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POLYHOMOLOGATION. A LIVING POLYMETHYLENE SYNTHESIS

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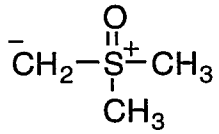
Supporting Data

Dimethyloxosulfonium methylide, 1, in toluene



Into a flame dried one neck 250 mL round bottom flask equipped with a magnetic stir bar was placed NaH (6.85 g, 60% by weight oil dispersion, 171 mmol) against a stream of argon. The NaH was washed three times with freshly distilled hexanes (3 x 100 mL) before introduction of freshly distilled toluene solvent (200 mL). After the installment of a water condenser, the trimethylsulfoxonium chloride (20.0 g, 156 mmol) was then loaded slowly against an argon stream into the reaction flask. The reaction mixture was heated to reflux for six hours. Then, the reaction mixture was transferred through a cannula into a Schlenck flask loaded with celite #545 (3 cm height) and vacuum filtered under argon to provide a clear solution (180 mL). Two parts of this solution (2 x 10 mL) were added into 50 mL H_2O respectively and titrated with 1N HCl by using phenolphthalein indicator. The concentration of the ylide solution was determined to be 0.71 M and the yield of the ylide was 82%.

Synthesis of hydroxylterminated polymethylene (DP = 50)[1]

Into a flame dried 100 mL one neck round bottom flask equipped with a magnetic stirrer and a rubber septa was added a solution of dimethyloxosulfonium methylide in toluene (50 mL, 0.64 M, 32 mmol) by syringe under argon. The solution was heated to 60 °C. To this was added a solution of triethylborane in THF (222 μL, 1 M, 0.22 mmol) in one portion via syringe to the reaction flask. After 10 min, an aliquot of the reaction mixture was withdrawn and added into distilled water containing phenolphthalein indicator. The reaction mixture was neutral. The reaction mixture was concentrated suspended in THF (50 mL) and heated at 60 °C. The oxidation was carried out by adding hydrogen peroxide (3.72 mL, 30%) slowly into the flask following addition of an aqueous solution of sodium hydroxide (1.86 mL, 6 N). After 3 h, the polymer was precipitated by the addition of acetonitrile, filtered and dried at 70 °C in vacuum oven to yield 451 mg (94%). ^{1}H NMR (500 MHz, d_8-toluene) δ 3.36 (t, 2 H, HO-C$\underline{H}_2$-), 1.32 (b, 125 H, $CH_3(C\underline{H}_2)_nCH_2OH$), 0.87 (m, 4 H, C$\underline{H}_3CH_2$-, -CH(C$\underline{H}_3$)-).

Synthesis of hydroxyterminated polymethylene (DP = 117)

In a similar manner, dimethyloxosulfonium methylide in toluene (50 mL, 0.47 M, 23.5 mmol) and triethylborane in THF (68 μL, 1 M, 0.068 mmol), after precipitation by the addition of acetonitrile, gave 337 mg (100%). ^{1}H NMR (500 MHz, d_8-toluene) δ 3.36 (t, 2 H, HO-C$\underline{H}_2$-), 1.32 (b, 291 H, $CH_3(C\underline{H}_2)_nCH_2OH$), 0.87 (m, 8 H, C$\underline{H}_3CH_2$-, -CH(C$\underline{H}_3$)-).

Synthesis of hydroxylterminated polymethylene (DP = 232)

In a similar manner, dimethyloxosulfonium methylide in toluene (50 mL, 0.47 M, 23.5 mmol) and triethylborane in THF (34 μL, 1 M, 0.034 mmol) gave 334 mg (100%). ^{1}H NMR (500 MHz, d_8-toluene) δ 3.36 (t, 2 H, HO-C$\underline{H}_2$-), 1.32 (b, 598 H, $CH_3(C\underline{H}_2)_nCH_2OH$), 0.87 (m, 16 H, C$\underline{H}_3CH_2$-, -CH(C$\underline{H}_3$)-).

Synthesis of α, ω-hydroxylmethoxyphenyl polymethylene using toluene as solvent[1]

Into a flame dried 100mL one neck round bottom flask equipped with a magnetic stirrer and a rubber septa was added a solution of dimethyloxosulfonium methylide in toluene (50 mL, 0.33 M, 16.5 mmol) by syringe under argon. The solution was heated by a oil bath at 60 °C. Then, a solution of tri(2-4-methoxyphenyl-ethyl) borane in THF (100 μL, 0.95 M, 0.095 mmol) was syringed into the reaction flask and the polyhomologation started. After 10 min., an aliquot of the reaction mixture was withdrawn and added into the distilled water with phenolphthalein indicator. The reaction mixture was neutral. Then, the reaction mixture was concentrated by rotavaporation, dissolved in THF (50 mL) and heated at 60 °C with the installation of condenser. The oxidation was carried out by adding hydrogen peroxide (1.93 mL, 30%) slowly into the flask after addition of sodium hydroxide aqueous solution (0.97 mL, 6 N). After three hours reaction, the polymer was precipitated by the addition of acetonitrile, filtered and dried at 70 °C in vacuo oven to yield 250 mg (100%). ^{1}H NMR (300 MHz, d_8-toluene) δ 6.98-6.95 (m, 2H, aromatic), 6.74 (d, 2H, aromatic), 3.43 (s, 3H, -Ph-OC$\underline{H}_3$), 3.36 (t, 2H, -C$\underline{H}_2$-OH), 2.49 (t, 2H, -C$\underline{H}_2$-Ph-OCH$_3$), 1.33 (s, 153H, -(C$\underline{H}_2$)$_n$-), 0.91 (d, 2.5H, -CH(C$\underline{H}_3$)-).

1. A typical reaction scale is 30 to 50 mmole. There is no reason that we know of that would prevent scale up providing precautions are taken to account for the reactions exothermicity. K. J. Shea, J. R. Walker, H. Zhu U.S. Patent No. 5, 476, 915, Dec. 19, 1995.

DEUTERATED POLYMER. COPOLYMERS

Trimethylsulfoxonium chloride-*d*9 (1)

A solution of trimethylsulfoxonium chloride (10.0 g, 77.7 mmol) in D_2O (20 mL) containing a catalytic amount of NaOD (1 mol%) was stirred at rt. for 6 hr. The water was removed by rotary evaporation, the resulting solid was dissolved in fresh D_2O (20 mL), stirred for 6 hr and concentrated in vacuum. This

Trimethylsulfoxonium methylide-*d*8

Trimethylsulfoxonium chloride-*d*9 (5 g, 36.5 mmol) was added to a stirred suspension of NaH (1.50 g, 38 mmol, 60% dispersion in mineral oil, prewashed with hexane) in toluene (30 mL). The resulting mixture was stirred for 15 min, then heated to reflux for 6 h. After this period, the reaction mixture was cooled to rt. and filtered through a celite path under N_2. The reaction flask and the filter cake were washed with toluene (10 mL). Two 2 mL portions of this solution were hydrolyzed with water (5 mL) and titrated with 0.10 N HCl using phenolphthalein as indicator. The concentration was 0.83 N (91%).

***p*-$MeOC_6H_4CH_2CH_2(CD_2)_{50}CD_2OH$**

A solution of Trimethylsulfoxonium methylide-*d*8 (9.0 mL, 7.5 mmol, 0.83 M in toluene) was heated to 50 °C and treated with borane **4** (250 μL, 50 μmol, 0.20 M in THF). After 5 min, a aliquot of the reaction mixture was hydrolyzed with water/phenolphthalein, and no color was observed, indicating that the reaction was complete. The reaction mixture was cooled to rt. and concentrated in vacuum. The residue was suspended in THF (5 mL) and treated with 3 N NaOH (83 μL, 0.250 mmol) and 33% H_2O_2 (25 μl, 0.250 mmol). The resulting suspension was heated to 50 °C and stirred for 2 hr at that temperature. After this period, the reaction mixture was cooled to rt. and CH_3CN (40 mL) was added to precipitate the polymer. The polymer was filtered and washed with CH_3CN and MeOH to give 120 mg (91%) of a white solid.

^{1}H NMR δ 6.97 (d, 2 H); 6.73 (d, 2 H, J = 9.6 Hz, Ar); 3.40 (s, 3 H, CH_3O); 2.48 (t, 2 H, J = 7.6 Hz, $ArCH_2$); 1.55 (t, 2 H, J = 7.6 Hz, CH_2CH_2Ar); 1.26 (s, 10 H, CH_2).

Synthesis of α, ω-hydroxylmethoxyphenyl copolymethylene polyperdeuterio polymethylene

In a procedure similar to that described for the perdeuterio polymer above, 25 eq. of ylide **1** was first reacted. Following consumption of the ylide (5 min.) a warm solution of 25 eq. of the perdeuterio (94% isotopic purity) was added as rapidly as possible. Following consumption of this ylide (10 min.), the polyhomologated organoborane was oxidized and worked up as described previously.