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# DIARYL DITELLURIDES FROM GRIGNARD REAGENTS AND ELEMENTAL TELLURIUM

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## SUMMARY

The one step reaction of aromatic Grignard reagents with elemental tellurium in tetrahydrofuran, followed by oxidation of the intermediates, produced diphenyl ditelluride in 80% yield and $(RC_6H_4)_2Te_2$ (R=4-$CH_3$, 2-$CH_3$, 2-Cl, 4-Br, 4-F, 3-F, 4-$C_6H_5$) in yields ranging from 15 to 58%. Several other aromatic Grignard reagents and all aliphatic derivatives tested failed to react. Diethyl and dibutyl ether are not suitable as solvents.

## INTRODUCTION

Diorganyl ditellurides, $R_2Te_2$, are convenient, stable starting materials for various tellurium containing compounds like organyl tellurium trihalides, tellurinic acids, symmetric and unsymmetric diorganyl tellurides, diorganyl tellurium dihalides and transition metal complexes. A detailed discussion of the reactions of diorganyl ditellurides is available in the literature[1]. Dialkyl ditellurides can be obtained from sodium ditelluride and alkyl halides. The principal method for the synthesis of aromatic ditellurides is the reduction of aryltellurium trihalides. The trihalides are easily prepared from aromatic hydrocarbons, when they bear the activating groups RO, RS, HO, RC(O)NH, or $R_2N$, and tellurium tetrachloride, while in the absence of such a group arylmercuric chlorides must be employed. The pertinent literature references for these reactions can be found in Ref. 2.

A short route to diorganyl ditellurides would be the reaction of Grignard reagents with elemental tellurium followed by hydrolysis and oxidation of the reaction mixture. It has been known for a long time, that phenylmagnesium bromide reacts with tellurium[3-8]. The rather unstable (phenyltelluro)magnesium bromide formed in these reactions has been employed to synthesize ethyl phenyl[4], phenyl alkynyl[5,6], diphenyl[1,6] and bis(trimethylsilyl) tellurides[7]. The only somewhat detailed investigation of the reaction between tellurium and phenylmagnesium bromide was carried out by Petragnani and de Moura Campos[8]. They extracted the hydrolyzed reaction mixture obtained from $C_6H_5MgBr$ and tellurium with benzene. The extract treated

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with sulfuryl chloride produced varying but relatively small amounts of phenyltellurium trichloride and diphenyltellurium dichloride.

A careful study of the reaction of phenylmagnesium bromide with elemental tellurium was therefore undertaken to find a convenient method for the direct synthesis of diphenyl ditelluride. Other Grignard reagents were then tested for their suitability in ditelluride syntheses.

## RESULTS AND DISCUSSION

The preparation of diaryl ditellurides is described by eqn. (1) and (2).

$$\text{Ar–MgBr} + \text{Te} \rightarrow \text{Ar–Te–MgBr} \qquad (1)$$

$$2\,\text{ArTeMgBr} \xrightarrow{O_2} \text{Ar}_2\text{Te}_2 + \text{MgBr}_2 + \text{MgO} \qquad (2)$$

The highest yields were obtained when the reactions were carried out in tetrahydrofuran with a 3–4% tellurium excess. With diethyl ether as the solvent most of the tellurium remained unreacted even after extended refluxing of the heterogeneous mixture. The presence of limited amounts of oxygen during the reaction between the Grignard reagent and tellurium is essential. Oxygen in large excess over the stoichiometrically required quantity resulted in the formation of a white, insoluble gummy precipitate, drastically reducing the ditelluride yield. The oxygen fed to the reaction mixtures in portions was taken up quickly until approximately one liter had been consumed per 0.1 mole of reagents. Immediate hydrolysis with aqueous ammonium chloride solution or dilute hydrochloric acid precipitated large amounts of tellurium as observed earlier[3,8]. In order to obtain good yields, it is imperative that the work-up procedure as described in the experimental section is closely followed. Cooling the mixtures to 0° after the reaction had started was found to be beneficial. Difficulties sometimes encountered in initiating the reactions were overcome by adding small amounts of benzoyl peroxide to the reaction mixture. The highest yields in reactions with phenylmagnesium bromide were obtained with 0.25 moles each of tellurium and Grignard reagent.

Tellurium was also reacted with phenylmagnesium bromide under a nitrogen atmosphere. A yellowish-white precipitate was formed. After all the tellurium had been consumed, air was bubbled through the heterogeneous mixture giving the ditelluride in yields of approximately 20%. Attempts to synthesize diphenyl ditelluride in dibutyl ether according to the conditions employed in the reaction in tetrahydrofuran failed. Even refluxing the dibutyl ether solution of phenylmagnesium bromide with tellurium did not give any ditelluride.

In order to determine the suitability of the conditions found optimal for the synthesis of diphenyl ditelluride for the preparation of aliphatic and aromatic ditellurides, the reaction was carried out with eighteen other Grignard reagents. Ditellurides were obtained only from $(\text{R–C}_6\text{H}_4)\text{MgBr}$ ($\text{R} = 4\text{-CH}_3$, $2\text{-CH}_3$, 2-Cl, 4-Br, 4-F, 3-F, $4\text{-C}_6\text{H}_5$) (Table 1). The yields were all lower than obtained in reactions with phenylmagnesium bromide. In most cases a substantial amount of unreacted tellurium was recovered. The yields did not improve when the reactions were run under conditions different from the optimal ones for the phenyl case. Tellurium was recovered almost quantitatively when 2-fluorenyl-, 1-naphthyl-, 2,5-diphenylphenyl-, 2,4,6-triphenylphenyl-, R–phenyl- (R = 3-$CH_3$, 2-F, 4-$CH_3O$) and pentafluorophenylmagnesium bromide were employed. The Grignard reagents derived from butyl chloride and octyl and pentyl bromide were also unreactive even in the presence of peroxide. Butylmagnesium chloride also failed to react with tellurium in THF under an atmosphere of nitrogen.

TABLE 1

DIARYL DITELLURIDES, $R_2Te_2$

| *R* | *M.p.* (°*C*) | *Yield*[a] (%) | *Analysis: found (calcd.)* (%) | |
|---|---|---|---|---|
| | | | *C* | *H* |
| Phenyl | 66 | 50–85 | 35.1<br>(35.2) | 2.4<br>(2.4) |
| 4-Methylphenyl | 51 | 49 | 38.3<br>(38.4) | 3.2<br>(3.2) |
| 2-Methylphenyl | Oil | 12 | 40.6[b]<br>(38.4) | 3.4<br>(3.2) |
| 2-Chlorophenyl[c] | Oil | 25 | [b] | [b] |
| 4-Bromophenyl | 153 | 20 | 25.7<br>(25.4) | 1.3<br>(1.4) |
| 4-Fluorophenyl[c] | 77 | 58 | 32.6<br>(32.3) | 1.9<br>(1.8) |
| 3-Fluorophenyl[c] | 44 | 29 | 32.3<br>(32.3) | 1.8<br>(1.8) |
| 4-Biphenylyl[c] | 216 | 15 | 50.0[b]<br>(51.3) | 2.8<br>(3.2) |

[a] Yield of pure, recrystallized product based on total tellurium employed. [b] See text for discussion. [c] Not previously reported in literature.

The results obtained make it unlikely, that the reactivity of the Grignard reagent towards elemental tellurium is influenced by the carbanion character of the organic group. If the concentration of negative charge on the carbon atom would determine the reactivity, then aliphatic Grignard reagents should be more reactive than aromatic derivatives. Alkylmagnesium halides are not only unreactive towards elemental tellurium, they have also been found to be inert towards diorganyl ditellurides. Ditellurides experience Te–Te bond cleavage with arylmagnesium halides[9]. The addition of 1,2-bis(dimethylamino)ethane, a reagent, which increases the negative charge on the carbanion, to a phenylmagnesium bromide solution did not impede the reaction with tellurium, but lowered the yield of ditelluride. Electron withdrawing and electron donating substituents in the phenyl rings both lower the yields.

The possibility of a radical mechanism in these reactions has been discussed[8]. Although final evidence for such a mechanism is not available, the observed initiation of the reaction by benzoyl peroxide points towards the participation of radicals in these reactions. Addition of 0.01 moles of anhydrous cobalt(II) chloride to the Grignard reagent followed immediately by the tellurium powder reduced the yield of ditelluride drastically. Cobalt chloride is known to induce coupling of the organyl groups of Grignard reagents via a radical mechanism[10], but did not enhance the attack of the organic groups on elemental tellurium. It is likely, that the transition state involved in these reactions is more influenced by solvation and steric factors than by electronic effects caused by the substituents in the phenyl ring. The fact that *ortho* substituted compounds formed in lower yields than the corresponding *para* compounds suggests the importance of steric factors.

Bis(2-methylphenyl) and bis(2-chlorophenyl) ditellurides were isolated only as oils, which could not be purified. The same difficulties with *ortho* substituted diphenyl ditellurides, prepared from the appropriate phenyllithium compound and tellurium, were encountered by Piette and Renson[11]. Treatment of the crude oils with bromine in carbon tetrachloride produced the aryltellurium tribromides, for which correct analytical results were obtained.

4-Biphenylylmagnesium bromide reacted easily with tellurium. The red precipitate which was formed was extracted with acetonitrile, and the residue recrystallized several times from dichloromethane. The carbon analysis of the best sample was still 1.3% low. The mass spectrum of the compound however, confirmed its identity. Impurities like bis(biphenylyl) telluride and biphenyl should increase the carbon value. Elemental tellurium could not have been present in the recrystallized samples since tellurium is insoluble in organic solvents. Bis(biphenylyl) tritelluride could be the cause of the low carbon analysis. Although diorganyl tritellurides have not been isolated yet, we have detected diphenyl tritelluride in the mass spectrum of diphenyl ditelluride. A bis(biphenylyl) tritelluride molecular ion was not found in the mass spectrum of the ditelluride. The tritelluride probably decomposed at the high probe temperature required to obtain the spectrum of the ditelluride. Details of the mass spectral investigations of these aromatic ditellurides will be published later.

Petragnani[9] showed that diaryl ditellurides are cleaved by an excess of aromatic Grignard reagent in diethyl ether solution according to eqn. (3).

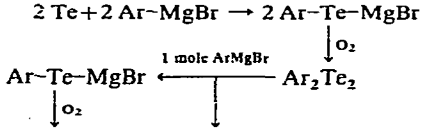
$$Ar_2Te_2 + Ar'MgBr \longrightarrow Ar{-}Te{-}Ar' + ArTeMgBr \qquad (3)$$

Since an excess of Grignard reagent was always present during the ditelluride syntheses [eqn. (1, 2)] the cleavage reaction (3) could have reduced the ditelluride yield.

Assuming that the formation of diaryl ditellurides [eqn. (1, 2)] and their cleavage [eqn. (3)] proceeds until all the Grignard reagent is used up one would expect to obtain one mole of diaryl telluride, 0.5 moles of diaryl ditelluride and one mole of unreacted tellurium from a reaction mixture initially containing three moles each of the Grignard reagent and tellurium. (Scheme 1.)

SCHEME 1

*Starting materials*: 3 moles Te+3 moles ArMgBr



*End products* ½ mole $Ar_2Te_2$ 1 mole Ar–Te–Ar 1 mole of Te unreacted

Diphenyl ditelluride was in fact cleaved by an excess of phenylmagnesium bromide in THF in the presence of oxygen. To ascertain whether such a cleavage reaction took place during the ditelluride syntheses the organic mother liquors and the aqueous solutions obtained upon hydrolysis of the reaction mixtures were further investigated.

The oils obtained after evaporating the organic liquors were dissolved in chloroform and treated with bromine in order to convert the ditellurides into aryltellurium tribromides and the tellurides into diaryltellurium dibromides. The resulting yellow solids were extracted with ethanol, which dissolves only the tribromides. In this manner 0.1 g of diphenyltellurium dibromide was recovered from a reaction of 0.3 moles of phenylmagnesium bromide. Similar reactions with 0.15 moles of (4-methylphenyl)magnesium bromide and 0.1 mole of 4-fluorophenylmagnesium bromide did not yield any dibromides. Diaryltellurium oxides, $Ar_2TeO$, which could be formed from the cleavage product, diaryl ditelluride, and oxygen are somewhat soluble in water. Treatment of the aqueous solutions with hydriodic acid, which converts the tellurium oxides into insoluble tellurium diiodides, failed to precipitate any solid. In an experiment, in which bis(4-methylphenyl)tellurium oxide was added to the hydrolyzate, the diaryltellurium diiodide was immediately precipitated upon addition of hydriodic acid. The amount of diaryl telluride required by Scheme 1 was never isolated. Although elemental tellurium was recovered in some cases, it seems unlikely that the cleavage reaction eqn. (3) is taking place to any appreciable extent. The maximum yield of ditelluride obtainable according to Scheme 1 is 33%. Several of the ditellurides (Table 1) were isolated in substantially higher yields. Scheme 1, therefore, does not describe the major path of the reaction between equimolar amounts of tellurium and Grignard reagents. Preliminary experiments with an excess of phenylmagnesium bromide gave diphenyl ditelluride in much lower yields.

Reactions were carried out with equimolar quantities of diphenyl ditelluride, tellurium and phenylmagnesium bromide in THF under the conditions described for the synthesis of diphenyl ditelluride in order to establish whether the Grignard reagents would react preferentially with tellurium. The results were inconclusive. When a mixture of 30 g (0.072 moles) diphenyl ditelluride and 9.2 g (0.072 moles) tellurium was added to a THF solution, containing 0.072 moles of phenylmagnesium bromide, 7.7 g (0.06 moles) of tellurium and 11 g (0.072 moles) ditelluride were recovered. Bromination of the oily residue produced 20 g (0.045 moles) phenyltellurium tribromide and 12.5 g (0.022 moles) diphenyltellurium dibromide. In a similar reaction employing 0.018 moles of the reagents only traces of tellurium were observed. At the present time the system tellurium/aromatic Grignard reagent/diaryl ditelluride is not well understood and clarification of the reaction mechanism must await further studies employing tellurium tracers.

## EXPERIMENTAL

### *Reagents*

Tellurium powder (99.9%), Noranda Brand, was supplied by Canadian Copper Refiners, Ltd. Fisher Scientific "Certified" tetrahydrofuran and the "Reagent Grade" organic halides were used without further purification, Magnesium shavings were purchased from Matheson Coleman & Bell.

### *Grignard reagents*

All Grignard reagents were prepared in tetrahydrofuran from the aromatic bromides and the stoichiometrically required amount of magnesium. The concentrations of the Grignard solutions were determined by hydrolysis and acid titration. The Grignard reagents were obtained in approximately 80% yield.

*Diphenyl ditelluride*

Phenylmagnesium bromide (0.25 moles) in tetrahydrofuran (250 ml) at room temperature was placed in a 500 ml Erlenmeyer flask, which was kept open to the atmosphere. Tellurium powder (33 g, 0.25 moles) was stirred into the Grignard solution. The reaction started in a few minutes. As soon as some ditelluride had formed as indicated by the appearance of a red color the solution was cooled to 0°. The flask was then closed with a rubber stopper into which a glass tube provided with a stopcock and connected to a balloon containing 2.5 l of oxygen had been inserted. From time to time the stopcock was opened to allow oxygen to flow into the flask. After one hour all the oxygen had been consumed. The mixture was then warmed to room temperature and stirred for an additional 1.5 h. After pouring it into a large beaker the mixture was allowed to stand overnight in the hood in contact with the atmosphere. The solid, red residue was treated with an aqueous ammonium chloride solution. From this heterogeneous mixture the diphenyl ditelluride was extracted with diethyl ether. Orange-red crystals of diphenyl ditelluride were obtained upon evaporation of the ether. One crystallization from 95% ethanol gave the analytically pure ditelluride.

*Other ditellurides*

All the other ditellurides listed in Table 1 were prepared as described above, but employing only 0.1 mole each of the Grignard reagents and tellurium and 1 liter of oxygen.

*Organyl tellurium tribromides*

The oily bis(2-methylphenyl) and bis(2-chlorophenyl) ditellurides were dissolved in carbon tetrachloride. A solution of bromine in carbon tetrachloride was dropped into the ditelluride solution until the bromine color persisted. The yellow tribromides precipitated quantitatively. They were washed with carbon tetrachloride and recrystallized from methanol (R = 2-$CH_3$, 2-Cl) or $CHCl_3/C_2H_5OH$ (R = 4-F). (R-$C_6H_4$)$TeBr_3$ [R: m.p.; elemental analyses, found (calcd.) (%): 2-$CH_3$, 131° (dec.); C, 18.7 (18.3); H, 1.5 (1.5). 2-Cl, 178° (dec.); C, 15.2 (15.1); H, 0.7 (0.8). 4-F, 291° (dec.); C, 16.0 (15.6); H, 0.8 (0.8).

*Bis(biphenylyl) ditelluride*

Elemental tellurium (11.5 g, 0.09 moles) was added to 150 ml of a tetrahydrofuran solution containing 0.09 moles of 4-biphenylylmagnesium bromide. This reaction was carried out as described for diphenyl ditelluride. The product (30 g) was a red powder insoluble in THF. The crude material was extracted with acetonitrile and the residue recrystallized from dichloromethane until the material appeared homogeneous under a microscope.

*Bis(biphenylyl) telluride*

The crude ditelluride obtained above was mixed with an equal volume of copper powder and heated in an oil bath to 210°. The cooled material was then ground and boiled with acetonitrile. On cooling white crystals of the telluride precipitated. Repeated recrystallizations failed to give an entirely pure sample. The best sample with a melting point of 167–168° was analyzed. (Found: C, 65.7; H, 3.9. $C_{24}H_{18}Te$ calcd.: C, 66.4; H, 4.1%.)

*Cleavage of diphenyl ditelluride by phenylmagnesium bromide*

To phenylmagnesium bromide (0.08 moles) in 100 ml THF was added diphenyl ditelluride (0.015 moles). The red color of the ditelluride disappeared immediately. The reaction mixture was stirred for 2 h at room temperature, then transferred into a beaker and allowed to stand overnight in contact with the atmosphere. The residue was treated with aqueous hydrochloric acid. Extraction with ether produced a faint yellow oil, which was dissolved in chloroform and reacted with bromine. Diphenyltellurium dibromide (75% yield, m.p. 208°[12]) was isolated.

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