Journal of Organometallic Chemistry, 190 (1980) C64—C66

Preliminary communication

PREPARATION OF THE DIMETHYLPHENYLTELLURONIUM AND TRIPHENYLTELLURONIUM IONS BY DIRECT PHENYLATION WITH $NaBPh_4$

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(Received January 11th, 1980)

Summary

New reactions are described for the formation of C—Te bonds by the use of an organoborate. Accordingly, dimethyltellurium dichloride, Me_2TeCl_2, and diphenyltellurium dichloride, Ph_2TeCl_2, undergo direct and facile phenylation reactions with sodium tetraphenylborate at room temperature in methanol and water, respectively, to produce dimethylphenyltelluronium and triphenyltelluronium tetraphenylborate, respectively. Tellurium tetrachloride in benzene undergoes triarylation with excess $NaBPh_4$ to yield $Ph_3Te^+BPh_4^-$.

A variety of tellurium compounds undergo reactions with reagents such as RMgX, RX and R_2M to form carbon—tellurium bonds [1]. Tellurium tetrachloride and diaryltellurium dichlorides, for example, react with aromatic Grignard reagents to form triaryltelluronium compounds.

We have discovered a rapid and facile procedure for the phenylation of tellurium(IV) using the tetraphenylborate ion. Intermolecular transfer reactions of organoborates are relatively uncommon [2, 3] and direct phenylation by BPh_4^-, for example, is known in only a few instances, such as in the reactions of $HgCl_2$, Br_2 and H^+ to form PhHgCl, PhBr and C_6H_6, respectively. The reactions of $TeCl_4$, Me_2TeCl_2 and Ph_2TeCl_2 with BPh_4^- provide the first examples of C—Te bond formation via the use of an organoborate, and serve to extend the chemistry of the replacement of boron to new and different electrophiles.

Dimethyltellurium dichloride reacts with sodium tetraphenylborate to form the new compound dimethylphenyltelluronium tetraphenylborate. In a typical reaction, 2 mmol (0.46 g) of Me_2TeCl_2 dissolved in 30 ml absolute methanol (reagent grade) was added with stirring to 5 mmol (1.7 g) of $NaBPh_4$ in 30 ml of the same solvent at room temperature. Precipitation occurred within minutes.

After one to two hours the product was collected by filtration and recrystallized from hot methyl ethyl ketone (MEK). The yield based on the complete conversion of the dichloride to the tetraphenylborate, was 55% after one hour and 65% after two hours. Considerably decreased yields were noted after 24 hours, indicating competing reactions. The same product results if an excess of Me_2TeCl_2 is used, for example, in 1/1 mol ratio, or if the reaction is run in the dark. In these and the reactions below, moisture was not rigorously excluded. Me_2TeCl_2 and Ph_2TeCl_2 (Organometallics, Inc.) were recrystallized from MeOH; $TeCl_4$ and $NaBPh_4$ (99.5%) were used as received.

Characterization studies of the new compound were performed on samples recrystallized from hot MEK. Dimethylphenyltelluronium tetraphenylborate is a white crystalline solid which is insoluble in water like the corresponding Me_3Te^+ and Ph_3Te^+ salts [4]. In addition to correct elemental analyses (H, B, C, Te), the new compound shows ^1H magnetic resonance signals in DMSO-d_6 (TMS, external, 24°C) at 2.35 ppm (sharp singlet), 6.8—7.4 ppm (multiplet) and 7.4—8.0 ppm (multiplet) in a 6/20/5 ratio, respectively. The cation phenyl-proton multiplet is downfield from the anion phenyl-proton multiplet, consistent with the larger deshielding effect expected in the cation. $Me_2PhTeBPh_4$ is less soluble in MeOH than the corresponding chloride and, therefore, precipitates even in the presence of excess Me_2TeCl_2. Similar behavior was noted for the Me_3Te^+ and Ph_3Te^+ ions [4, 5]. Replacement of BPh_4^- with I^- produced Me_2PhTeI which was synthesized previously by the reaction of PhTeLi with methyl iodide [6].

Unit cell data for the compound are as follows: monoclinic, space group $P2_1/n$, a 9.098(2), b 17.990(2), c 16.266(4) Å, β 97.25(2)°, $Z = 4$, V 2641 Å^3, D_{cald} 1.393 g/cm^3 and D_{meas} 1.39(2) g/cm^3 (23°C). $Me_2PhTeBPh_4$ decomposes upon heating above 200°C with the apparent decomposition range (liquefaction and bubbling) markedly dependent upon heating rate.

In addition to the arylation of the dialkyltellurium dichloride, sodium tetraphenylborate will also arylate the diphenyl compound, Ph_2TeCl_2. Typically, a filtered solution containing approximately 0.5 g of Ph_2TeCl_2 dissolved in 150 ml of hot water was added to 20 ml of H_2O containing 2 g of $NaBPh_4$ to form a white precipitate. After stirring, the reaction mixture was filtered and washed with water. The product was recrystallized from acetonitrile in yields of 40 to 50%. The reaction of Ph_2TeCl_2 in water with pseudohalide ions gave compounds of the type $(Ph_2TeX)_2O$ [7].

Tellurium tetrachloride, which is one of the most widely used reagents for the synthesis of tellurium compounds, also undergoes arylation with sodium tetraphenylborate. In the presence of excess $NaBPh_4$, $Ph_3Te^+BPh_4^-$ is formed. In a typical reaction, 4 mmol of solid $NaBPh_4$ was added to one mmol of $TeCl_4$ dissolved in 60 ml of benzene to form a gray precipitate. The reaction mixture was shaken vigorously for 24 h or longer, filtered and washed with water. The product was extracted with acetone and precipitated with H_2O. Small amounts of elemental crystalline tellurium (0.02 g), identified by X-ray diffraction, remained in the filter. The product was recrystallized from acetonitrile in yields of 30 to 50%. We have not ruled out the formation of monoaryl or diaryl species in this reaction or when an excess of $TeCl_4$ is used.

Triphenyltelluronium tetraphenylborate was identified by comparison of its

X-ray powder pattern with that of a previously prepared and characterized sample [4], and by ^{1}H magnetic resonance in DMSO-d_6. In addition to the BPh_4^- multiplet (vide supra) a sharp signal was observed at 7.6 ppm in a 3/4 ratio. The NMR spectrum of a previously prepared sample was identical. Triphenyltelluronium tetraphenylborate decomposes upon heating above 200°C and cannot be conveniently identified by its thermal behavior.

The new reactions reported here for the formation of C—Te bonds appear to provide a general and expedient method for the synthesis of triorganotelluronium salts. Utilization of mixed diorganotellurium dihalides, for example, offers a viable route to the preparation of chiral RR′R″TeX compounds. Some new research opportunities in organochalcogen and organoboron chemistry are also suggested by extension of the present reaction to include other tellurium compounds and other organoborates, such as the alkenylborates, $RCH{=}CHB(R')_2Me^-$. In addition, we note that $NaBPh_4$ also reacts with various selenium compounds which suggests application of the organoborate reaction to the formation of C—Se bonds as well. Further explorations of these reactions are expected to provide new methods for the insertion of selenium and tellurium in organic compounds.

Acknowledgement

We thank the referees for their helpful comments, some of which were incorporated into the manuscript.

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