

SHORT
COMMUNICATIONS

Synthesis of Bis(2-amino-5-R-phenyl) Ditellurides

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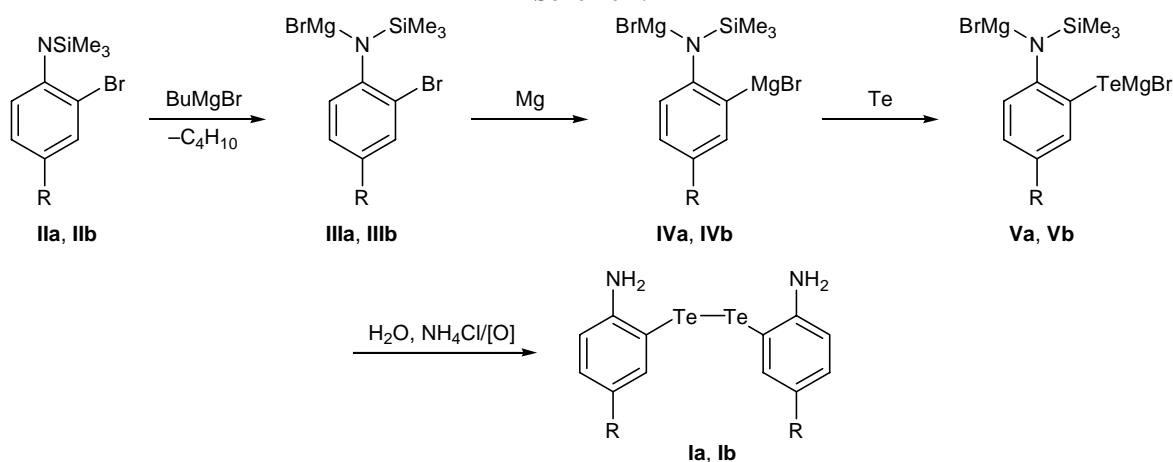
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Aromatic compounds having an amino group and a tellurium-containing moiety in the *ortho* positions with respect to each other are promising synthons for the preparation of tellurium heterocycles with two heteroatoms; they can also be used as soft ligands for the synthesis of coordination compounds. Up to now, only two methods for the synthesis of such amino tellurium compounds have been reported. Bis(2-amino-phenyl) ditelluride [1] was synthesized in three steps including mercuriation of azobenzene at the *ortho* position; reaction of the chloromercurio derivative thus formed with tellurium tetrachloride to obtain 2-(phenylazo)phenyltellurium trichloride; and treatment of the latter with NaBH₄, which resulted in simultaneous reduction of the trichlorotellurium moiety to ditelluride and of the azo group to amino. The other method for the synthesis of bis(2-amino-5-R-phenyl) ditellurides is based on mercuriation of *para*-substituted anilines, followed by reaction of 2-chloromercurio-4-R-anilines with TeBr₄ and reduction of the resulting tellurium tribromides with hydrazine hydrate [2]. However, these procedures are not free from some disadvantages. In

particular, intermediate products in each step should be thoroughly purified, and the overall yields of the target products do not exceed 45–57%.

We have developed a more convenient (from the preparative viewpoint) procedure for the synthesis of bis(2-aminophenyl) ditelluride (**Ia**) and bis(2-amino-5-methylphenyl) ditelluride (**Ib**). As starting compounds we used readily accessible and hydrolytically stable *N*-trimethylsilyl-2-bromoanilines **IIa** and **IIb**. The reaction sequence shown in Scheme 1 is implemented as a one-pot process. The reaction of **IIa** and **IIb** with an equimolar amount of butylmagnesium bromide in THF gives *N*-bromomagnesio-*N*-trimethylsilyl-2-bromoanilines **IIIa** and **IIIb** which are converted into dimagnesium derivatives **IVa** and **IVb** by treatment with magnesium. Compounds **IVa** and **IVb** react with tellurium powder to afford bromomagnesium tellurolates **Va** and **Vb**, and hydrolysis of the latter involves removal of the trimethylsilyl protection and oxidation with atmospheric oxygen of intermediate tellurophenols to target ditellurides **Ia** and **Ib**. The yield of ditellurides **Ia** and **Ib** ranges from 65 to 67%.

Scheme 1.



Bis(2-amino-5-methylphenyl) ditelluride (Ib).

Butyl bromide, 13.7 g (0.1 mol), was added dropwise under stirring to a mixture of 2.43 g (0.1 mol) of magnesium and 250 ml of THF. When the reaction was complete, the mixture was cooled to 10°C, and 25.8 g (0.1 mol) of aniline **Ib** was added at such a rate that the temperature did not exceed 15°C. The mixture was stirred until butane no longer evolved, heated for 1 h, and cooled to 20°C, 2.43 g (0.1 mol) of magnesium was added, 0.1 ml of 1,2-dibromoethane was added to initiate the reaction, and the mixture was carefully heated to maintain it evenly boiling; the magnesium dissolved completely in 3.5–4 h. The mixture was cooled to 20°C, 12.76 g (0.1 mol) of tellurium powder was added, and the mixture was heated for 0.5 h under reflux, cooled, and poured into 500 ml of a saturated aqueous solution of ammonium chloride. Air was then bubbled through the solution over a period of 2 h, and the mixture was extracted with diethyl ether (150 ml). The extract was washed with water, dried over anhydrous sodium sulfate, and evaporated, and the residue was recrystallized from toluene–hexane (1:1). Yield 15.19 g (65%). Red needles, mp 118–119°C; published

data [2]: mp 116°C. ¹H NMR spectrum, δ, ppm: 2.17 s (3H, CH₃), 4.04 br.s (2H, NH₂), 6.63 d (1H, 3-H, ³J = 8.1 Hz), 6.92 d.d (1H, 4-H, ³J = 8.1, ⁴J = 1.9 Hz), 7.46 d (1H, 6-H, ⁴J = 1.9 Hz).

Bis(2-aminophenyl) ditelluride (Ia) was synthesized in a similar way. Yield 67%. Purple needles, mp 102°C (from toluene–hexane, 1:1); published data [1]: mp 100°C.

The ¹H NMR spectra were recorded on a Varian Unity-300 spectrometer (300 MHz) using CDCl₃ as solvent; the chemical shifts were measured relative to the residual proton signal of the solvent.

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