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^{1}H NMR SPECTRA OF SOME ARYLTELLURIUM COMPOUNDS

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Summary

The ^{1}H NMR spectra of some anisyl- and phenetyl-tellurium derivatives confirm that *para*-substitution of methoxybenzene (anisole) and ethoxybenzene (phenetole) occurs on reaction with tellurium tetrachloride. Some new aryltellurium(IV) halides are reported.

Introduction

Phenetole [1] and anisole [2] undergo quasi-Friedel—Crafts reactions with tellurium tetrachloride in boiling organic solvents to form yellow aryltellurium(IV) trichlorides. Further reactions at higher temperatures and in the absence of solvent give diaryltellurium(IV) dichlorides [1,2]. The trichlorides and dichlorides react with stoichiometric quantities of silver fluoride to form aryltellurium(IV) trifluorides and diaryltellurium(IV) difluorides.

Hydrolysis of the trichlorides gives aryltellurium(IV) oxochlorides [3,4], oxohydroxides [3] or tellurinic anhydrides [4], and of the dichlorides gives diaryltellurium(IV) oxochlorides, dihydroxides, or telluroxides [5-7]. The hydrolysis products are converted into trihalides and dihalides on reaction with aqueous HCl, HBr, and HI.

Phenyl- and *p*-tolyl-tellurium(IV) trichlorides are prepared from arylmercury(II) chlorides and tellurium tetrachloride [8]. The reduction of aryltellurium(IV) trichlorides by aqueous $K_2S_2O_5$ gives red-brown diaryl ditellurides(II) [1,2,8] which react with an excess of bromine or iodine to give the aryltellurium(IV) trihalides [9,10]. Dianisyl ditelluride(II) reacts with methyl iodide to give anisyldimethyltellurium(IV) iodide and anisylmethyltellurium(IV) diiodide [1], and it is shown below that the other ditellurides behave similarly:

$$Ar_2Te_2 + 3MeI \rightarrow ArMe_2TeI + ArMeTeI_2$$

Reduction of dianisyl- and diphenetyl-tellurium(IV) dichlorides with zinc dust in boiling benzene [2,7] and reactions of phenyl- and *p*-tolyl-mercury(II)

TABLE 1

^{1}H NMR CHEMICAL SHIFTS FOR ARYL PROTONS IN DMSO

Ar compound	p-MeC$_6$H$_4$		p-MeOC$_6$H$_4$		p-EtOC$_6$H$_4$	
	δA	δB	δA	δB	δA	δB
Ar_2Te	7.51	7.03	7.75	6.98	7.73	6.98
Ar_2Te_2	7.71	7.09	7.86	6.99	7.64	6.78
Ar_2TeF_2			7.93	7.26	7.92	7.23
Ar_2TeCl_2	7.83	7.32	7.98	7.17	7.88	7.09
Ar_2TeBr_2	7.88	7.29	8.14	7.24	8.10	7.21
Ar_2TeI_2	7.89	7.24	8.87	7.07	8.05	7.16
$ArTeF_3$			8.08	7.26	8.20	7.20
$ArTeCl_3$	8.09	7.18	8.35	7.16	8.32	7.13
$ArTeBr_3$	8.23	7.15	8.50	7.01	8.60	7.20
$ArTeI_3$	8.19	7.41	8.26	6.85	8.22	6.91
$ArMe_2TeI$	7.93	7.56	7.80	7.11	7.80	7.05
$ArMeTeI_2$	7.83	6.67	8.00	7.08	7.92	7.01

with elemental tellurium [11,12] give diaryl tellurides(II) which react with chlorine, bromine, and iodine to give diaryltellurium(IV) dihalides [5,7,11-16].

Results and discussion

This work confirms that substitution of anisole and phenetole by tellurium(IV) occurs exclusively at *para* positions. The ^{1}H NMR spectra of the substitution products show four line AABB signals characteristic of 1,4-disubstituted benzenes, J_{AB} 8—9 Hz, which resemble those of corresponding p-tolyl derivatives. The protons in *ortho* positions to tellurium appear as broad doublets at lower field.

Chemical shifts with respect to TMS, of the aryl protons of some typical compounds in DMSO-d_6 are recorded in Table 1. All the aryltellurium compounds are soluble in DMSO; some are soluble in CCl_4 and C_6H_6. The differences in chemical shifts, δA — δB, increase in the order DMSO < CCl_4 < C_6H_6, and for a particular solvent, in the order $Ar_2Te < Ar_2TeX_2 < ArTeX_3$.

Experimental

Methods of preparation of typical new organotellurium compounds are described below. Analytical data for new compounds are summarised in Table 2. Other organotellurium compounds were prepared by standard methods [1-16].

Di-p-phenetyltellurium(IV) difluoride. Di-p-phenetyltellurium(IV) dichloride (0.88 g, 1.99 mmol) was added in small quantities to a mixture of silver fluoride (0.5 g, 4.0 mmol) in dry toluene (30 ml) which was boiled under reflux (1 h). Silver chloride (0.51 g, 3.55 mmol) was removed by filtration. The addition of the cold, clear, concentrated filtrate to light petroleum (b.p. 60-80°C) gave colourless crystalline di-p-phenetyltellurium(IV) difluoride (0.13 g, 0.32 mmol), m.p. 169-170°C.

Dimethyl-p-phenetyltellurium(IV) iodide and methyl-p-phenetyltellurium-

TABLE 2

ANALYTICAL DATA FOR NEW COMPOUNDS

Compound	m.p. (°C)	Found (%)			Molecular formula	Calcd. (%)		
		C	H	Hal		C	H	Hal
p-$MeOC_6H_4TeF_3$	176-178	29.22	2.59		$C_7H_7F_3OTe$	28.84	2.46	19.54
(*p*-$MeOC_6H_4)_2TeF_2$	120-121	42.73	3.58		$C_{14}H_{14}F_2O_2Te$	44.30	3.69	10.01
p-$EtOC_6H_4TeF_3$	204	30.92	2.91		$C_8H_9F_3OTe$	31.44	2.95	18.65
(*p*-$EtOC_6H_4)_2TeF_2$	169-170	46.92	4.28		$C_{16}H_{18}F_2O_2Te$	47.15	4.41	9.32
$PhMe_2TeI$	168	26.45	3.09	35.32	$C_8H_{11}ITe$	26.57	3.04	35.09
$PhMeTeI_2$	145	18.36	1.79	51.95	$C_7H_8I_2Te$	17.76	1.69	53.60
p-$TolMe_2TeI$	154	28.79	3.62	32.12	$C_9H_{13}ITe$	28.78	3.46	33.79
p-$TolMeTeI_2$	126-127	20.11	2.15	52.14	$C_8H_{10}I_2Te$	19.71	2.07	52.05
p-$EtOC_6H_4Me_2TeI$	163	29.06	3.63	32.29	$C_{10}H_{15}IOTe$	29.62	3.70	31.29
p-$EtOC_6H_4MeTeI_2$	108	21.47	2.43	50.07	$C_9H_{12}I_2OTe$	20.89	2.32	49.05

(IV) diiodide. Di-*p*-phenetyl ditelluride(II) (1 g, 1.98 mmol) was boiled under reflux with an excess of methyl iodide (50 g). The yellow microcrystalline precipitate was removed by filtration and washed with benzene (2 × 15 ml) to give yellow dimethyl-*p*-phenetyltellurium(IV) iodide (0.89 g, 2.19 mmol), m.p. 163°C. Addition of the cold red filtrate to light petroleum (b.p. 60-80°C) (30 ml) gave red needles of methyl-*p*-phenetyltellurium(IV) diiodide (0.34 g, 0.66 mmol), m.p. 108°C.

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