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PHENYLALKYL TELLURIDES

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Summary

Phenyllithium telluride, generated from diphenyl ditelluride in tetrahydrofuran solution and lithium metal, was treated with alkyl halides to produce alkylphenyl tellurides, C_6H_5TeR (R = CH_3, C_2H_5, C_3H_7, i-C_3H_7, C_4H_9, $C_{14}H_{29}$), as light sensitive yellow oils in yields ranging from 62 to 81%. The tetradecyl derivative could not be purified by distillation and was, therefore, converted to the diiodide. The heat sensitive alkylphenyltellurium dihalides, $RC_6H_5TeX_2$, were obtained by treating the tellurides with iodine (R = CH_3, C_2H_5, C_3H_7, i-C_3H_7, C_4H_9, $C_{14}H_{29}$) or bromine (R = C_4H_9). Ultraviolet-visible and NMR spectral data of the tellurides are reported.

Introduction

A number of arylalkyl tellurides, ArTeR, have been prepared by a variety of methods, including the reaction of aryl-alkali-metal tellurides, ArTeM (M = Li, Na), with aliphatic halides, the thermal decomposition of appropriate triorganyl telluronium salts, the condensation of organyl tellurium trichlorides with organyl mercury chlorides, and the reaction of diphenyl ditelluride with dialkylmercury compounds [1]. The most convenient method for the preparation of these arylalkyl tellurides seems to be the reaction of an aryllithium telluride with an alkyl halide. Aryllithium tellurides have been obtained from aryllithium compounds and elemental tellurium [2]. Diphenyl ditelluride has been reported to be cleaved by lithium to form phenyllithium telluride [3]. Since many diaryl ditellurides can now be synthesized in good yields from elemental tellurium and aromatic Grignard reagents [4] or by reduction of aryltellurium trihalides [5], which in turn are easily formed by condensation of tellurium tetrachloride with aromatic hydrocarbons with [6] or without the assistance of aluminum chloride

[7], we investigated the cleavage of the Te—Te bond by lithium in diaryl ditellurides and prepared and characterized a number of arylalkyl tellurides and their dihalides.

Experimental

Reagents and instrumentation

Diphenyl ditelluride was prepared from phenylmagnesium bromide and elemental tellurium [4]. Alkyl halides were obtained commercially and used without further purification. Tetrahydrofuran was dried over sodium with benzophenone as an indicator. This solvent was distilled before use. Reagent grade carbon tetrachloride was stored over molecular sieves. Proton NMR spectra were recorded on a Varian Model T-60 spectrometer employing solutions (10-20% volume) in carbon tetrachloride with TMS as internal standard. Ultraviolet spectra were recorded in cyclohexane solutions on a Cary 118 UV-visible spectrometer. Analyses were performed either by Galbraith Laboratories, Inc. or by Chemanalytics, Inc.

Phenyllithium telluride

Diphenyl ditelluride (4.1 g, 0.01 mol) was dissolved in dry tetrahydrofuran (100 ml) and placed into a 250 ml three-necked flask equipped with a high-speed wire stirrer and a nitrogen inlet tube. The solution was kept under an inert atmosphere of nitrogen. Freshly cut, small pieces of lithium metal (1.4 g, 0.02 mol) were added through the third neck, which was then stoppered. The mixture was stirred for 6 to 8 h at room temperature. After this time the initially dark red solution had become yellowish-brown. The unreacted lithium metal is removed by transferring the reaction mixture into a dropping funnel and then carefully draining the solution back into the flask. The pieces of lithium metal remain in the dropping funnel. Alternatively, the excess metal can be removed with a bent spatula from the mixture maintained under an atmosphere of nitrogen.

Alkylphenyl tellurides

To the solution of phenyllithium telluride, prepared as described above, the appropriate neat alkyl halide (0.02 mol) was added dropwise with stirring. The reaction mixture was then stirred for another 0.5 h at room temperature. After a reflux condenser had been connected to the flask, the mixture was refluxed for 30 min to complete the reaction. The solvent was then distilled off. Water (10 ml) and ether (25 ml) were then added to the residue. After thorough mixing the organic layer was separated, the ether removed by distillation and the oily residue fractionated in vacuo. The alkylphenyl tellurides were obtained as light yellow oils in good yields (see Table 1).

Alkylphenyltellurium diiodides

The alkylphenyl tellurides (0.005 mol) dissolved in carbon tetrachloride (10 ml) were placed in a round-bottomed flask (250 ml) equipped with a nitrogen inlet tube, a magnetic stirrer and a dropping funnel. Iodine (1.27 g, 0.005 mol) was dissolved in carbon tetrachloride (75 ml) and this solution dropped

TABLE 1

ALKYLPHENYL TELLURIDES AND ALKYLPHENYLTELLURIUM DIIODIDES

Compound: RTeAr					Compound: $ArRTeI_2$			
R	Yield (%)	B.p. (°C/Torr)	Analysis found (calcd.) (%)		Yield (%)	M.p. (°C)	Analysis found (calcd.) (%)	
			C	H			C	H
CH_3[a]	62	64/1.1	38.07 (38.26)	3.63 (3.67)	65	152-154	17.68 (17.76)	1.73 (1.70)
C_2H_5[b]	67	94/4	41.15 (41.10)	4.32 (4.31)	64	102	20.05 (19.71)	2.02 (2.07)
C_3H_7[b]	81	88/1.5	44.18 (43.62)	5.09 (4.88)	62	102	21.26 (21.56)	2.24 (2.41)
i-C_3H_7	71	78/1.3	43.54 (43.62)	4.92 (4.88)	46	103-104	21.88 (21.56)	2.22 (2.41)
C_4H_9[b]	79	108/2	45 60 (45.88)	5.40 (5.39)	84	82-84	23.54 (23.29)	2.79 (2.74)
$C_{14}H_{29}$[b]					70	74	36.46 (36.62)	5.04 (5.22)

[a] Iodide employed. [b] Bromide used.

into the stirred telluride solution. The reaction mixture was concentrated by evaporation in vacuo at room temperature to 10 ml. The precipitated diiodides were filtered and washed with carbon tetrachloride. After drying, the diiodides were analytically pure (Table 1).

Phenyltetradecyltellurium diiodide

Neat tetradecyl bromide (5.5 g, 0.02 mol) was treated with phenyllithium telluride (0.02 mol) in tetrahydrofuran. Extraction of the inorganic salts with water, separation of the organic layer and removal of the solvent, produced a dark red oily residue, which was dissolved in carbon tetrachloride (10 ml) and treated with iodine (5.08 g, 0.02 mol) in carbon tetrachloride (250 ml). All the carbon tetrachloride was removed in vacuo at room temperature, the residue dissolved in benzene (80 ml) and the benzene solution concentrated to 10 ml at room temperature in vacuo. The precipitated phenyltetradecyltellurium diiodide was filtered and washed with a small amount of carbon tetrachloride. This product was analytically pure.

Butylphenyltellurium dibromide

Butylphenyl telluride (2.0 g, 0.0076 mol) was dissolved in carbon tetrachloride (10 ml) and treated with bromine (1.22 g, 0.0076 mol) in carbon tetrachloride (25 ml). The solvent was completely removed in vacuo at room temperature. The oily residue was dissolved in benzene (10 ml). Hexane was added dropwise until no more precipitate formed. The yellow crystals were filtered and dried at room temperature. The product (3.05 g, 95% yield) was analytically pure and melted at 74-75°. Anal. found: C, 28.48; H, 3.23. $C_{10}H_{14}Br_2Te$ calcd.: C, 28.49; H, 3.35.

TABLE 2

UV AND NMR DATA FOR ALKYLPHENYL TELLURIDES

R	UV λ_{max} (Å) (ε)	NMR shifts (ppm)[c]				
		CH_3	α-CH_x	β-CH_2	C_6H_5	
CH_3	3305(734); 2695(5040); 2547[a] (3200); 2245(8780)	2.16s			6.96-7.25[f]	7.43-7.75
C_2H_5	3296(683); 2697(3720); 2533[a] (2330); 2270(12800)	1.63t	2.82q[d]		6.98-7.30	7.53-7.83
C_3H_7	3293(691); 2711(3810); 2533[a,b] (2260); 2251(12600)	0.98t	2.90t[e]	1.75m	7.02-7.30	7.57-7.80
i-C_3H_7	3339(610); 2708(2510); 2520[a] (1920); 2277(16000)	1.58d	3.52(st)[g]		7.03-7.33	7.62-7.90
C_4H_9	3284(725); 2700(3840); 2531[a] (2360); 2241(12400)	0.88t	2.88t[g]	1.08-2.05m	7.00-7.28	7.53-7.80

[a] Shoulder on 2700 Å band. [b] This shoulder arises from a band centered at ≈2500 Å(ε ≈ 1100). [c] s, singlet; d, doublet, t, triplet, q, quadruplet; st, septet; m, multiplet. [d] J 7.5 Hz. [e] $J(CH_2CH_2)$ 7.5 Hz. [f] Three protons [g] J 7.0 Hz.

Discussion

Phenyllithium telluride is obtained on stirring a tetrahydrofuran solution of diphenyl ditelluride with lithium metal (eqn. 1). The rate of the ditelluride

$$C_6H_5TeTeC_6H_5 + 2\ Li \rightarrow 2\ C_6H_5TeLi \qquad (1)$$

cleavage reaction is increased when the solution is mixed well with a stirrer made by bending 15 gauge stiff wire into two loops. Stirring with a magnetic stirrer did not produce the desired yellow-brown solution characteristic of phenyllithium telluride after more than 24 h. Tetrahydrofuran appears to be the solvent of choice. Diphenyl ditelluride was not cleaved by lithium in diethyl ether.

Phenyllithium telluride was never isolated but reacted immediately with alkyl halides. The alkylphenyl tellurides formed easily in good yields. In the case of higher halides a brief reflux period will drive the reaction to completion. With the exception of the tetradecyl derivative all the alkylphenyl tellurides listed in Table 1 have been purified by vacuum distillation. The freshly distilled compounds are pale yellow oils. The lower members of the series have a disagreeable odor. These tellurides seem to be decomposed by light acquiring a red color in as short as a days time, even when stored under nitrogen in sealed ampoules. A sample stored in the dark for six months did not show any noticable discoloration. A mass spectrum of a discolored sample contained peaks indicating the presence of diphenyl ditelluride, whereas the spectrum of the sample stored in the dark was devoid of these peaks. The decomposition probably proceeds according to eqn. 2.

$$2\ C_6H_5TeR \rightarrow C_6H_5TeTeC_6H_5 + R\text{-}\text{-}R \qquad (2)$$

Phenyitetradecyl telluride could not be purified by vacuum distillation as extensive decomposition occurred above 100°. The crude telluride therefore was converted to the phenyltetradecyltellurium diiodide.

The conversion of the alkylphenyl tellurides to the tellurium diiodides proceeds readily upon mixing of the carbon tetrachloride solutions of the reagents. The lower members of the series precipitate on formation while the higher homologues are obtained by concentration of the reaction mixtures. Additional product can be obtained by evaporating the mother liquors. The solvent must be removed at or below room temperature in a vacuum. Higher temperatures will decompose the thermally labile alkylphenyltellurium diiodides. Table 1 presents pertinent data for these compounds.

The ultraviolet-visible spectra of the alkylphenyl tellurides (Table 2) show three absorption maxima at approximately 3300, 2700 and 2250 Å and a shoulder at 2530 Å on the short wavelength side of the 2700 Å band. The molar absorbances at these maxima increase with decreasing wavelength and are of approximately the same magnitude for comparable bands for the ethyl, propyl and butyl derivatives. The absorbances for the methyl and i-propyl compounds differ considerably from the other three tellurides. The UV data previously reported [8] for ethylphenyl telluride are, with exception of the absorbance for the 2533 Å band, in good agreement with the values of Table 2. The phenyl group bonded to the tellurium atom seems to be responsible for the 3300 and 2700 Å bands, since dimethyl telluride has its longest wavelength absorption maximum at 2575 Å [9]. The longest wavelength band of the alkylphenyl tellurides at 3300 Å, which is responsible for the yellow color of these materials, is considerably shifted from the longwave maximum of diphenyl ditelluride, which occurs at 4000 Å.

Proton NMR data are listed in Table 2. The phenyl proton signals appear as two sets of multiplets centered at 7.15 ppm (3H) and 7.65 ppm (2H). The α-CH_2 protons of the ethyl, propyl and butyl derivatives resonate between 2.82 and 2.90 ppm. The spectral data previously reported for the i-propyl and butyl compounds [10] agree reasonably well with the values reported in Table 2.

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