

ALKALINE HYDROLYSIS OF DIARYL DITELLURIDES UNDER PHASE TRANSFER CONDITIONS; SYNTHESIS OF ALKYL ARYL TELLURIDES *

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Summary

The disproportionation reaction of diaryl ditellurides $[(C_6H_5Te)_2, (p-CH_3C_6H_4Te)_2, (p-CH_3OC_6H_4Te)_2, (p-C_2H_5OC_6H_4Te)_2, (2-naphthyl-Te)_2]$ with sodium hydroxide under phase transfer conditions at room temperature is described for the first time. The phase transfer catalyst used is 2HT-75, a trade name for a mixture of dialkyldimethylammonium chlorides. The intermediates aryl tellurolates react "in situ" with alkyl halides to give the corresponding alkyl aryl tellurides (ArTeR) in 52–72% yield. The following compounds were prepared: Ar = C_6H_5 , R = $CH_3(CH_2)_3CH_2$, $(CH_3)_2CHCH_2CH_2$, $(CH_3)_2CHCH_2$, $CH_3CHBrCH_2CH_2$, $CH_3(CH_2)_8CH_2$, $C_6H_5CH_2$, $ClCH_2$, $C_6H_5CH_2CH_2$, $CH_2=CHCH_2$, $C_6H_5CH=CHCH_2$, $C_6H_5SeCH_2$, $CH_2CH_2CH_2CH=CHCH$; Ar = $p-CH_3C_6H_4$, R = $CH_3(CH_2)_2CH_2$; Ar = $p-CH_3OC_6H_4$, R = $CH_3(CH_2)_2CH_2$; Ar = $p-C_2H_5OC_6H_4$, R = $CH_3(CH_2)_2CH_2$; Ar = 2-naphthyl, R = $CH_3(CH_2)_2CH_2$.

Introduction

The alkaline hydrolysis of diaryl disulfides [1,2] and diaryl diselenides [3] has been thoroughly investigated. The reactions were performed with sodium or potassium hydroxide in refluxing water or ethanol. The dichalcogenides were transformed into arene thiolate or selenolate (eq. 1) [2,3]



(Y = S, Se; M = Na, K)

We recently adapted this reaction to the preparation of alkyl aryl sulfides [4] and

* Preliminary results were reported at the "Fourth International Conference on the Organic Chemistry of Selenium and Tellurium" Birmingham, England, July 1983.

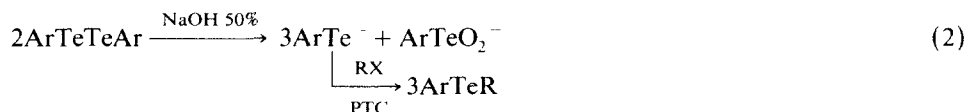
selenides [5]. The disproportionation (eq. 1) was performed in the presence of a phase transfer catalyst (PTC) and an alkylating agent.

Analogous alkaline hydrolysis of diaryl ditellurides has not yet been described in the literature.

The favorable results obtained with phase transfer catalysts in the reaction of diphenyl disulfide and diaryl diselenides with sodium hydroxide prompted us to investigate the alkaline hydrolysis of diaryl ditellurides under similar conditions to generate arenetellurolates and then to obtain alkyl aryl tellurides.

Results and discussion

Diaryl ditellurides react rapidly in THF at room temperature with 50% aqueous sodium hydroxide in the presence of an alkyl halide and a phase transfer catalyst as indicated by the discharge of the red color of the reaction mixture (eq. 2)



The catalyst used was 2HT-75, a trade name for a mixture of dialkyldimethylammonium chlorides [6]. After the reactions were complete the phases were separated and the aqueous layer was extracted with methylene chloride. The organic phases were combined, dried and evaporated. The residue was chromatographed on a silica gel column with hexane as the eluent and finally distilled at reduced pressure. In certain cases the tellurides were purified by preparative TLC.

The use of methylene chloride as solvent (30 ml of CH_2Cl_2 per mmol of diphenyl ditelluride) led to the exclusive formation of α -chloromethyl phenyl telluride. Use of a lower ratio (15 ml of CH_2Cl_2 per mmol of diphenyl ditelluride) led to a mixture of α -chloromethyl phenyl telluride and bis(phenyltelluro)methane [7] in a 6/1 ratio (determined by ^1H NMR).

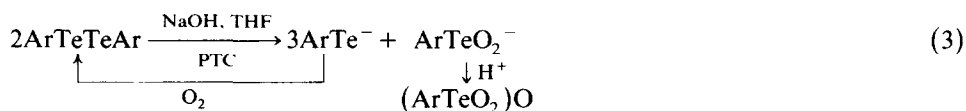
The tellurides listed in Table 1 are pale yellow oils with the exception of (phenylseleno)methyl phenyl telluride, which is solid. Aryl alkyl tellurides are relatively stable. However benzyl and allyl tellurides readily decomposed during the workup in air affording α,β -unsaturated carbonyl compounds, which were formed by oxidation of the allylic group bonded to the tellurium atom. These tellurides could be isolated under an inert atmosphere and were identified by ^1H NMR.

Diphenyl ditelluride and cyclohexyl bromide did not produce any cyclohexyl phenyl telluride after 20 h. In the case of 1,3-dibromobutane only the primary carbon was attacked by benzene telluroate. However, 3-bromocyclohexene reacted under these conditions to give the corresponding telluride.

The reactions were performed with alkyl halides and diaryl ditellurides in a molar ratio of 2/1. Stoichiometry requires 1.5 moles of alkyl halides per mole of ditelluride (eq. 2). In the case of the less volatile alkyl halides the excess halide (17–22%) was recovered. Neutralization of the aqueous phase with hydrochloric acid precipitated benzenetellurinic anhydride [8,9,10], which could be reduced to diphenyl ditelluride with potassium metabisulfite.

In the absence of an alkyl halide and in the presence of oxygen the reaction gave after neutralization as the only reaction product benzenetellurinic anhydride. Under

these conditions benzenetelluroate was oxidized to the ditelluride, which was again transformed to the benzenetellurinate (eq. 3).



The simple preparative procedure and low cost of the reagents make the method described in this work attractive when compared with the described ones available for the preparation of alkyl aryl tellurides [11].

Experimental

^1H NMR spectra were recorded on a Perkin–Elmer–Hitachi R-20, Varian EM-390 and Varian XL100 spectrometers in CCl_4 solutions with Me_4Si as internal standard; IR spectra of films in NaCl were obtained with a Perkin–Elmer 735 grating spectrophotometer. All the alkyl halides were distilled prior to use. Best results were achieved when the 50% sodium hydroxide solution was freshly prepared. Merck Silica Gel 60E was used for column chromatography and Silica Gel 60PF 254 for preparative TLC.

2HT-75 was supplied by Herga Indústrias Químicas S/A., Rio de Janeiro, Brasil. Diphenyl ditelluride [12], bis(*p*-methoxyphenyl) ditelluride [13], di-*p*-tolyl ditelluride [12] and di-2-naphthyl ditelluride [14] were prepared according to published procedures.

Synthesis of alkyl phenyl tellurides under phase transfer conditions. General procedure

To a solution of diaryl ditelluride (1 mmol) in tetrahydrofuran (7.5 ml), under a nitrogen atmosphere, was added in sequence the phase transfer catalyst (30 mg), 50% aqueous sodium hydroxide solution (7.5 ml) and the alkyl halide (2 mmol). The reaction mixture was vigorously stirred at room temperature for the time indicated in Table 1. The phases were separated and the aqueous layer was extracted with CH_2Cl_2 (30 ml). The organic phases were combined, dried with Na_2SO_4 and the solvent evaporated in a rotatory evaporator. The excess of alkyl halide was removed in a vacuum pump and the residue filtered through a column (15 cm length, 1 cm $\varnothing$) of silica gel (7 g) using petroleum ether (30–60°C) as eluent. The eluent was evaporated and the residue distilled in a Kugelrohr oven under oil pump vacuum to give the alkyl aryl tellurides. The benzylic and allylic tellurides were handled under nitrogen and were not distilled. The yields are listed in Table 1.

The aqueous phase from the preparation of phenyl *n*-butyl telluride was cooled in an ice bath and neutralized with concentrated hydrochloric acid. Tellurinic anhydride precipitated as a white solid (50 mg 24% yield, based on diphenyl ditelluride) which was dried under vacuum at 100 °C for 1 h. Recrystallization from glacial acetic acid furnished crystals that melted at 224–226°C (lit. [8] 220–225°C).

Reaction of diphenyl ditelluride with sodium hydroxide under phase transfer conditions

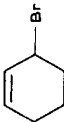
A mixture of diphenyl ditelluride (2.04 g, 5 mmol) and 2HT-75 (0.15 g) in THF (38 ml) and 50% aqueous sodium hydroxide (38 ml) was vigorously stirred in an open beaker. After 3 h of stirring the initially dark red mixture turned milky-white.

(Continued on p. 266)

TABLE 1

PREPARATION OF ALKYL ARYL TELLURIDES FROM DIARYL DITELLURIDES, SODIUM HYDROXIDE AND ALKYL HALIDES IN THE PRESENCE OF A PHASE TRANSFER CATALYST

Compound	RX	Reaction time (h)	Yield (%)	B.p. ^a or m.p. (°C/Torr)	Analyses (Found (calcd.) (%))		¹ H NMR, δ (ppm), <i>J</i> (Hz), TMS internal ^f
					C	H	
(C ₆ H ₅) ₂ (n-C ₄ H ₉)Te [16] ^g	n-C ₄ H ₉ Br	1.3	66	106–110/2.2	46.12 (45.87)	5.37 (5.39)	0.86(t, <i>J</i> 7, 3H), 1.4–1.9 (m, 4H), 2.84(t, <i>J</i> 7, 2H), 6.9–7.8(m, 5H) ^f
(<i>p</i> -CH ₃ OC ₆ H ₄)(n-C ₄ H ₉)Te	n-C ₄ H ₉ Br	1.3	58	120–125/1	45.20 (45.27)	5.49 (5.52)	0.85(t, <i>J</i> 7, 3H), 1.1–1.8 (m, 4H), 2.82(t, <i>J</i> 7, 2H), 3.82(s, 3H), 6.80(d, <i>J</i> 9, 2H), 7.72(d, <i>J</i> 9, 2H) ^f
(<i>p</i> -C ₂ H ₅ OC ₆ H ₄)(n-C ₄ H ₉)Te [16] ^g	n-C ₄ H ₉ Br	1.3	72	130–133/2	47.27 (47.12)	5.87 (5.93)	0.80(t, <i>J</i> 7, 3H), 1.0–2.0 (m, 7H), 2.60(t, <i>J</i> 7, 2H), 3.46(q, <i>J</i> 7, 2H), 6.04(d, <i>J</i> 9, 2H), 7.33(d, <i>J</i> 9, 2H) ^h
(<i>p</i> -CH ₃ C ₆ H ₄)(n-C ₄ H ₉)Te [16] ^g	n-C ₄ H ₉ Br	1.3	60	128–133/8	47.73 (47.89)	5.73 (5.84)	0.71(t, <i>J</i> 5, 3H), 1.0–2.0 (m, 4H), 2.10(s, 3H), 2.66(t, <i>J</i> 7, 2H), 6.63 (d, <i>J</i> 8, 2H), 7.33(d, <i>J</i> 8, 2H) ^h
2-Naphthyl(n-C ₄ H ₉)Te	n-C ₄ H ₉ Br	2.0	64	120–125/1	53.96 (53.91)	5.09 (5.17)	0.70(t, <i>J</i> 5, 3H), 0.8–2.0 (m, 4H), 2.66(t, <i>J</i> 7, 2H), 6.8–7.6(m, 6H), 7.90(s, 1H) ^h
(C ₆ H ₅) ₂ [(CH ₃) ₂ CHCH ₂ CH ₂]Te	(CH ₃) ₂ CHCH ₂ CH ₂ Br	1.3	65	80–87/1	47.71 (47.89)	5.45 (5.84)	0.84(d, <i>J</i> 7, 6H), 1.4–1.8 (m, 3H), 2.7–3.0(m, 2H), 7.0–7.2(m, 3H), 7.5–7.8 (m, 2H) ^f
(C ₆ H ₅) ₂ [(CH ₃) ₂ CHCH ₂]Te	(CH ₃) ₂ CHCH ₂ Br	1.3	57	73–78/1	45.68 (45.87)	5.35 (5.39)	0.98(d, <i>J</i> 6, 6H), 1.7–2.3 (m, 1H), 2.86(d, <i>J</i> 7, 2H), 7.0–7.2(m, 3H), 7.6–7.8 (m, 2H) ^d

$(C_6H_5)_3X(CH_3CHBrCH_2CH_2)_2Te$	$CH_3CHBrCH_2CH_2Br$	1.3	61	108–115/0.5	35.10 (35.25)	3.72 (3.84)	1.63(d, J 7, 3H), 1.9–2.4 (m, 2H), 2.7–3.3(m, 2H), 3.9–4.4(m, 1H), 7.1–7.4 (m, 3H), 7.6–7.9(m, 2H), ['] 0.6–2.0(m, 19H), 2.80(t, J 7, 2H), 6.8–7.3(m, 3H), 7.4–7.6(m, 2H) ^h
$(C_6H_5)_3X(CH_3(CH_2)_8CH_2)_2Te$ [17] ^g	$CH_3(CH_2)_8CH_2Br$	1.3	57	^b	55.42 (55.54)	7.45 (7.57)	
$(C_6H_5)_3X(C_6H_5CH_2)_2Te$ [18] ^g	$C_6H_5CH_2Cl$	0.5	56	—	^{c,e}		4.00(s, 2H), 6.7–7.1(m, 8H), 7.2–7.5(m, 2H) ^h
$(C_6H_5)_3X(ClCH_2)_2Te$	CH_2Cl_2	2.0	52	—	^c		4.66(s, 2H), 6.7–7.2(m, 3H), 7.3–7.8(m, 2H) ^h
$(C_6H_5)_3X(C_6H_5CH_2CH_2)_2Te$	$C_6H_5CH_2CH_2Br$	1.3	60	^b	54.20 (54.26)	4.35 (4.55)	3.16(s, 4H), 7.0–7.5 (m, 8H), 7.6–7.9(m, 2H) [']
$(C_6H_5)_3X(CH_2=CHCH_2)_2Te$ [17] ^g	$CH_2=CHCH_2Br$	0.5	60	—	^{c,e}		3.30(d, J 8, 2H), 4.2–4.7 (m, 2H), 5.3–6.1(m, 1H), 6.7–7.1(m, 3H), 7.2–7.6 (m, 2H) ^h
$(C_6H_5)_3Te-$ 		0.5	59	—	^{c,e}		1.3–2.3(m, 6H), 3.8–4.2 (m, 1H), 5.1–6.0(m, 2H), 6.8–7.1(m, 3H), 7.3–7.8 (m, 2H) ^h
$(C_6H_5)_3X(C_6H_5CH=CHCH_2)_2Te$	$C_6H_5CH=CHCH_2Cl$	0.5	61	—	^{c,e}		3.53(d, J 7, 2H), 5.5–6.5 (m, 2H), 6.7–7.3(m, 6H), 7.3–7.7(m, 4H) ^h
$(C_6H_5)_3X(C_6H_5SeCH_2)_2Te$ [19] ^g	$C_6H_5SeCH_2Br$	0.8	56	50–51 ^d	41.60 (41.66)	3.19 (3.22)	4.00(s, 2H), 6.8–7.7(m, 10H) ^h

^a Distilled in a Kugelrohr oven. ^b Purified by preparative TLC. ^c Unstable compounds; CH analyses not obtained. ^d Recrystallized from petroleum ether (30–60°C) at –78°C. ^e Isolated under a nitrogen atmosphere. ^f The ¹H NMR shift of the groups linked to tellurium agree with the shifts reported for analogous tellurium compounds [15]. ^g These compounds have been previously prepared. ^h Spectra registered on a Perkin–Elmer Hitachi R-20 spectrometer. ['] Spectra registered on a Varian EM-390 spectrometer. ^j Spectra registered on a Varian XL-100 spectrometer.

At this point 60 ml of water and 60 ml of ethyl ether were added with stirring. The phases were separated and the aqueous phase was cooled in an ice bath and neutralized with concentrated hydrochloric acid. At pH 7 the tellurinic anhydride precipitated as a white solid, which was dried in vacuum at 100°C for 1 h (yield 2.05 g, 89%). After recrystallization from glacial acetic acid the material melted at 224–226°C (lit. [8] 220–225°C). The infrared spectrum showed no absorption at 3060 cm⁻¹ attributed to $\nu(\text{OH})$ in aromatic tellurinic acids [10].

Reduction of benzenetellurinic anhydride to diphenyl ditelluride

To a suspension of the benzenetellurinic anhydride (2.0 g, 4.3 mmol) in water (20 ml) was added ether (20 ml) and potassium metabisulfite (2.0 g, 9.0 mmol). The mixture was stirred for 1 h at room temperature, then diluted with water (30 ml) and extracted with ether (2 × 20 ml). The organic phase was washed with water dried with sodium sulphate and evaporated, furnishing diphenyl ditelluride (1.60 g, 94%). M.p. 64°C (lit. [12] 67°C).

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