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Homolytic reactions of diorganotellurium and diorganoditellurium compounds in solution; an EPR study

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Abstract

The thermal and photochemical decompositions of dialkyltelluriums and dialkylditelluriums in *t*-butylbenzene solvent have been studied by EPR spectroscopy. On photolysis, di-*t*-butyl, diallyl, allyl methyl, and dibenzyl tellurium showed EPR spectra of *t*-butyl, allyl, allyl, and benzyl radicals respectively. Alkyl radicals were not detected directly on thermolysis in the range 300–370 K but, primary, secondary, and tertiary alkyl, benzyl and allyl telluriums gave spin adducts of the corresponding alkyl radical with nitrosodurene. Dimethyl tellurium was unreactive in the same temperature range. The rates of thermal decomposition of the diorgano telluriums at 315 K were found to be in the following order, as judged by the intensity of the spin adduct spectra: ${}^t\text{Bu}_2\text{Te} \sim {}^t\text{BuTeMe} > (\text{allyl})_2\text{Te} \sim \text{allylTeMe} > {}^s\text{Bu}_2\text{Te} > (\text{benzyl})_2\text{Te} > {}^i\text{Pr}_2\text{Te} > \text{Et}_2\text{Te} > \text{Me}_2\text{Te}$. For dihex-5-enyltellurium the results were consistent with formation and cyclisation of hex-5-enyl and hex-5-enetelluryl radicals. In the case of dipent-4-enyltellurium, the results suggested that both *exo*- and *endo*-cyclisation of the pentene telluryl radicals were important. Di-isopropyl- and di-*t*-butyl-ditelluriums gave spin adducts of the corresponding alkyl radicals on thermolysis in the same temperature range as the monoalkyltelluriums.

Introduction

The thermal and photochemical decomposition of dialkyltelluriums in the gas phase has attracted much interest [1,2] because of the importance of these materials for the MOVPE growth of II–IV semiconductors. It is believed that the mechanism of thermal decomposition involves homolysis of the Te–C bond to give free radicals [3]. Several free radical reactions of dialkyltelluriums have been reported in solution. For example, the reduction of alkyl(phenyl)telluriums by triphenyltin hydride gave alkanes [4]. Diallyltellurium decomposed at 180°C with

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formation of hexa-1,5-diene [5]. Free radicals generated from acyl derivatives of *N*-hydroxy-2-thiopyridone reacted with diisopropyl tellurium to release isopropyl radicals which were subsequently trapped by addition to alkenes [6]. Few, if any, well characterised homolytic reactions of dialkylditelluriums have been described [7].

We examined the thermal and photochemical decomposition of a range of dialkyltelluriums and dialkylditelluriums in solution. In addition, peroxide and ditin initiators were used and the reactive intermediates were monitored by EPR spectroscopy. Free alkyl radicals were directly detected in a few cases, and were identified by spin trapping for all dialkyltelluriums except dimethyl.

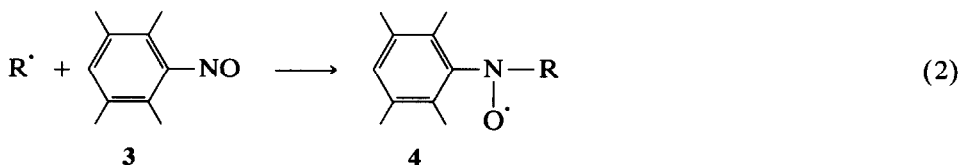
Results and discussion

Dialkyltelluriums

The dialkyltelluriums **1a–g** and **2e,f** were prepared as described previously [3,8]. A sample of each was distilled into a Spectrosil tube containing *t*-butylbenzene as solvent and the mixture was carefully freed from traces of oxygen by a series of freeze-pump-thaw cycles. The samples were heated in the range 300–370 K in the cavity of the EPR spectrometer, but no signals were observed for any of these compounds. That reaction had occurred was shown by the darkening of the

R_2Te		$RTeMe$
1	a; R = Me b; R = Et c; R = ⁱ Pr d; R = ^s Bu	e; R = ^t Bu f; R = allyl g; R = PhCH ₂
		2

colour and, for the ^tBu (**1e**), allyl (**1f**), and ⁱPr (**1c**) compounds, by the formation of tellurium mirrors. Evidently, the concentration of free alkyl radicals was below the spectrometer detection limit. To confirm this, samples were also prepared in *t*-butylbenzene saturated with nitrosodurene **3**, which is usually the best spin trap for alkyl radicals [9]. For **1a** no spectra were obtained up to *ca.* 380 K, but for the others, **1b–g**, strong spectra of the spin adducts **4** of the corresponding alkyl radicals were observed.



The spectra showed cleanly one trapped radical in each case, except on prolonged heating at $T > 350$ K when additional species, probably from secondary reactions, began to build up. The EPR parameters, which were in good agreement with literature values [10] are collected in Table 1. As expected, the H_{β} hyperfine splittings (hfs) of all the radicals **4** decreased with decreasing temperature. For the mixed dialkyltelluriums **2** only the spin adduct of the more stable alkyl radical, *i.e.* allyl for **2f**, and *t*-butyl for **2e**, was observed. The evidence is strong therefore that

Table 1

EPR parameters of nitrosodurene spin adducts of alkyl radicals ^a

Radical	<i>T</i> /K	<i>a</i> (N)	<i>a</i> (H _β) ^b
4b	350	1.37	1.12(2H)
4c	350	1.36	0.80(1H)
4d	350	1.38	0.81(1H)
4e	350	1.38	—
4f	320	1.38	1.06(2H)
4g	350	1.37	0.83(2H)

^a All *g*-factors 2.006 ± 0.001 ; hfs in mT. ^b H_β hfs decreased with decrease in *T*; at 300 K values were: 4b; 1.02, 4c; 0.66, 4d; 0.69, 4f; 1.04, 4g; 0.78 mT.

thermolysis of dialkyltelluriums in solution occurs by homolysis of the C–Te bond; but that higher temperatures are necessary for homolysis of the Te–Me bond. The fact that only the more stabilised radical was detected from 2e and 2f indicates that at *T* < 370 K initial reaction is by one bond rather than two bond fission.

The intensity of the EPR signals of the spin adducts increased with increasing temperature and with time of thermolysis. For *T* < 350 K the rates of decomposition were sufficiently slow that the change in signal intensity with time was negligible in comparison with the time taken to record the spectra (*ca.* 100s). The normalised signal intensities *I*(4) as a function of temperature are shown in Fig. 1 as an Arrhenius type plot. *I*(4) depends on (i) the alkyl radical concentration, (ii) the efficiency with which 3 traps each radical, (iii) the rate of decay of each spin adduct radical, (iv) the concentration of spin trap, (v) instrumental parameters. Factors (iv) and (v) were constant for each experiment. Nitrosodurene traps all

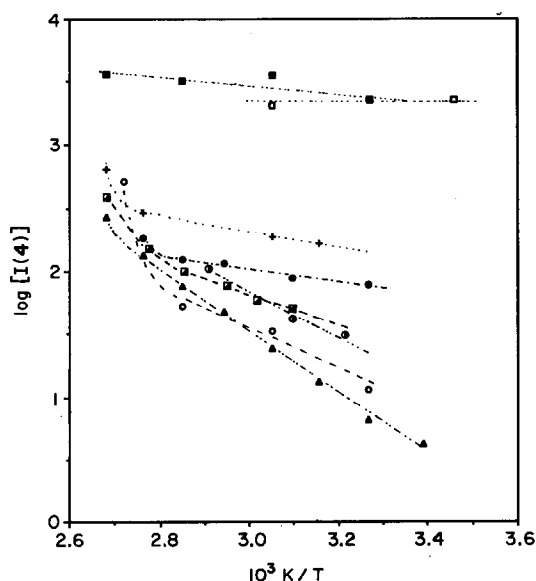


Fig. 1. Arrhenius type plot of spin adduct normalised signal intensities *I*(4). ▲ Et₂Te, ● ⁱPr₂Te, ● ^sBu₂Te, □ ^tBu₂Te, + (allyl)₂Te, ▣ (benzyl)₂Te, ○ ⁱPr₂Te₂, ■ ^tBu₂Te₂.

Table 2

Relative rates of thermolysis of dialkyl tellurium compounds estimated from spin adduct intensities I(4)

Compound	Rel. Rate ^a	SE ^b	T _d /°C ^c
Me ₂ Te	< 0.02	0.0	500
Et ₂ Te	1.0	18	400
¹ Pr ₂ Te	2.8	27	320
^s Bu ₂ Te	5.7	24	–
^t Bu ₂ Te	150	37	250
^t BuTeMe	290		
(allyl) ₂ Te	12	78	180
allylTeMe	11		
(benzyl) ₂ Te	3.2	71	
Me ₂ Te ₂	< 0.02		
¹ Pr ₂ Te ₂	1.6		
^t Bu ₂ Te ₂	170		

^a Rate of thermal decomposition relative to that of Et₂Te at 315 K. ^b Stabilisation energy of radical, relative to that of methyl radicals, in kJ mol⁻¹, from gas phase thermodynamic data [13]. ^c Approximate temperature for HgTe growth by gas phase thermal decomposition under MOVPE conditions.

types of alkyl radical very rapidly, although there may be small differences for primary, secondary and tertiary radicals [9]. To a first approximation however, the I(4) values should be proportional to the alkyl radical concentrations. This in turn is governed by their rates of formation and termination, including reaction of 4 with R[•], which will be the main process leading to decay of 4. All the radicals in this study were small alkyls whose termination rates with each other [11] and with nitroxide radicals [12] will be essentially diffusion-controlled and hence the I(4) values will give an approximate measure of the rate of thermal decomposition of each dialkyl tellurium. Figure 1 shows that in the range 300–350 K satisfactory linear plots of log[I(4)] *vs.* 10³ T/K were obtained. At higher temperatures the plots curved upwards, almost certainly because the time dependence of I(4) became important. The I(4) values decrease in the order ^tBu₂Te > (allyl)₂Te > ^sBu₂Te > (benzyl)₂Te > ¹Pr₂Te > Et₂Te. Apart from the allyl and benzyl cases, these intensities indicate that, as expected, thermolysis to give tertiary radicals is more rapid than thermolysis to give secondary radicals etc. Table 2 shows relative rates of decomposition calculated from the I(4) values at 315 K. Because of the complex interplay of factors affecting the spin adduct intensities, these numbers can only be regarded as a very rough guide. In the main the relative rates increase in line with the increasing thermodynamic stabilisation energies (SE) of the product alkyl radicals [13] (Table 2). Similarly, the relative rates also correlate with the temperatures at which satisfactory rates of growth of HgTe could be achieved from gas phase decomposition of the dialkyl telluriums under MOVPE conditions [1], again with the exception of the allyl compounds.

The estimated relative rates for 1f and 1g in solution are lower than that of 1e, even though SE(allyl) and SE(benzyl) are much greater than SE(^tBu). There are two possible explanations of this anomaly. Firstly, allyl and benzyl radicals are stabilised by resonance delocalisation of the unpaired electron. Thus, the incipient radical centre must be completely planar before this delocalisation can take full effect. This will take significantly more molecular reorganisation than in the t-butyl

case. As the $\text{CH}_2\text{-Te}$ bond of **1f**, **1g** or **2f** lengthens, the configuration at C^α must change from tetrahedral to planar before resonance stabilisation can come into play. For the *t*-butyl case the stabilisation is due to inductive and steric effects, which can operate to some extent in the ground state even before the $\text{Me}_3\text{C-Te}$ bond is stretched. Furthermore, the *t*-butyl radical is pyramidal in its lowest energy conformation so that comparatively little reorganisation of the carbon structure is involved on homolysis. The relative thermolysis rates will depend on how far the Te-C bond has been stretched in the transition state of homolysis. If the transition state is "early" with only minor bond stretching, the resonance delocalisation of the final allyl or benzyl radical can have little effect in lowering the activation energy, and hence the slower relative rates of decomposition of **1f** and **1g** are explained. An alternative explanation is that the allyl and benzyl radicals may not be efficiently trapped by nitrosodurene, so that the I(4) value is not a true measure of the relative rate of decomposition of the diorganotellurium. It is known that there is little difference in the rate of trapping for primary, secondary and tertiary alkyl radicals [9], but delocalised radicals such as allyl and benzyl have not been examined in this respect.

The temperature at which TeHg is deposited from $(\text{allyl})_2\text{Te}$ is also lower, under MOVPE conditions, than the temperature required in the $\text{t-Bu}_2\text{Te}$ case (Table 2). In the MOVPE experiments the reactions may be partly heterogeneous and subject to catalysis at surfaces, so that the lack of complete correlation with the solution phase data is hardly surprising. However, the Arrhenius type plots of Fig. 1 do suggest that the lines for **1e** and **1f** may cross at higher temperatures. Thus, at the much higher temperatures of the gas phase decompositions the relative rates for **1e** and **1f** may be in reverse order to that obtained at 315 K.

The tellurium-centred radicals $\text{RTe}^\cdot$ are also formed in the homolysis step. We found no evidence of spin adducts $\text{RTeN(O}^\cdot\text{)duryl}$ from any of the dialkyl telluriums. Aryl-thio nitroxides $\text{RSN(O}^\cdot\text{)aryl}$ are usually very short-lived; for example, $\text{PhSN(O}^\cdot\text{)duryl}$ has a half-life of only 3.4 s at room temperature [14]. It is likely therefore that the spin adducts of telluryl radicals are too transient for EPR detection in the temperature range of these experiments. Tellurium mirrors were deposited in many of the thermolyses so that the alkyltelluryl radicals possibly undergo a further decomposition step (3) to give more alkyl radicals.



Alternatively, the Te may be formed by combination of two $\text{RTe}^\cdot$ radicals and subsequent extrusion of the metal:



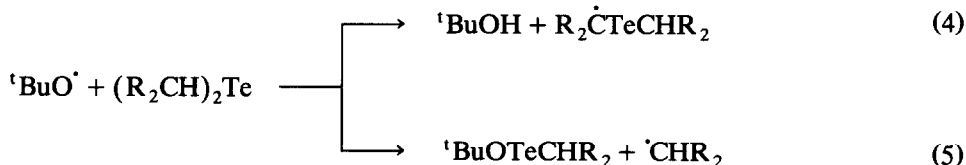
Primary alkyltelluryl radicals must have significant lifetimes because ring-closed products derived from unsaturated examples have been identified (see below):

Photolyses of **1a-g** and **2e,f** in *t*-butylbenzene solution by light from a high pressure mercury lamp were also examined in the range 220–350 K. Compound **1a** showed no reaction, **1b-1d** deposited Te mirrors, but no EPR signals were observed. For **1e** and **1g** weak spectra of *t*-butyl and of benzyl radicals were obtained; **1f** and **2f** gave strong spectra of the allyl radical.

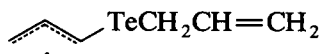
At higher temperatures deposition of Te was rapid which screened the solution from photolysis, caused baseline drift, and led to poor quality spectra. This method

of alkyl radical generation will only be useful for spectroscopic work for strongly stabilised radicals at $T < 300$ K. When spin trap **3** was included the same spin adducts were observed as in the thermal experiments. Attempts were made to observe the addition of alkyl radicals to alkenes. For example, **1b** was photolysed in the presence of acrylonitrile, but the adduct radical, $\text{EtCH}_2\text{CH}\cdot\text{CN}$, was not detected.

Photolyses were also carried out in the presence of di-*t*-butyl peroxide, without spin trap. The peroxide gives *t*-butoxyl radicals on photolysis which could potentially react with R_2Te in two ways. Either by abstraction of a hydrogen atom to give a telluraalkyl radical, eq. 4, or by homolytic substitution at tellurium ($S_{\text{H}2}$ reaction) with displacement of an alkyl radical, eq. 5.



For **1a** and **1c** no EPR signals were observed, although for the latter, a Te mirror was deposited. For **1f** a strong spectrum of the allyl radical was obtained. These results do not exclude the possibility of hydrogen abstraction but, if reaction 4 were important, we might have expected to detect the product radical, particularly for **1f** where the resonance stabilised species **5** would be formed.



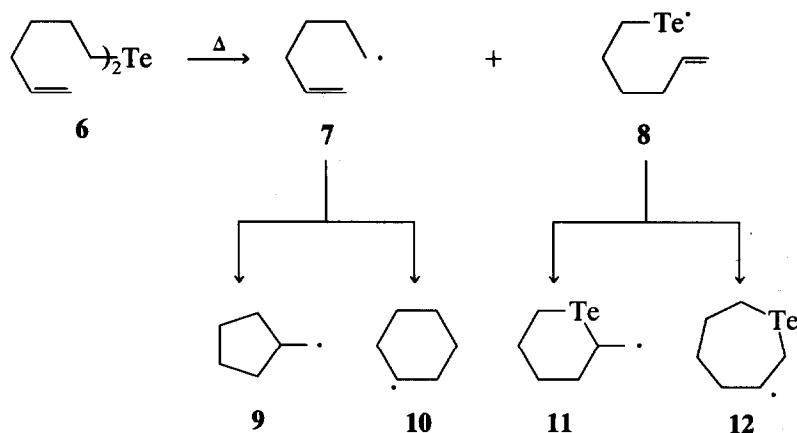
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Probably however, the EPR spectra of α -telluraalkyl radicals are broadened beyond detection by a large isotopic g shift due to interaction of the unpaired electron with the adjacent Te lone pair. This was found to be the case for analogous unhindered α -selenaalkyl radicals [15]. The allyl radicals detected in the reaction with **1f** could be due to direct photolysis (see above) or to the displacement reaction 5.

Dihex-5-enyl- and dipent-4-enyl-tellurium

On thermolysis or photolysis, solutions of **6** and **13** showed similar behaviour to that of Et_2Te . When spin trap **3** was included, the main spin adduct obtained on thermolysis of **6** was that of primary radicals [$a(\text{N}) = 1.37$, $a(2\text{H}) = 1.11$ mT at 360 K]. The rate of cyclisation of hex-5-enyl radicals **7** is such that spin adducts of both **7** and the product of *exo* ring closure, *i.e.* the cyclopentylmethyl radical **9** are observed in the range 270–340 K under EPR conditions [9] (see Scheme 1).

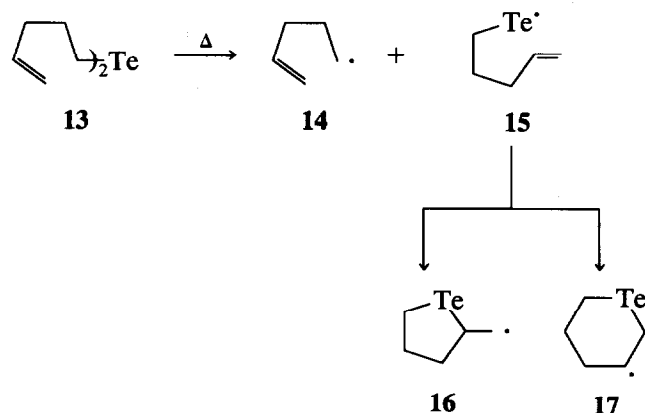
Therefore, at $T < 340$ K, our spectra represent overlapping spin adducts of the primary radicals **7** and **9**; at 360 K contributions from **7** are negligible. In the range 300–360 K the spin adduct of a secondary radical [$a(\text{N}) = 1.37$, $a(1\text{H}) = 0.72$ mT at 360 K] was also observed. The measured ratio of secondary to primary spin adducts was 0.18 ± 0.04 at 360 K. Radical **7** is known to cyclise to a minor extent in the *endo* mode giving **10**, but if the secondary spin adduct were solely due to **10** the ratio, calculated from the known ratio of **10** and **9** at 360 K [16], should be 0.02. The amount of secondary spin adduct substantially exceeds this, which indicates



Scheme 1.

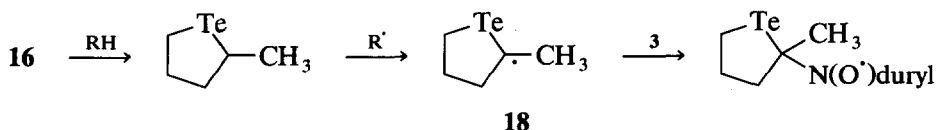
that additional secondary radicals are produced by another reaction. The hex-5-ene telluride radicals **8** may also cyclise in the *exo* mode to give primary radical **11** and in the *endo* mode to give secondary radical **12**. The EPR spectrum of the spin adduct of **11** would overlap that of the other primary radicals and would not be distinguishable. The secondary spin adduct detected here may well be that derived from **12**. Unsaturated radicals centred on non-first row elements are known to give more *endo* cyclisation in comparison with radicals centred on first row elements [16]. Both sulphur- [17] and selenium-centred radicals [18] cyclise to give major yields of the *endo* products.

When dipent-4-enyltelluride **13** was thermally decomposed in the presence of nitrosodurene two major spin adducts, a primary with $a(\text{N}) = 1.37$, $a(2\text{H}) = 1.08$ mT at 360 K, and a tertiary with $a(\text{N}) = 1.37$ mT, were observed together with minor amounts of at least one secondary spin adduct. The tertiary spin adduct increased in intensity with thermolysis time and dominated the spectrum at higher temperatures and after about 5 min thermolysis at lower temperatures. Thermolysis of **13** will give pent-4-enyl radicals **14** which do not cyclise and will give a



Scheme 2.

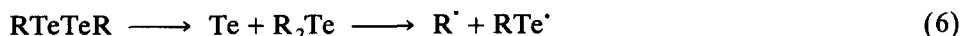
primary spin adduct at all temperatures. Pent-4-ene telluranyl radicals **15** (Scheme 2) will also be produced and may cyclise to give **16** and **17**. Thermal decomposition of **13** in the gas phase *in vacuo* [19], gave mainly 2-methyl telluracyclopentane derived from **16**, however, formation of both **16** and **17** in solution cannot be ruled out. Radical **16** would give a primary spin adduct indistinguishable from that derived from **14**. Radical **17** may be responsible for the minor secondary spin adduct detected. The large amount of tertiary spin adduct is difficult to account for. Possibly it is formed after **16** abstracts hydrogen from **13**, or other material (collectively designated RH), to give **18**, where R' may be any of the radicals in the system:



If this is correct then it is surprising that similar tertiary spin adducts are not observed for **6**, **1c**, and other dialkyl telluriums with tertiary hydrogens adjacent to tellurium.

Dialkylditelluriums

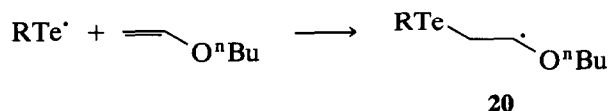
The thermal and photochemical decompositions of **19a–c** were examined under similar sets of conditions to those used for **1** and **2**.



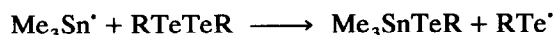
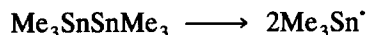
19, a; R = Me, **b;** R = ⁱPr, **c;** R = ^tBu

No EPR spectra were obtained from the dimethyl compound **19a**, with or without spin trap, although a tellurium mirror was deposited in the photolysis experiments. **19b** and **19c** gave spin adducts of the corresponding alkyl radicals on thermolysis in the range 300–370 K; the spin adducts were detected at lower temperatures on photolysis. Spin adducts of tellurium centred radicals were not detected (see above). The I(4) values were measured under the same conditions as for the dialkyl telluriums and the rates of decomposition of **19a–c**, relative to that of **1b**, were estimated in the same way (see Table 2). The relative rate for ¹Pr₂Te₂ is very similar to that of ¹Pr₂Te and the relative rate for ¹Bu₂Te₂ lies between that of ¹Bu₂Te and ¹BuTeMe. This might be taken to indicate that **19** decomposes by initial Te–C bond homolysis. However, the results are probably best explained by initial extrusion of Te, as demonstrated before [3], with subsequent decomposition of the R₂Te, eq. 6. This will explain why the relative rates are close to those observed for the corresponding dialkyltelluriums.

Alkyltelluranyl radicals are expected to be weakly electrophilic in character and might therefore add rapidly to alkenes with electron-releasing substituents. We attempted to trap RTe' with n-butyl vinyl ether:



but no adduct radicals were detected for $R = {}^i\text{Pr}$, or ${}^t\text{Bu}$. We also used hexamethylditin as an initiator in photolyses at *ca.* 230 K:



but radical **20** could not be detected in these circumstances either.

Experimental

The EPR spectra were recorded with a Bruker ER 200D spectrometer operating at 9.3 GHz with 100 kHz modulation. Samples of each organotellurium compound (*ca.* 100 mg) were distilled into a Spectrosil tube (o.d. = 4.0 mm) containing *t*-butylbenzene (*ca.* 1 ml). In the spin trapping experiments *t*-butylbenzene already saturated with nitrosodurene was employed. The samples were degassed by several freeze-pump-thaw cycles and transferred to the EPR cavity. In the photolysis experiments unfiltered light from a 500 W super pressure mercury lamp was employed. The line widths of the spin adducts were all virtually the same and therefore signal intensities $I(4)$ were determined by measuring the peak to peak height of a given line, multiplying by the multiplicity factor to obtain the intensity of the whole spectrum, and normalizing each spectrum to the same gain (2×10^5).

Dialkyltelluriums were prepared by published methods [8], as were ${}^i\text{Pr}_2\text{Te}_2$ [20] and ${}^t\text{Bu}_2\text{Te}_2$ [21].

Di-t-butyl tellurium.

t-Butyl lithium (90 g) in pentane was added dropwise to a solution of tellurium(IV) chloride (100 g) in ether at 0°C over 6 h. An exothermic reaction occurred and the mixture was stirred for 1 h after complete addition. The pale yellow solution was filtered, water was added to destroy any excess ${}^t\text{BuLi}$, the organic layer was separated and dried (CaCl_2), and the solvent was evaporated. The residual oil was purified by vacuum distillation to give **1e** (62%) as a deep yellow oil [22].

Dimethylditellurium

Tellurium powder (40.3 g, 0.32 mol), sodium formaldehyde sulfoxide (Rongalite C) (58.4 g, 0.38 mol) and sodium hydroxide (50.0 g, 1.25 mol) were dissolved in deaerated, distilled water (300 cm³), heated to 110°C for 1 h and then cooled rapidly. CTAB (0.75 g, 2.0 mmol) in diethyl ether (500 cm³) was added, followed by dropwise addition of CH_3I (22 cm³, 0.35 mol). The reaction mixture was stirred overnight at room temperature, then heated to 40°C for 2 h, followed by stirring at room temperature for 3 h. The ether layer was removed, ether (250 cm³) was added to the aqueous layer, together with CTAB (0.5 g) and CH_3I (5 cm³). The mixture was then warmed to 30°C and stirred for *ca.* 2 h. The ether layers were combined and the aqueous layer was again extracted with diethyl ether containing CH_3I (5 cm³) and CTAB (0.5 g). The ether layers, which were orange black in colour, were dried (CaCl_2 and CaH_2). Removal of the ether gave a red-black oil

(35 g), which was distilled *in vacuo* to give Me_2Te (8.0 g, 16%) and Me_2Te_2 (25.5 g, 57%).

Acknowledgment

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