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NOTE

THE PREPARATION AND SOME PROPERTIES OF DIMETHYL DITELLURIDE

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In connection with a study of organo-substituted tellurium(IV) halides there developed a need for dimethyl ditelluride, $(CH_3)_2Te_2$, a substance not previously described in the literature. While a large number of dialkyl selenides are known, the only aliphatic ditellurides which have been reported are di-n-butyl ditelluride[1] and the derivatives of acetic and propionic acids[2,3]. In this note an adaptation of a recent method for dialkyl sulfides, selenides and tellurides[4] is described which gives $(CH_3)_2Te_2$ in moderate yields. This compound is of interest because of the opportunities it affords for the examination of the chemical reactivity of the Te–Te bond in a simple molecule and for the spectroscopic identification of the stretching frequency of this bond.

EXPERIMENTAL AND RESULTS

Clean sodium metal (3.2 g, 0.14 mole) was added to 100 ml of anhydrous ammonia at −78° in a 500-ml flask equipped with a reflux condensor, stirrer, and dropping funnel. After stirring the mixture for 1 h high purity, powdered tellurium (18.2 g, 0.14 mole) was added in 0.5 g portions. Methyl iodide (24 g, 0.17 mole) was then added in dropwise manner over a 20 min period with stirring to the dark green solution. After removal of the cooling bath and the evaporation of the ammonia, water was added to the residue, and the mixture extracted four times with 50 ml portions of diethyl ether. The deep red ether extract was dried overnight using anhydrous calcium chloride; the solvent was removed from one-half of this extract by vacuum distillation. The product (3.8 g, 13 mmole, 38% yield based upon Te) was collected at 68° under vacuum. (Found: Te, 87.6; cryoscopic mol. wt. in benzene, 274. $C_2H_6Te_2$ calcd.: Te, 89.5%; mol. wt., 285.) The freshly prepared ditelluride is a heavy, dark red liquid which solidifies after standing a few days at room temperature. The liquid is regenerated by subjecting the solid to vacuum distillation under the above conditions. The infrared spectrum determined using a thin layer of the liquid between KBr and polyethylene windows showed absorptions as follows: 3010 w–m, 2920 s, 2795 w–m, 2390 w–m, 1710 vw, 1410 s, 1205 vs, 818 vs, 505 m, 122 w–m, 61 w cm^{-1}. The proton NMR spectrum of a carbon tetrachloride solution of the ditelluride consists of a single peak at 2.71 ppm (TMS internal standard).

Dropwise addition of a large excess of bromine to 20 ml of a benzene solution containing $(CH_3)_2Te_2$ (0.41 g, 1.4 mmole), followed by removal of solvent and excess bromine by vacuum distillation at room temperature, gave green, crystalline methyltellurium tribromide[5], CH_3TeBr_3, in quantitative yield. Recrystallization from methylene chloride gave 0.53 g of this substance which darkens and decomposes above 140°. In other trials it was observed that both tellurium tetrabromide and methyl bromide may also be formed when the reaction occurs either in the absence of a solvent, or in a concentrated diethyl ether solution.

Using standard vacuum line procedures a large excess of boron tribromide was condensed into a trap containing 10 ml of a benzene solution of the ditelluride (0.91 g, 3.2 mmole). Warmed slowly to room temperature the yellow mixture darkens progressively over a 1 h period, and yields a black precipitate. Removal of solvent and excess BBr_3 (infrared spectra of the volatile material indicated the presence of no species other than C_6H_6 and BBr_3) resulted in 1.73 g of the black solid. The weight gain corresponds to a 1 : 1 mole ratio of BBr_3 to $(CH_3)_2Te_2$. The infrared spectrum of this material is identical with that of the white 1 : 1 BBr_3 adduct of $(CH_3)_2Te$[6].

DISCUSSION

In a report of the infrared spectrum of diphenyl ditelluride[7], $(C_6H_5)_2Te_2$, the spectral range examined was too limited to permit the identification of the Te–Te stretching frequency. However, a Raman investigation of ditellurium decafluoride[8], Te_2Fe_{10}, led to the assignment of 168 cm^{-1} to the infrared-inactive Te–Te mode. It is reasonable to expect that the skeletal structure of the $(CH_3)_2Te_2$ molecule is either non-planar (C_2) or planar *cis* (C_{2v}) and, accordingly, the Te–Te stretching frequency should be active in the infrared. Examination of the spectrum suggests that the weak–medium absorption at 122 cm^{-1} is the preferred choice for this fundamental.

The proton resonance of 2.71 ppm found for $(CH_3)_2Te_2$ is somewhat further downfield than that observed for dimethyl disulfide[9], 2.38 ppm, or for dimethyl diselenide[10], 2.53 ppm. The failure to observe any proton resonance at about 1.8 ppm, expected to be the approximate proton resonance for $(CH_3)_2Te$ based upon the known shifts for the analogous sulfide and selenide[10], argues for the absence of $(CH_3)_2Te$ in the $(CH_3)_2Te_2$ prepared here.

Although CH_3TeBr_3 was in all cases the principal product of the bromination of $(CH_3)_2Te_2$ the reactivity of the C–Te bond as well as that of the Te–Te bond is indicated by the appearance of $TeBr_4$ and CH_3Br as secondary products under the indicated conditions.

The dark reaction product obtained in the attempt to demonstrate Lewis basicity of $(CH_3)_2Te_2$ toward BBr_3 is most readily interpreted as a 1 : 1 mole ratio mixture of elementary tellurium and the stable adduct, $(CH_3)_2Te \cdot BBr_3$, resulting from the disproportionation of the ditelluride.

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