Electronic Supplementary Information for Dalton Transactions

SUPPORTING INFORMATION

4,4’-Bipyridazine: a new twist for the synthesis of coordination polymers

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Detailed procedure for preparation of 1,2,4,5-tetrazine.

Unsubstituted 1,2,4,5-tetrazine may be viewed as a valuable starting compound for synthesis of a number of new pyridazine derivatives, including such polyfunctional compounds as polypyridazines (e.g. 4,4’-bipyridazine as a simple prototype) and condenced pyridazines [1].

Present very simple and efficient method for the preparation of unsubstituted 1,2,4,5-tetrazine rationally combines two literature procedures [2, 3]. However, it was possible significantly simplify the preparation and to avoid any column chromatography separations. This method was best reproducible and the synthesis was successfully repeated in our laboratory for dozens times.

120 mL of cold hydrazine hydrate was added for 10 min at 0°C and with stirring to 93.6 g of solid formamidinium acetate. The initially formed clear solution solidified after 5-8 min strirring and it was left for 1 h at r.t. Then 60 mL of ice water was added and the mixture was stirred for an additional hour in an ice bath. The solid was filtered on a Büchner funnel with suction and was made as dry as possible by efficient pressing. In spite of oxidation of this intermediate product in air, it was not necessary to use inert atmosphere technique.

The solid was dissolved in 300 mL of cold glacial acetic acid and 31 g of solid $NaNO_2$ was added in small portions for 2 h at 0°C (ice bath) and with stirring. After additional 1.5 h of stirring at this temperature, the mixture was pre-cooled to -18°C and 450 mL of ice water was added at once [*Efficient pre-cooling was an important step since the addition of water effects rapid and pronounced rise of temperature, after 1-2 minutes: from -18°C to +15°C. When, without the pre-cooling, in some experiments the reaction mixture temperature exceeded 30°C, the yield of the product was significantly lower*]. The solution was extracted with 5 × 400 mL of cold CH_2Cl_2, the combined extracts were washed with 1.5 L of saturated $NaHCO_3$ solution and with 1 L water, and then dried overnight over $CaCl_2$ in a refrigerator. The red-violet solution was gently evaporated to a volume of 60-70 mL by distillation of the solvent from a 500 mL flask through a 60 cm Vigreux column [*the red-colored distillates were used for extractions of the next batch*]. The residual liquid was transferred into 250 mL flask. Some solvent remained was evaporated *in vacuo* and the solid left was sublimed at r.t. and 1.0 Torr directly from the flask on a cooling finger (-40°, acetone/liquid N_2) yielding the pure product as deep-red very volatile crystals (See Figure S1). The typical yields were 8.5-10 g.

This product significantly decomposes at r.t. in air for a period of 2-3 weeks, but may be stored for indefinitely long term in a refrigerator (-20°C).

1 I.A. Gural'skiy, P.V. Solntsev, H. Krautscheid and K.V. Domasevitch, *Chem. Commun.*, 2006, 4808.

2 A.T.M. Marcelis, H.C. van der Plas, *J. Heterocyclic Chem.* **1987**, *24*, 545.

3 J. Sauer, D.K. Heldmann, J. Hetzenegger, J. Krauthan, H. Sichert, J. Schuster, *Eur. J. Org. Chem.* **1998**, 2885.

Figure S1. Final step of 1,2,4,5-tetrazine preparation: The foto demonstrates a very simple equipment for isolation of pure tetrazine (in a 10-15 g scale) by direct sublimation at room temperature of the residue after evaporation of the solvent. As a cooling finger we have employed a usual 60 cm adapter for condensation of liquid ammonia, charged with acetone and liquid nitrogen for supporting temperature in the range -40-50°C. Note the extremely high volatility of the deep-red product, which was best illustrated here by coloration of all transparent vacuum tubing in pink to red.