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^{125}Te NMR SPECTRA OF TELLURIUM HETEROCYCLES

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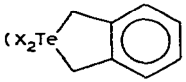
Summary

The ^{125}Te chemical shifts and ^{125}Te—^{1}H coupling constants for the heterocycle 1,3-dihydrobenzo[*c*]tellurophene and its dihalo oxidation products



; X = Cl , Br , I)

have been measured and shown to correlate with the oxidation state of the tellurium and the electronegativity of the halo substituent. Halogen exchange in mixed dihalides has also been monitored by ^{125}Te NMR. Examination of typical Te-compounds in the oxidation states —II, +II and +IV reveals a chemical shift range of 3,500 ppm.

Introduction

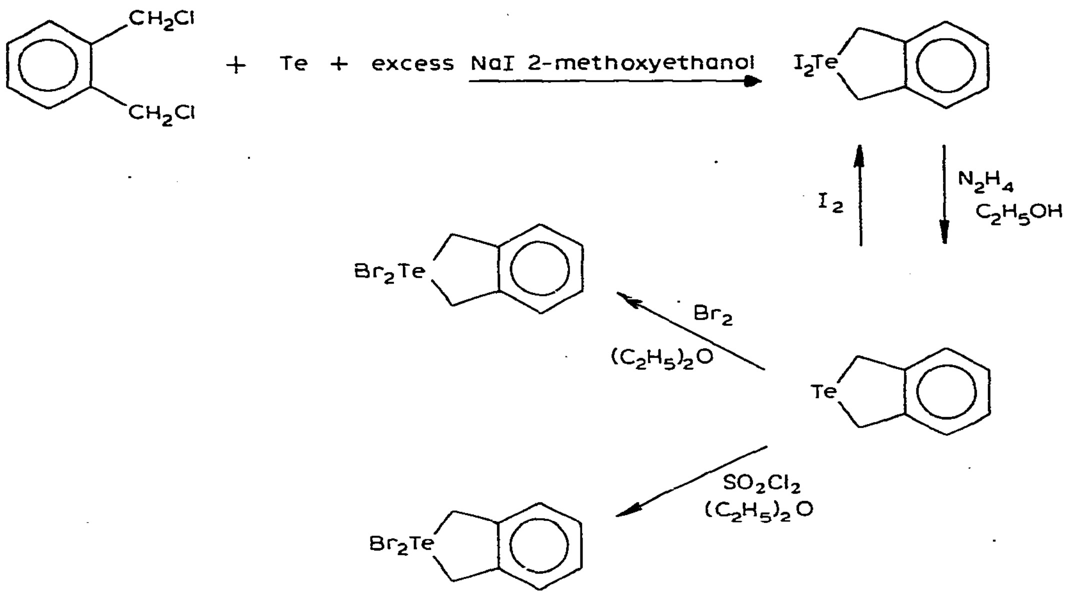
Despite its favorable NMR properties ($I = 1/2$, natural abundance 7%), relatively few direct observations of ^{125}Te in organometallic compounds have been reported [1]. In contrast, a number of investigators have studied the ^{77}Se-NMR spectra of a broad range of compounds in a variety of chemical environments [2]. These studies have established the utility of ^{77}Se-NMR in obtaining structural information, as a result of the wide range of chemical shifts observed (i.e., ca. 1,800). We have recently begun systematic ^{125}Te NMR studies of organotellurium compounds which can be used as ligands for various class B transition metal ions.

Here we report preliminary findings for a series of heterocyclic organotellurium compounds which illustrate the large dependence of the tellurium chemical shifts and coupling constants on oxidation state and systematic variations in molecular structure. We also draw attention to the general usefulness of dynamic ^{125}Te NMR in establishing chemical exchange processes involving tellurium either as a central atom (vide infra) or as a ligand (such as in transition metal-dialkyltellurium complexes).

Results and discussion

Preparation of the heterocycles

The tellurium heterocycle 1,3-dihydrobenzo[*c*]tellurophene was first prepared by alkylation of a Na_2Te suspension in DMF (prepared by the reaction of the elements in liquid ammonia followed by evaporation of the solvent and addition of DMF) with α,α'-dibromo-*o*-xylene [3]. A more convenient synthesis of this heterocycle has recently been reported [4], involving the reduction of the readily accessible diiodide (Scheme 1):



This synthesis of diiodide using a high-boiling solvent and excess NaI avoids the use of a sealed-tube reaction as previously reported for a number of dialkyl tellurium diiodides [5]. We reduced the diiodide with hydrazine in ethanol, and recrystallization of the crude product from warm ethanol gave the analytically pure product in 67% yield (m.p. 44°C) [3]. The Te^{II} heterocycle can be readily oxidized to the dihalo derivatives in ether, with SO_2Cl_2, Br_2, or I_2 as the oxidants (Scheme 1).

Tellurium-125 NMR Parameters

The ^{125}Te spectra of all four heterocycles display a quintet due to coupling to the methylene protons (cf. Fig. 1), consistent with the integrity of the heterocyclic structure in the dihalides. The dihalides display greater coupling constants than the parent compound, and fine structure due to small long-range couplings to the aromatic protons (~2—3 Hz) begins to appear. Any long-range couplings in the parent compound must be considerably less than the linewidth (~1 Hz) of the components of the quintet.

A correlation between halogen electronegativities and tellurium chemical shifts is observed. Inspection of Table 1 shows that chlorine induces the largest

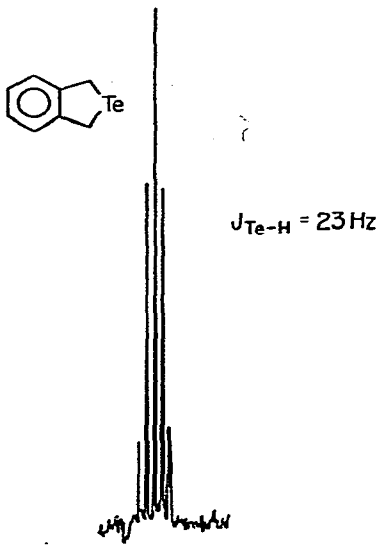
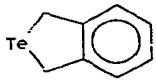
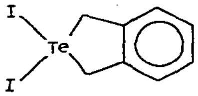
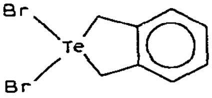
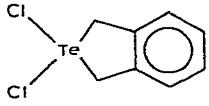
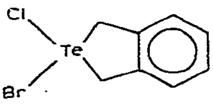


Fig. 1. ^{125}Te NMR spectrum of C_8H_8Te in $CDCl_3$. 100 transients; 3.6 sec delay, no proton decoupling.

TABLE 1

^{125}Te NMR PARAMETERS

Compound	Chemical shift [a]	Coupling constants (Hz) [d]	Halogen electronegativity [b]
	0	23	—
	561.5	34	2.65
	671.4	40	2.95
	724.7	40	3.15
	~703 [c]	—	—

[a] All measurements were made using DMF-d_7 as solvent. Chemical shifts are to lower field of the parent Te^{II} heterocycle. [b] Pauling electronegativities. [c] In equilibrium with the dichloride. [d] Some Te—H coupling constants have been previously reported from ^{1}H NMR studies [7].

downfield shift, iodine the smallest. This observation is analogous to the behavior of ^{13}C shifts in alkyl halides.

The chemical shifts of all four heterocycles considered in this paper are dependent to a certain extent on solvent, concentration, and temperature. One possible explanation would be the existence of association equilibria, a view consistent with the observation of Ziolo and Günther [4] that the molecular weight of the iodide in acetone is concentration dependent.

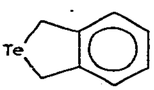
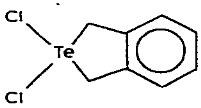
The chemical shifts of the heterocycles are compared with those of some representative tellurium compounds in Table 2. The shifts are given with respect to tellurium diethyldithiocarbamate, $Te(S_2CNEt_2)_2$, in $CDCl_3$ (1 *M*) used as external reference. A negative sign indicates an upfield shift from the reference. The most shielded Te nucleus observed by us to date is the Te^{2-} ion. The least shielded species observed so far is the tellurite ion $Te^{IV}O_3^{2-}$. These extremes span a chemical shift range of ~3.500 pm. Within this range the parent heterocycle correlates well with other diakyl tellurides and its chemical shift occurs at a higher field than that of diaryl tellurides. The dihalides of alkyl tellurides, though formally in the +IV oxidation state, overlap in part in their chemical shift range with strongly deshielded, divalent tellurium species such as the dialkyldithiocarbamates and the alkylxanthates.

The larger coupling constants observed for the Te^{IV} compounds reflect the increasing *s*-character of tellurium bonding orbitals compared to Te^{II}, which used pure *p*-orbitals for bonding [6].

Halogen exchange is observed when saturated DMF solutions of dichloride and dibromide are mixed. The halogen exchange rate is slow on the NMR time scale; thus the dichloride and chlorobromide signals are distinctly observable, although broadened (~110 Hz). The results of this preliminary qualitative experiment are shown in Fig. 2. Quantitative dynamic ^{125}Te NMR experiments on this and similar systems are in progress. A more extensive study of the NMR

TABLE 2

CHEMICAL SHIFTS OF REPRESENTATIVE TELLURIUM COMPOUNDS [a]

Formal oxidation state	Compound	Chemical shift
—II	Te^{2-} in D_2O	—2581.8
+II	$Te(CH_2CH_2CH_2Si(CH_3)_2)_2$	—613.0
		—564.6
	$TePh_2$	—145.6
+IV		+160.1
	TeO_3^{2-}	+892.4

[a] Chemical shifts measured with respect to external $Te(S_2CNEt_2)_2$. A negative sign indicates an upfield shift.

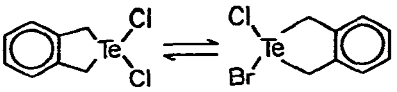


Fig. 2. ^{125}Te NMR spectra of an equilibrium mixture of $C_8H_8TeCl_2$ and $C_8H_8TeBrCl$ in DMF-d_7. 10,000 transients; 3.6 sec delay; proton noise decoupling.

properties of ^{125}Te in organotellurium compounds will be presented in an upcoming paper.

Experimental

Tellurium powder, TeO_2, K_2TeO_4 and diphenyl telluride were obtained from Alfa Products. All other reagents were obtained from Eastman Organic Chemicals. Bis(diethyldithiocarbamato)tellurium [9], bis(3-trimethylsilylpropyl)-telluride [8] and 1,1-diiodo-3,4-benzo-1-telluracyclopentane [4] were prepared as previously described.

1,3-dihydrobenzo[c]tellurophene

To a suspension of $C_8H_8TeI_2$ (7.3 g, 0.015 mol) in 350 ml of ethanol and 30 ml of water was added dropwise a solution of hydrazine (1.75 g, 0.055 mol) in 30 ml of ethanol. The resulting solution was warmed gently until all the red crystals of the diiodide disappeared. The reaction solution was then poured into 1 l of water and extracted with three-400 ml portions of ether. The combined ether extracts were washed with water, dried over $MgSO_4$ and concentrated to dryness on a rotary evaporator. The resulting yellow powder (2.8 g) was recrystallized from 125 ml of methanol (45°C) to give 2.1 g of very pale yellow flakes, m.p. 44°C (lit. 44—46°C [3]). Anal. Found: C, 41.4; H, 3.6; Te, 55.2; C_8H_8Te calcd.: C, 41.46; H, 3.48; Te, 55.06%.

1,1-dibromo-3,4-benzo-1-telluracyclopentane

To a solution of C_8H_8Te (1.1 g, 0.004 mol) in 125 ml of ether was added dropwise a solution of Br_2 (0.76 g, 0.0048 mol) in 20 ml of ether. A pale yellow precipitate formed immediately; the solution was evaporated to dryness and the residue was recrystallized from 350 ml of 1 : 1 methanol/methylene chloride to give 1.3 g (69.9%) of white microcrystals, m.p., blackens above 230°C. Anal.: found: C, 24.3; H, 2.0; Br, 39.8; Te, 31.9; mol. wt., 392 (field desorption mass spectroscopy based on ^{130}Te and ^{79}Br) $C_8H_8Br_2Te$, Calcd.: C, 24.54; H, 2.06; Br, 40.81; Te, 32.59%; mol. wt. 391.54.

The dichloro analog was prepared by a similar oxidation reaction with SO_2Cl_2, the product being obtained as white needles in 65% yield after recrystallization from toluene, m.p. 265—270°C dec. Anal: Found: C, 32.2; H, 2.9; Cl, 23.3; Te, 42.0; mol. wt. 304 (field desorption mass spectroscopy) $C_8H_8Cl_2Te$ calcd.: C, 31.75; H, 2.66; Cl, 23.42; Te, 42.16%.

Na_2Te solution in D_2O

A suspension of Te powder (3 g, 0.0235 g atom) in 50 ml of D_2O containing 8 g NaOH and 3 g $NaBH_4$ was refluxed under Ar in a Schlenk flask fitted with a 10 mm NMR tube ca. 2″ above the level of the reaction solution and extending out 90° from the flask. When the reduction was complete, as evidenced by the formation of a clear, pale yellow solution, a portion of the Na_2Te solution was decanted into the NMR tube side arm and sealed.

Physical measurements

Microanalyses were performed by the Analytical Sciences Division of the Kodak Research Laboratories. Field desorption mass spectra were recorded on a Varian MAT 731 mass spectrometer.

^{125}Te NMR spectra were obtained using a Bruker HX-90 spectrometer, with home-built electronics for multinuclear operation. Typically, 1.5—2 ml samples of 0.1 *M* solutions were run in 10 mm tubes, with the exception of the sparingly soluble dibromide. The temperature was maintained at 32°C and controlled within ±1°C.

The chemical shifts for the heterocycles are reported with reference to the parent compound. In general, however, we have found tellurium diethyldithiocarbamate, $Te(S_2CNEt_2)_2$, to be a convenient reference. It is stable in solution and soluble in most organic solvents. Its chemical shift, assigned arbitrarily as zero, falls approximately in the middle of the Te chemical shift range.

Acknowledgment

We would like to thank Mr. R. Gohlke for obtaining the field desorption mass spectra.

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