_7\)\(^+\), 100), 65 (C\(_5\)H\(_5\)\(^+\), 11). The data match to the previously described compound. The data match to the previously described compound.\(^{18}\)

Dibenzyldisulfide (3o) [150-60-7] \(\text{C}_{14}\text{H}_{14}\text{S}_{2}\), LRMS (EI) \(m/z\) (rel. int.) 246 ([M\(^+\)], 5), 181 (C\(_9\)H\(_9\)S\(_2\)\(^+\), 7), 91 (C\(_7\)H\(_7\)\(^+\), 100), 65 (C\(_5\)H\(_5\)\(^+\), 12).\(^{15}\)


