

Improved preparation of diaryl ditellurides

Lars Engman ^{*} and Joachim Persson

Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm (Sweden)

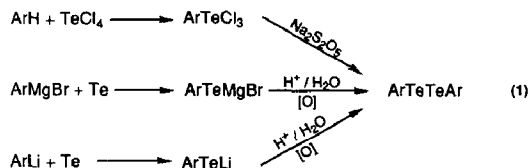
(Received December 7th, 1989)

Abstract

Diaryl ditellurides have been synthesized from aryl bromides via lithiation, tellurium insertion, and ferricyanide oxidation of the resulting lithium arenetelluroates.

Introduction

Diaryl ditellurides are useful, relatively stable, starting materials for many tellurium-containing compounds [1] and reagents [2]. The standard method for their preparation involves reduction of an aryltellurium trichloride, which is readily available from tellurium tetrachloride and the corresponding aromatic compound (eq. 1). However, owing to the low reactivity of TeCl_4 , only ditellurides bearing activating substituents are readily obtained by this route.



Elemental tellurium has long been known to insert into the carbon–metal bonds of aromatic Grignard reagents and organolithium compounds [3]. After hydrolysis of the resulting metal telluroates and oxidative workup, diaryl ditellurides are formed (eq. 1). However, Grignard reagents combine with elemental tellurium only in the presence of small amounts of oxygen. The isolated yields of ditellurides are often modest, and many aromatic Grignard reagents fail to react with elemental tellurium [4].

Early attempts to prepare diaryl ditellurides from organolithium reagents gave only modest yields of diaryl ditellurides when ethyl ether was used as the solvent and the aryllithium compound was prepared from aromatic halides by reaction of an aryl halide with lithium [5,6]. More recent studies indicate that tetrahydrofuran is

Table 1

Diaryl ditellurides **2** prepared.

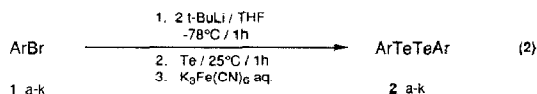
Product	Ar	Yield ^a (%)	M.p. (°C)	Lit. M.p. (°C)
2a	Phenyl	83	64–65	66–67 [5]
2b	4-Chlorophenyl	73	114–116	114 [14]
2c	4-Bromophenyl	67	151–152	153 [4]
2d	4-Methoxyphenyl	50	58–59	59–60 [13]
2e	3-Methylphenyl	80	33–34	32 [6]
2f	4-Methylphenyl	60	51–52	51 [4]
2g	4-Fluorophenyl	55	74–75	77 [4]
2h	4-(Trifluoromethyl)phenyl	80	85	^b
2i	4-(Dimethylamino)phenyl	61	137	^c
2j	1-Naphthyl	66	119–120	119–122 [5]
2k	4-Biphenyl	84	210–212	216 [4]

^a Yield of isolated product **2**, based on **1**, before recrystallisation. ^b Anal. Found: C, 30.72; H, 1.35. C₇H₄F₃Te calcd.: C, 30.83; H, 1.48%. ¹H NMR δ 7.42 (d, 2H), 7.89 (d, 2H) ppm. ^c Anal. Found: C, 38.92; H, 3.98. C₈H₁₀NTe calcd.: C, 38.78; H, 4.07%. ¹H NMR δ 2.97 (s, 6H), 6.54 (d, 2H), 7.64 (d, 2H) ppm.

a better solvent for the insertion reaction [7]. The preparation of aryllithium reagents can also be improved by using *t*-butyllithium in a halogen–metal exchange [3,8–10]. The oxidation of tellurols to the corresponding ditellurides is efficiently brought about by use of aqueous potassium ferricyanide, K₃Fe(CN)₆, as demonstrated in the syntheses of bis(2-pyridyl) ditelluride [3] and dimesityl ditelluride [10].

Results and discussion

We find the following procedure convenient for the high yield preparation of diaryl ditellurides **2** in which the aryl group can either be an electron-donating or an electron-withdrawing substituent (eq. 2). The aryl bromides **1** were treated under



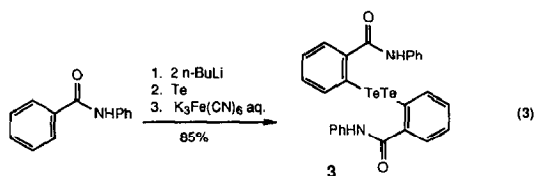
argon with two equivalents of *t*-butyllithium at -78°C . After addition of finely ground elemental tellurium, the mixture was stirred at ambient temperature to give a coloured solution of the corresponding lithium tellurolate. Oxidation was effected by adding the mixture to aqueous potassium ferricyanide. After extraction with methylene chloride, the crude products were passed through short columns of silica to remove traces of elemental tellurium. Yields, melting points, and ¹H NMR and analytical data (new compounds only) are shown in Table 1.

The ferricyanide oxidation reaction, which is a clean process with tellurols, has previously been used with less success for the oxidation of areneselenols to the corresponding diaryl diselenides. However, the problems can be circumvented by using an alternative procedure [9].

The incompatibility of certain aryl substituents with organolithium reagents seems to be the main restriction of our ditelluride synthesis. Also, *ortho*-dihaloaromatics are expected to be poor substrates owing to competing benzyne

formation [8]. On the other hand, the method should be useful for the preparation of diaryl ditellurides carrying metalation directing groups in the *ortho*-position. The aryl lithium compounds in these cases are prepared via proton abstraction rather than halogen metal exchange.

Christiaens and coworkers [11] recently showed that 2-phenyloxazolines and 2-phenylthiazolines can be lithiated in the *ortho*-position and elemental tellurium inserted into the carbon–lithium bonds. However, no attempts were made to oxidize the lithium tellurolates. To demonstrate the applicability of our ditelluride synthesis, elemental tellurium was added to a solution of the orange-red dianion prepared from benzanilide and two equivalents of *n*-butyllithium [12] (see eq. 3). After



completion of the insertion reaction, the reaction mixture was added to an aqueous solution of $K_3Fe(CN)_6$ to give the insoluble crystalline ditelluride **3** in 85% yield.

Experimental

The aryl bromides were commercial products. *t*-Butyllithium (1.7 *M* in pentane) and *n*-butyllithium (2.5 *M* in hexanes) were purchased from Aldrich Chemical Co. Tetrahydrofuran was freshly distilled from sodium/benzophenone prior to use. Analytical TLC plates and silica gel (230–400 mesh) were purchased from Merck. Melting points were determined with a Büchi 510 apparatus and are uncorrected. NMR spectra were obtained with Bruker WP 200 and AM 400 instruments. They were recorded in $CDCl_3$ solutions containing tetramethylsilane as internal standard. Elemental analyses were performed by Analytical Laboratories, Engelskirchen, Germany.

Bis(4-methoxyphenyl)ditelluride (2d); typical procedure. *t*-Butyllithium (10 ml 1.7 *M*, 17.0 mmol) was added dropwise to a stirred solution of 4-bromoanisole (**1d**; 1.59 g, 8.5 mmol) in THF (40 ml) at $-78^\circ C$ under argon. After 1 h, the cooling bath was removed and the mixture allowed to warm to room temperature during 30 min. Finely ground elemental tellurium (1.08 g, 8.5 mmol) was then added rapidly while a brisk stream of argon was passed through the open system to prevent admission of air. After 1 h when only traces of tellurium remained, the mixture was poured into a separatory funnel containing $K_3Fe(CN)_6$ (2.80 g, 8.5 mmol) in water (150 ml). The ditelluride product was extracted with methylene chloride (100 ml + 2 $\times$ 50 ml). After drying of the combined extracts ($CaCl_2$), evaporation on silica (10 g) and flash chromatography (SiO_2 ; hexane/ CH_2Cl_2 8/2) gave 0.99 g (50%) of ditelluride **2d**, m.p. 58 – $59^\circ C$ (Lit. [13] m.p. 59 – $60^\circ C$). The material was recrystallized from ethanol.

In the preparation of bis(4-biphenyl) ditelluride (**2k**), the product was obtained as a crystalline solid when the solution of the lithium tellurolate was added to aqueous potassium ferricyanide. After filtration, the product was recrystallized from DMSO.

2,2'-Ditellurobis(benzanilide) (3). To a stirred solution of benzanilide (1.0 g, 5.1 mmol) in dry THF (35 ml) under Ar at 0 °C was added n-butyllithium (4.1 ml 2.5 M, 10.2 mmol). After 30 min finely ground elemental tellurium (0.65 g, 5.1 mmol) was added to the orange-red solution while a brisk stream of argon was passed through the open system. The solid material was almost consumed after 1 h, and the yellowish-green solution was added to a beaker containing $K_3Fe(CN)_6$ (1.70 g, 5.2 mmol) in water (150 ml). The precipitated material was filtered off to give, after washing with methylene chloride and drying, 1.40 g (85%) of ditelluride 3. An analytical sample, m.p. > 300 °C, was obtained by recrystallization from 1,2-dichlorobenzene. Found: C, 48.43; H, 2.95. $C_{13}H_{10}NOTe$ calc.: C, 48.22; H, 3.11%. IR (KBr): 3316 (NH); 1631 (C=O) cm^{-1} .

Acknowledgments

Financial support from the National Swedish Board for Technical Development and the Swedish Natural Science Council is gratefully acknowledged.

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