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Triselenium dicyanide from malononitrile and selenium dioxide. One-pot synthesis of selenocyanates

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Abstract—Triselenium dicyanide is formed by the interaction of malononitrile and selenium dioxide in dimethylsulfoxide or dimethylformamide. Addition of aromatic amines, indoles and some active methylene compounds to this reaction mixture gives the corresponding selenocyanates in one-pot.

Triselenium dicyanide (TSD) is used as a selenocyanating reagent for the synthesis of aromatic[1] and metalloorganic[2] selenocyanates. TSD has been well-known for a long time.[3] All the methods described for its synthesis are based on inorganic selenocyano compounds as starting materials. TSD has been obtained by oxidation of potassium selenocyanate with chlorine or bromine,[3] dinitrogen tetroxide,[4] iodine pentafluoride,[5] by oxidation of silver selenocyanate with iodine,[1] by interaction of selenium dibromide and silver cyanide,[6] by disproportionation of selenocyanogen,[3] by thermal decomposition of sulphenyl selenocyanates[7,8] and by electrooxidation of the selenocyanate anion.[9]

We have discovered that TSD may be obtained very easily by interaction of malononitrile (1 mol) with selenium dioxide (1.5–2 mol) in dimethylsulfoxide or dimethylformamide.[10] The reaction is exothermic and evolution of CO_2 and N_2 are observed as during the oxidative coupling of malononitrile with SeO_2 in the presence of organic bases;[11] more time is required to start the exothermic reaction leading to TSD than for the oxidative coupling.

TSD may be isolated from the reaction mixture after dilution with water; the yield 36% is not very high probably because of the instability of TSD against water. We discovered, however, that the reaction mixture may be used for selenocyanation of the organic substrates without isolation of the TSD. Aromatic amines with a free *para*-position, indoles with a free 3-position and some active methylene compounds may be used as substrates. The corresponding selenocyanates **2**–**6** were formed with good yields in most cases if these substrates were added to the reaction mixture after the exothermic reaction between malononitrile and selenium dioxide[12] (Scheme 1). Selenocyanates were isolated after dilution of the reaction mixtures with water and were purified by recrystallization.

Anthranilic and *meta*-aminobenzoic acid react normally under these conditions, but *o*- and *p*-nitroanilines are inactive. Reactions proceed regioselectively only *para* to the amino-group in aromatic amines, in the 3-position for indoles and at the methylene group for dibenzoylmethane, acetylacetone and barbituric acid, as well as for bindone; dimedone reacts nonselectively.

Addition of selenium dioxide to the mixture of malononitrile and dimethylaniline in DMSO following the procedure for the oxidative coupling of malononitrile[11] led to another result: a mixture of four compounds was formed: selenocyanate **2b**, di(*p*-dimethylaminophenyl)selenide **7**, di(*p*-dimethylaminophenyl)malononitrile **8** and a small amount of 4-(1,2,2-tricyanovinyl)dimethylaniline **9**; the pentacyanopropenide salt was not detected[13] (Scheme 2). A mixture of the same

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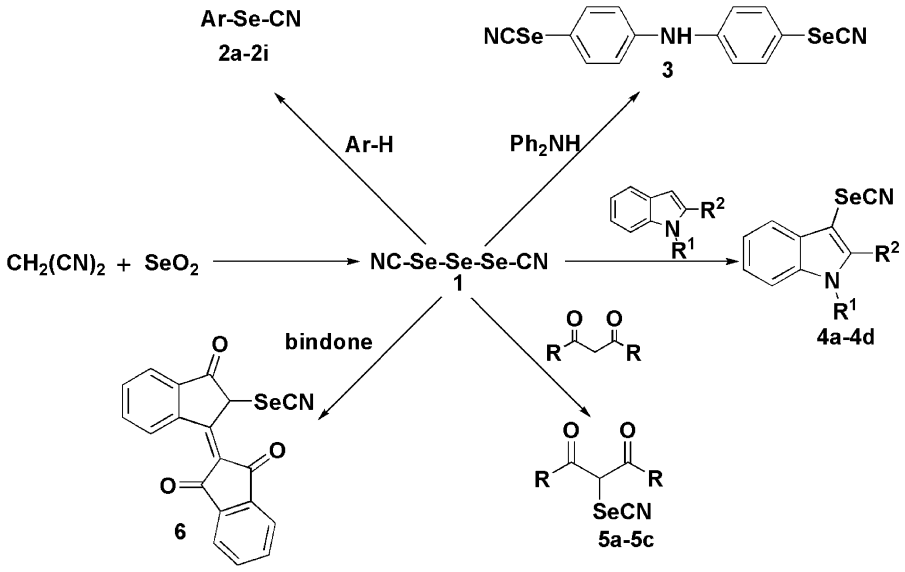
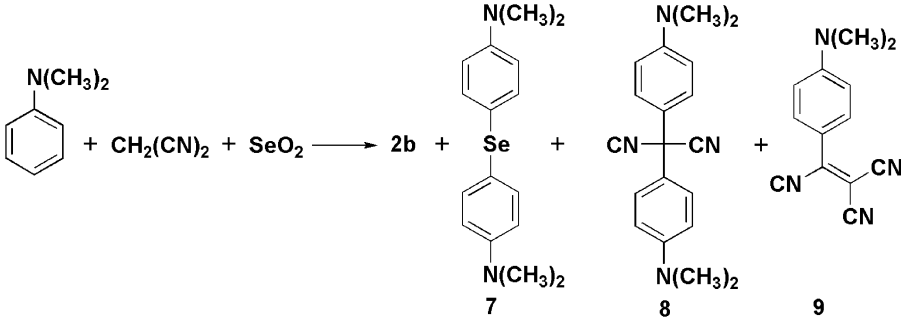


Ar = **2a** 4-aminophenyl; **2b** 4-dimethylaminophenyl; **2c** 4-morpholinophenyl; **2d** 4-amino-3-methylphenyl; **2e** 4-aminonaphthyl; **2f** 4-dimethylaminonaphthyl; **2g** 4-amino-3-carboxyphenyl; **2h** 4-amino-2-carboxyphenyl; **2i** 4-amino-3-hydroxymethyl;

4a R^1=R^2=H; **4b** R^1=H, R^2=Me; **4c** R^1=H, R^2=-COOEt; **4d** R^1-R^2=-$(CH_2)_3CO$-;

5a R= Me; **5b R=** Ph; **5c R+R=** -NH-CO-NH-.

Scheme 1.



Scheme 2.

compounds (in other proportions) was formed when *i*-PrOH was used instead of DMSO.

Selenocyanates are important in selenoorganic chemistry; they may be transformed to various selenoorganic derivatives.[14] Several methods are known for the synthesis of aromatic selenocyanates: reactions of diazonium salts with potassium selenocyanate;[15] reactions of iodarenes with potassium selenocyanate catalyzed by copper(I) iodide;[16] photo-induced substitution of halogen is in halogenarenes by selenocyanate anion;[17] reaction of diselenium dicyanide (selenocyanogene) with indole[18a,b] and the reaction of activated aromatic substrates with triselenium dicyanide as mentioned above.[1] This proposed one-pot synthesis is based on the same reaction as the last method, however, it is very simple and convenient.

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10. *Triselenium dicyanide from malononitrile and selenium dioxide*. Selenium dioxide (0.67 g, 6 mmol) was added with stirring to solution of malononitrile (0.2 g, 3 mmol) in DMSO (2 mL). The mixture became reddish after 5 min, an exothermic reaction with vigorous gas evolution began during the next 10 min. The volume of gas was 52 mL, half of the volume was absorbed by a water solution of NaOH. The mixture was diluted with water (6 mL) and after cooling, a yellow precipitate was formed within 5 min. The precipitate was filtered, dried and crystallized from benzene, 0.21 g (1.1 mmol) of TSD was obtained; mp 133–134 °C, lit. mp 133–134 °C;[5] IR (KBr, cm^{-1}) 2141, 511, lit. 2131, 513;[5] 2141.[19] The substance **1** was identical with a sample of triselenium dicyanide obtained by the published method.[19] The same yield of TSD was obtained using DMF instead DMSO.
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12. *Synthesis of selenocyanates in one-pot*. (a) From aromatic amines and indoles: selenium dioxide (0.34 g, 3 mmol) was reacted with malononitrile (0.1 g, 1.5 mmol) in DMSO as described above. The aromatic substrate (2.25 mmol) was added with stirring to the reaction mixture after termination of the exothermic reaction. The homogeneous solution was diluted with water (5–10 mL) after 15–40 min and the precipitate was filtered, dried and crystallized. (b) From active methylene compounds: the reaction was carried out in the same manner but the mole ratio malononitrile:SeO_2 1:1.5 and DMF was used instead of DMSO.
    The selected data for compounds are listed as follows—yield, %; melting point, °C (solvent for recrystallization) (literature melting point, °C); ^{1}H NMR (250 MHz, DMSO for **2g**, **2h**, **5c**, $CDCl_3$ for others), APCI/MS for **2–4** or API-ES/MS for **5–6**:
    Compound **2a**—75; 88–89 (50% MeOH) (90–92); ^{1}H NMR spectra are in close agreement with the literature;[18] $[M+H]^+$ *m/z* 199.
    Compound **2b**—65; 100–102 (50% *i*-PrOH) (104–105); ^{1}H NMR spectra are in close agreement with the of literature;[18] $[M+H]^+$ *m/z* 228.
    Compound **2c**—85; 120–122 (*i*-PrOH); δ 3.21 (t, $J = 4.89$, 4H, $-CH_2-$); 3.85 (t, $J = 4.89$, 4H, $-CH_2-$); 6.87 (dt, $J_1 = 9.0$, $J2 = 2.2$, 2H, H-3, 5); 7.56 (dt, $J_1 = 9.2$ $J_2 = 2.2$, 2H, H-2, 6); $[M+H]^+$ *m/z* 269.
    Compound **2d**—93; 92–94 (50% MeOH) (92–93); ^{1}H NMR spectra are in close agreement with the literature;[18] $[M+H]^+$ *m/z* 213.
    Compound **2e**—99; 150–152 (C_6H_6) (160–170 dec); ^{1}H NMR spectra are in close agreement with the literature;[18] $[M+H]^+$ *m/z* 249.
    Compound **2f**—96; 60–62 (MeOH); δ 2.93 (s, 6H, H–Me); 6.97 (d, $J = 8.0$, 1H, H-3); 7.57 (t, $J = 8.3$, 1H, H-6); 7.65 (t, $J = 8.3$, 1H, H-7); 7.91 (d, $J = 8.0$, 1H, H-2); 8.23 (m, 1H, H-5); 8.27 (m, 1H, H-8); $[M+H]^+$ *m/z* 277.
    Compound **2g**—85; 170–172 dec (80% EtOH); δ 6.09 (ws, 1H, H–COOH), 6.70 (d, $J = 8.8$, 1H, H-5); 7.60 (dd, $J_1 = 8.6$, $J_2 = 2.2$, 1H, H-6); 8.25 (d, $J = 2.2$, 1H, H-2); $[M-H]^-$ *m/z* 241.
    Compound **2h**—76; 176–180 dec (50% DMFA); δ 3.35 (ws, 2H, $-NH_2$), 6.95 (dd, $J_1 = 2.7$, $J_2 = 8.6$, 1H, H-5), 7.34 (d, $J = 2.7$, 1H, H-3), 7.47 (d, $J = 8.6$, 1H, H-6), 8.34 (d, 1H, –COOH); $[M-H]^-$ *m/z* 241.
    Compound **2i**—78; 91–92 (C_6H_6); δ 1.17 (s, 1H, H–OH), 4.50 (s, 2H, $-NH_2$), 4.65 (s, 2H, $-CH_2-$), 6.67 (d, $J = 8.0$, 1H, H-5); 7.43 (m, 2H, H-2, 6); $[M+H]^+$ *m/z* 229.
    Compound **3**—94; 145–146 (C_6H_6); δ 6.12 (s, 1H, –NH–); 7.10 (d, $J = 8.8$, 4H, H-2, 2′, 6, 6′); 7.59 (d, $J = 8.8$, 4H, H-3, 3′, 5, 5′); $[M+H]^+$ *m/z* 378.
    Compound **4a**—94; 99–100 (50% MeOH) (98.5–100); ^{1}H NMR spectra are in close agreement with the literature;[18a] $[M+H]^+$ *m/z* 221.
    Compound **4b**—56; 125–126 (50% MeOH) (126–127); ^{1}H NMR spectra are in close agreement with the literature;[18b] $[M+H]^+$ *m/z* 236.
    Compound **4c**—60; 123–124 (50% EtOH); δ 1.48 (t, $J = 7.2$, 3H, $-CH_3$); 4.49 (q, $J = 7.2$, 2H, $-CH_2-$); 7.32 (m, 1H, H-7); 7.46 (m, 2H, H-5, 6); 8.05 (d, $J = 9.28$, 1H, H-4); 9.25 (s, 1H, –NH–); $[M+H]^+$ *m/z* 294.
    Compound **4d**—76; 118.5–120 (EtOH); δ 2.46 (q, $J = 6.1$, 2H, $-CH_2-$); 2.79 (t, $J = 6.1$, 2H, $-CH_2-CO-$); 4.28 (t, $J = 6.1$, 2H, $-CH_2-N$); 7.31 (t, $J = 7.81$, 1H, H-5); 7.42 (d, $J = 8.06$, 1H, H-7); 7.50 (t, $J = 7.94$, 1H, H-6); 8.32 (d, $J = 8.3$, 1H, H-4); $[M+H]^+$ *m/z* 291.
    Compound **5a**—46; 76–78 (hexane–C_6H_6) (78–80); δ 2.56 (s, 6H, $-CH_3$), 11.07 (s, 1H, –CH); $[M-H]^-$ *m/z* 204.
    Compound **5b**—84; 102–104 (hexane–C_6H_6); δ 6.79 (s, 1H, –CH–), 7.49 (t, $J = 7.6$; 4H, Ar-H), 7.65 (m, 2H, Ar-H), 7.97 (d, $J = 7.3$, 4H, Ar-H); $[M-H]^-$ *m/z* 328.
    Compound **5c**—42; 190–200 °C dec (re-precipitation with water from DMF); δ 8.31 (s, 1H, –CH–), 10.45 (s, 2H, –NH–); $[M-H]^-$ *m/z* 232.
    Compound **6**—59; 186–190 °C dec (C_6H_6); δ 5.61 (s, 1H, –CH–), 7.98 (m, 7H, Ar-H), 9.67 (d, $J = 8.0$; 1H, Ar-H); $[M-H]^-$ *m/z* 378.
    In all the IR-spectra the absorption of the SeCN-group was observed at 2144–2155 cm^{-1}. Selenium isotope multiplicity of quasi-molecular ion signals were observed in all the mass-spectra. We cite the significances for quasi-molecular ions containing isotope ^{80}Se.
13. *Simultaneous reaction of malononitrile, dimethylaniline and selenium dioxide*: selenium dioxide 0.44 g (4 mmol) was added with stirring to solution of malononitrile 0.13 g (2 mmol) and dimethylaniline 0.48 g (4 mmol) in DMSO (4 mL). The reaction mixture rapidly became dark-red in colour and after 10 min it was diluted with water, the resulting crude precipitate was filtered, dried and separated by preparative thin-layer chromatography on alumina (hexane–ethyl acetate 3:1). Compounds **2b** and **7** were isolated as individual substances in 0.07 g (6%) and 0.36 g (56%) amounts; attempts to separate compounds **8** and **9** were unsuccessful, their structures were established by mass-spectral data.
    Compound **7** yield 56%; 118–120 °C mp (from *i*-PrOH); IR (KBr, cm^{-1}) 3019, 3007, 1593, 1500; ^{1}H NMR (250 MHz,$CDCl_3$) δ 2.92 (s, 12H, $-CH_3$); 6.61 (d, $J = 8.8$, 4H, Ar-H); 7.35 (d, $J = 8.8$, 4H, Ar-H); APCI MS (*m/z*) $[M+H]^+$ 321.
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