

Organic Tellurium-Centered Radicals Evidenced by EPR Spin Trapping and Mass Spectrometry Experiments: Insights into the Mechanism of the Hydrotelluration Reaction

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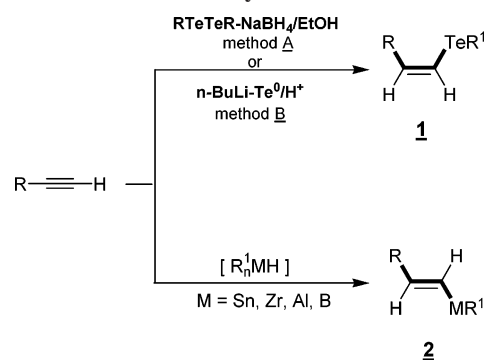
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The first experimental evidence for the formation of an organic tellurium-centered radical (RTe[•], R = Ph or ⁿBu groups) during the hydrotelluration of alkenes and alkynes is provided. The radicals were detected by electronic paramagnetic resonance (EPR), using DNBNS (3,5-dibromo-4-nitrosobenzene-sulfonate) as the spin trap. The radical adducts (DBNBS/ⁿTeⁿBu and DBNBS/ⁿTePh) presented an EPR spectrum characterized by a triplet of triplets due to one nitrogen and two equivalent hydrogen atoms ($a_N = 21.6$ G and $a_H = 0.7$ G) and a g value of 2.0060. The presence of tellurium radical adducts was confirmed by isotopic substitution (¹²⁵Te) and by electrospray and chemical ionization mass spectrometry and MS/MS analysis. The products showed isotopic patterns expected for compounds containing Br and Te. These results provide evidence for organic tellurium-centered radical formation and suggest that the hydrotelluration reactions occur by a free radical mechanism.

Introduction

The organic compounds of tellurium are becoming important synthetic tools. In the last decade a number of reviews have been published dealing with synthetic applications of these compounds,¹ both for functional group transformations and for stereocontrolled carbon–carbon double bond formation. Among the several synthetic methodologies using organotellurium compounds, the hydrotelluration of alkynes is the most employed in view of its unique features.² This reaction can be performed by RTeTeR–NaBH₄/EtOH (method A, R = Ph or ⁿBu)³ or by ⁿBuLi–Te⁰/H⁺ (method B),⁴ both with the same high regio- and stereoselectivity, leading to the exclusive formation of *Z*-vinylic tellurides **1**. Other hydrometalation reactions of synthetic interest such as hydrozirconation,⁵ hydroalumination,⁶ and hydroboration⁷ of alkynes give the *E*-vinylic derivatives **2** predominantly (Scheme 1).

Scheme 1. Hydrotelluration and Hydrometalations of Alkynes



This unique characteristic of the hydrotelluration reaction transformed vinylic tellurides **1** into the most studied class of organic tellurium compounds. The most important synthetic methodologies based on vinylic tellurides are their transformation into *Z*-vinylic organometallics, notably into *Z*-vinyllithiums⁸ and *Z*-vinylicyanocuprates,^{2a,9} and their stereospecific coupling

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reaction with alkynes and with sp^2 and sp carbanionic species promoted by Pd¹⁰ and by Ni.¹¹ These reactions were recently applied with success in the total synthesis of natural products.¹²

Contrasting with the interest in the synthetic applications of the hydrotelluration reaction, its mechanism has not been focused on. Up to now only speculations were made about the mechanism. Some authors suggested that the reaction occurs by an ionic mechanism,^{1a,13} and others suggested a free radical process.¹⁴ Organic tellurium-centered radicals have been proposed in several other reactions involving organic tellurium compounds;^{15,16} however there are no reports of their detection or characterization.

In this work the EPR spin trapping technique was used as a tool to detect the formation of organic tellurium-centered radicals during the hydrotelluration reaction. The detected DBNBS/ⁿ-TeR radical adducts (R = Ph and ⁿBu) had their structures further analyzed by isotopic substitution (¹²⁵Te) and by electrospray and chemical ionization mass spectrometry (ESI and

APCI-MS) and MS/MS analysis. Tellurium radicals generated by photolysis were also trapped with DBNBS, indicating that the spin trapping approach can be a general method for the detection of organic tellurium-centered radicals.

Experimental Section

Materials. All reagents and solvents were previously purified and dried in agreement with conventional methods. THF was distilled from sodium/benzophenone under nitrogen immediately before use. ⁿBuLi and ⁶BuLi were titrated with 1,10-phenanthroline prior to use.¹⁷ Nitrogen gas was deoxygenated and dried. All operations were carried out in flame-dried glassware. Column chromatography separations were carried out with Vetec silica gel 60 (0.063–0.200 mm, 70–230 mesh) or Acros Organics silica gel (0.035–0.075, pore diameter ca. 60 nm). Elemental tellurium (200 mesh) was obtained from Aldrich Chemical Co. and dried overnight in an oven at 100 °C. Elemental ¹²⁵Te isotope (powder) was purchased from Cambridge Isotopes Laboratories Inc. (MA) in 92% of isotopic purity grade. Dibutyl ditelluride (ⁿBuTeTeⁿBu) and diphenyl ditelluride (PhTeTePh) were prepared according to the literature procedures.¹⁸ DBNBS (3,5-dibromo-4-nitrosobenzene-sulfonate) was prepared from 3,5-dibromosulfanilic acid and glacial acetic acid by a procedure previously described,¹⁹ and its purity was evaluated according to the literature.²⁰ DMPO (2,2'-dimethylpyrrolidine-*N*-oxide, from Aldrich) was vacuum distilled previous to use.²¹ MNP (2-methyl-2-nitrosopropane) and PBN (*N*-tert-butyl- α -phenylnitron) were purchased from Sigma Chemical Co. and were used without purification. The following reagents were purchased from Aldrich Chemical Co.: sodium borohydride, phenylacetylene, propargyl alcohol, 1-hexyne, ethyl propiolate, ethoxyethene, vinyl acetate, Ce(NO₃)₂·2NH₄NO₃.

General Procedure for the Hydrotelluration Reactions with Sodium Borohydride: Method A. To a 25 mL two-necked, round-bottomed flask equipped with magnetic stirring, heating, and reflux condenser under a nitrogen atmosphere were added RTeTeR (R = Ph or ⁿBu, 0.3 mmol) and ethanol (not necessarily anhydrous, 2 mL). To this solution was added NaBH₄ (0.029 g, 0.75 mmol) in small portions until the solution color turned from dark red to pale yellow. After that, a solution of the appropriate alkyne or alkene (0.66 mmol) in deoxygenated ethanol (0.5 mL) was added, and the resulting mixtures were refluxed. Samples were removed under a nitrogen atmosphere from the reaction mixture for the spin trapping and MS experiments. The obtained vinyl tellurides [(*Z*)-butyl(styryl)tellane³ and (*Z*)-3-(butyltellanyl)prop-2-en-1-ol²²] were isolated and analyzed, giving spectroscopic data consistent with those previously reported.

General Procedure for the Hydrotelluration Reactions with ⁿBuLi and Elemental Tellurium: Method B. To a two-necked, round-bottomed flask equipped with magnetic stirring, heating, and reflux condenser under a nitrogen atmosphere were added elemental tellurium (0.127 g, 0.1 mmol) and THF (5 mL). ⁿBuLi (0.65 mL, 1 mmol of a 1.5 mol L⁻¹ solution in hexane) was added dropwise at room temperature to the obtained suspension. After 5 min of stirring a clear solution was formed. After that, deoxygenated ethanol (10 mL) and then the appropriate alkyne (1.2 mmol) were

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added. The resulting mixtures were refluxed for 2 h. Samples were removed from the reaction mixture under a nitrogen atmosphere for the spin trapping experiments. The hydrotelluration reactions with the ^{125}Te pure isotope were performed in a round-bottomed vial (0.5 mL), adapting the above procedure to a very small scale (5 mg, 40 μmol of ^{125}Te). Experiments using a saturated ethanolic solution of NaBH_4 (10 mL) instead of deoxygenated ethanol were also performed.

Generation of Organic Tellurium-Centered Radicals from RTeTeR and $\text{Ce}(\text{NO}_3)_4 \cdot 2\text{NH}_4\text{NO}_3$. The tellurium radical species were generated using the same experimental conditions used for the hydrotelluration of alkynes, but changing the alkyne solution by the Ce(IV) salt solution (16.4 mg, 0.05 mmol in 0.5 mL of ethanol). The reaction solutions were maintained under stirring at room temperature and under N_2 atmosphere.

EPR Spin Trapping during Hydrotelluration Reactions. EPR spectra were recorded at room temperature (22 ± 2 °C) on a Bruker EMX EPR (electron paramagnetic resonance) spectrometer equipped with a standard cavity, operating at X-band frequency, using a standard flat quartz cell. Instrumental conditions were usually 2.00×10^4 gain and 0.5 G modulation amplitude (or 0.3 G in some cases) and a resolution of 1024 points. The EPR spin trapping experiments were performed in neutral medium, using 50 mmol L^{-1} phosphate buffer, at pH = 7.4 or water solution, previously treated with Chelex-100 resin to remove contaminant metal ions. The stock solution of DBNBS and other spin traps were 0.10 mol L^{-1} in phosphate buffer or ethanol solution, maintained at low temperature. Both the stock and buffer solutions were previously purged with N_2 for 2–3 h. All buffer and aqueous stock solutions were prepared with distilled water purified with a Millipore Milli-Q system.

In a typical spin trapping experiment, a sample of the reaction mixture of the hydrotelluration reactions (20.0 mmol L^{-1} , final concentration of the RTeTeR) and the DBNBS-buffered solution (15.0 mmol L^{-1} , final concentration) were mixed in a polyethylene vial containing water or phosphate buffer solution (50 mmol L^{-1}) under constant N_2 purge. Then 200.0 μL of the resulting solution was immediately transferred to a flat quartz cell under N_2 . The EPR spectra were registered no later than 1 min after transfer. In some cases, the spectra were registered at different time intervals to monitor the EPR signal evolution. Appropriate controls were performed. Most important was to control possible addition reaction of the spin trap DBNBS to reagents and products of these reactions.

The magnetic field was calibrated with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, $g = 2.0056$).²³

EPR spectra simulations were performed with the software WinEPR SimFonia version 1.25 (WinEPR System, Bruker) or WinSim EPR calculations for MS-Windows NT, 95, version 0.96, from Public EPR Software Tools (NIH).

EPR Spin Trapping During Photolysis. EPR spectra were recorded under the same conditions described above. A mercury medium-pressure lamp (50 W, $\lambda_{\text{max}} = 366$ nm, Spindler & Hoyer, Germany) positioned 30 cm from the EPR spectrometer cavity was used. The following tellurium compounds in EtOH or EtOH/THF medium were photolyzed in the presence of the DBNBS spin trap buffered solution: $^n\text{BuTeH}$ (from reduction of $^n\text{BuTeTe}^n\text{Bu}$ with NaBH_4 in EtOH medium and from reaction of elemental tellurium with $^n\text{BuLi}$ in THF/EtOH medium) and PhTeH (from reduction of the PhTeTePh with NaBH_4 in EtOH medium). Photolysis of the spin trap or the solvents (EtOH and EtOH/THF) was performed as controls.

In a typical photolysis experiment, the RTeH solution (20.0 mmol L^{-1} , final concentration) of the tellurium species and the DBNBS spin trap buffered solution (15.0 mmol L^{-1} , final concentration) were mixed in a polyethylene vial containing water or phosphate

buffer solution (50 mmol L^{-1}) under constant N_2 purge. Then 200.0 μL of the resulting solution was immediately transferred to a flat quartz cell under N_2 . The EPR spectra were registered no later than 1 min after the lamp was turned on. In some cases, the spectra were registered at different time intervals to monitor the EPR signal evolution.

ESI, APCI, and MS/MS Experiments. The DBNBS/ $^n\text{Te}^n\text{Bu}$ and the DBNBS/ $^n\text{Te}^n\text{Ph}$ radical adducts were analyzed by a Quattro II Micromass mass spectrometer with Z-spray ion source (Manchester, UK). The DBNBS/ $^n\text{Te}^n\text{Bu}$ radical adduct solution was analyzed in the mass spectrometer by electrospray ionization (ESI) in the positive ion mode, and the DBNBS/ $^n\text{Te}^n\text{Ph}$ radical adduct solution was analyzed by atmospheric pressure chemical ionization (APCI) in the positive ion mode, both using methanol and formic acid 0.1% (9:1, v/v) as mobile phase. Analyses in the ESI mode were performed using the following parameters: source and desolvation temperature of 80 °C; flow rate of drying and nebulizing gas of 300 and 15 L/h, respectively; and a capillary potential of 3.5 kV. ESI full scan data were acquired at a sample cone voltage of 10 V, and daughter ions of a specific adduct were obtained using a collision energy of 15 eV. Analyses in the APCI mode were performed using the desolvation and source temperatures of 150 and 400 °C, respectively, capillary potential of 3.0 kV, and flow rate of drying and nebulizing gas of 300 and 15 L/h, respectively. APCI full scan data were acquired at a sample cone voltage of 50 V. Daughter ions of a specific adduct were obtained using a cone voltage of 50 V and collision energy of 15 eV. Parent ions of m/z 280, 282, and 284 were obtained using a cone voltage of 50 V and collision energy of 15 eV. All data were processed and simulated by Mass Lynx NT, version 3.2 software (Micromass, Altricham, U.K.).

Energy Bond Calculations. The Y–H energy bond calculations (Y = O and Te) were carried out with the Hyperchem v. 6.0 program. All compounds' geometry optimizations were performed by molecular mechanics using the MM+ method a. Then the semiempirical method PM3 was used to perform the energy minimization of the molecules. These molecules were submitted to conformational analysis, using the "Conformational Search" routine. Finally, the minor energy enthalpy geometries, obtained from the systematic search, were optimized using the PM3 Hamiltonian method b. The convergence limit used was 0.01.²⁴ The following values were obtained: EtO–H (94 kcal mol^{-1}), $^n\text{BuTe}$ –H (58 kcal mol^{-1}), and PhTe –H (54 kcal mol^{-1}).

Results and Discussion

Electronic Paramagnetic Resonance Studies. To verify the presence of radical species in the reaction mixture of the hydrotelluration reactions, we first employed the sodium borohydride method to generate the hydrotellurating system (method A, Scheme 1) and examined samples of the mixtures at room temperature by EPR in the absence and in the presence of different spin traps, namely, DMPO, MNP, PBN, and DBNBS. Only samples of the mixtures containing DBNBS produced detectable EPR signals (Figure 1). The detected spectra consisted of a triplet of triplets ($a_N = 21.6$ G, $a_H = 0.7$ G, and a g value of 2.0060, Figure 1), which can be attributed to the interaction of the electron spin with the nuclear spin of nitrogen and with the nuclear spin of the two equivalent hydrogens of DBNBS. Such EPR parameters are consistent with those of DBNBS radical adducts, although the value of the nitrogen hyperfine splitting constant is considerably higher than those previously reported, which are in the range of 12–17 G.²⁵ During the course of the

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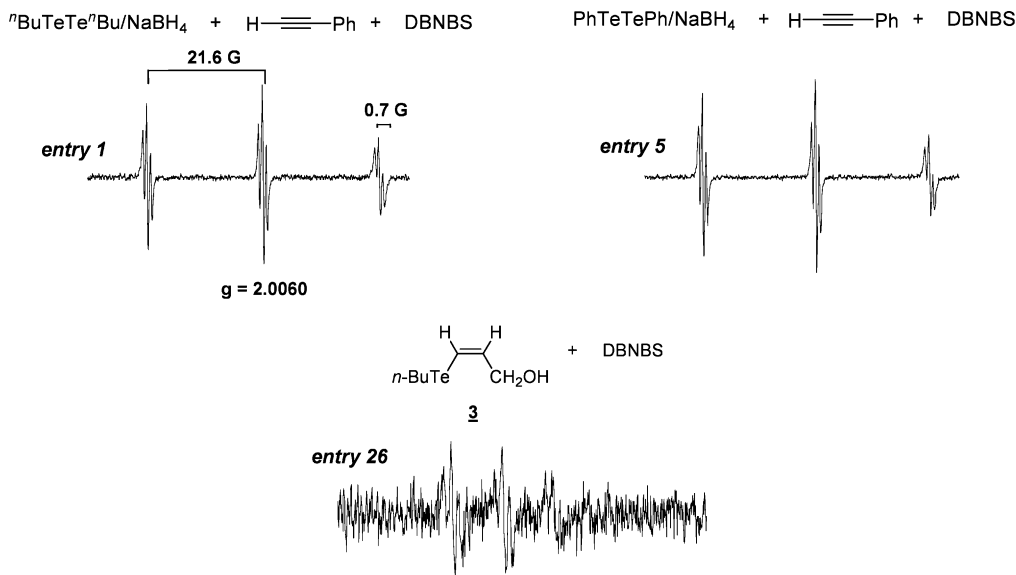


Figure 1. Representative EPR spectra of DBNBS radical adducts obtained during the hydrotelluration reactions of alkynes and a control experiment (for experimental conditions see Table 1).

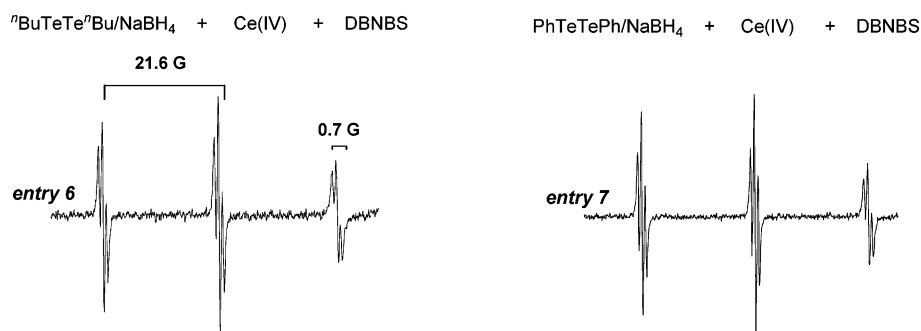


Figure 2. Representative EPR spectra of DBNBS radical adducts obtained during the oxidation of organic tellurium compounds with Ce(IV) (for experimental conditions see Table 1).

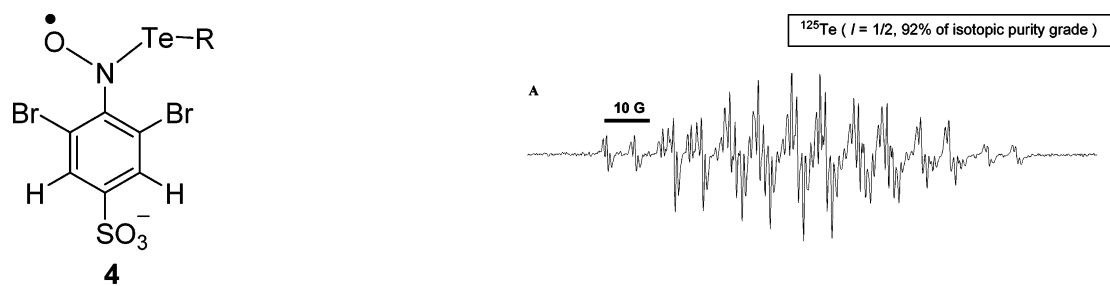


Figure 3. Proposed structure for the DBNBS/ ${}^n\text{TeR}$ radical adducts **4**, R = Ph or ${}^n\text{Bu}$.

hydrotelluration reaction (1–2 h, depending on the R alkyne group), the observed DBNBS radical adduct is likely to maintain the same instantaneous concentration, since samples of the reaction mixture of the hydrotelluration reactions taken at different times and mixed with DBNBS presented similar EPR signal intensity 1 min after the addition of the spin trap. Thereafter, the intensity of the EPR signal increased up to 2–3 min (about 1.5 times) and started decaying after 10–15 min, probably by the DBNBS radical adduct reduction as inferred from MS analysis. By the end of the reaction, when the alkene or the alkyne starting materials were consumed, a less intense EPR spectrum was observed probably due to radical consumption.

Figure 4. Representative EPR spectrum of DBNBS/ ${}^{125}\text{Te}^n\text{Bu}$ radical adduct of a sample of a hydrotelluration reaction using ${}^{125}\text{Te}$ ($I = 1/2$, 92% of isotopic purity grade). (A) Obtained spectrum (for experimental detail see Table 1). (B) Simulated spectrum of the DBNBS/ ${}^{125}\text{Te}^n\text{Bu}$ radical adduct ($a_N = 21.6$ G, $a_{\text{Te}} = 15.8$ G, $a_{\text{Br}} = 6.95$ G, and $a_{\text{H}} = 0.7$ G).

DBNBS is known to add to double bonds.^{26,27} Although the EPR parameters of the detected DBNBS radical adduct were

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Table 1. Reactions and Control Experiments Performed

entry	reaction ^{a-c}	DBNBS radical adducts EPR hyperfines (G)	
		a_N	a_H
1	ⁿ BuTeTe ⁿ Bu/NaBH ₄ + HC≡CPh	21.6	0.7
2	ⁿ BuTeTe ⁿ Bu/NaBH ₄ + HC≡C(CH ₂) ₃ CH ₃	21.6	0.7
3	ⁿ BuTeTe ⁿ Bu/NaBH ₄ + HC≡CCH ₂ OH	21.6	0.7
4	ⁿ BuTeTe ⁿ Bu/NaBH ₄ + HC≡CCO ₂ Et	21.6	0.7
5	PhTeTePh/NaBH ₄ + HC≡CPh	21.6	0.7
6 ^d	ⁿ BuTeTe ⁿ Bu/NaBH ₄ + Ce(IV)	21.6	0.7
7 ^d	PhTeTePh/NaBH ₄ + Ce(IV)	21.6	0.7
8	ⁿ BuTeTe ⁿ Bu/NaBH ₄ + H ₂ C=CHCO ₂ Me	21.6	0.7
9	ⁿ BuTeTe ⁿ Bu/NaBH ₄ + H ₂ C=CHOEt	21.6	0.7
10	ⁿ BuLi/Te ⁰ + HC≡CCO ₂ Et, EtOH	no signal	
11	ⁿ BuLi/Te ⁰ + HC≡CCO ₂ Et, EtOH/THF (9:1, v:v)	no signal	
12	ⁿ BuLi/Te ⁰ + HC≡CCO ₂ Et, EtOH/NaBH ₄	21.6	0.7
13 ^d	ⁿ BuLi/Te ⁰ + Ce(IV), EtOH	no signal	
14 ^d	ⁿ BuLi/Te ⁰ + Ce(IV), EtOH/NaBH ₄	21.6	0.7
15	ⁿ BuLi/ ¹²⁵ Te ⁰ + HC≡CPh, EtOH	no signal	
16	ⁿ BuLi/ ¹²⁵ Te ⁰ + HC≡CPh, EtOH	no signal	
17 ^e	ⁿ BuLi/ ¹²⁵ Te ⁰ + HC≡CPh, EtOH/NaBH ₄	21.6	0.7
18 ^e	ⁿ BuLi/ ¹²⁵ Te ⁰ + HC≡CPh, EtOH/NaBH ₄	21.6	0.7
19	ⁿ BuTeTe ⁿ Bu/NaBH ₄ , photolysis (50 W)	21.6	0.7
20	PhTeTePh/NaBH ₄ , photolysis (50 W)	21.6	0.7
21	ⁿ BuLi/Te ⁰ , photolysis (50 W)	21.6	0.7
22 ^f	HC≡CPh ethanolic solution	no signal	
23 ^f	HC≡CPh THF solution	no signal	
24 ^f	HC≡CCO ₂ Et ethanolic solution	no signal	
25 ^f	ⁿ BuTeCH=CHPh, ethanolic solution	no signal	
26 ^{f,g}	ⁿ BuTeCH=CH ₂ OH, ethanolic solution	8.4	0.7
27	ⁿ BuTeTe ⁿ Bu/NaBH ₄ , ethanolic solution	no signal	
28	PhTeTePh/NaBH ₄ , ethanolic solution	no signal	
29	ⁿ BuTeTe ⁿ Bu + HC≡CPh, ethanolic solution	no signal	
30	NaBH ₄ saturated ethanolic solution	no signal	
31	NaBH ₄ + HC≡CPh, ethanolic solution	no signal	
32 ^d	Ce(IV) ethanolic solution	no signal	

^a All the reactions and controls were performed with constant stirring and under a nitrogen atmosphere. All the spectra (except for the controls) were obtained after 1 min incubation of the mixture of the hydrotelluration reaction solutions (equivalent to 20 mmol L⁻¹ of RTeTeR, at rt and under reflux conditions) with 15 mmol L⁻¹ DBNBS solution. Instrumental conditions: microwave power, 20 mW; time constant, 20.48 ms; modulation amplitude, 0.5 G; gain, 3.17 × 10⁴; 1 or 4 scans. ^b All the hydrotelluration reactions were also examined by direct EPR at low temperature (-196 °C). ^c In almost all the entries, parallel experiments with the spin traps MNP, PBN, and DMPO (dissolved in ethanol, phosphate buffer, or water) were performed, but no EPR signals were detected even with scan accumulation and high equipment gain. ^d Ce(NO₃)₄·2NH₄NO₃. ^e $a_N = 21.6$ G, $a_H = 0.7$ G, with additional $a_{Te} = 15.8$ G and $a_{Br} = 6.95$ G parameters, obtained from a reasonable computer simulation (Figure 4). ^f Unsaturated compound solution (20 mmol L⁻¹). ^g Very weak hyperfine signal, with a_H difficult to observe even after several scans.

not consistent with those of carbon-centered radical adducts, it was important to completely exclude spin trap addition to the unsaturated compounds present in the reaction medium. This was accomplished by performing control experiments, which showed that incubation of alkenes and alkynes with DBNBS, in the absence of hydrotellurating systems (method A or method B, Scheme 1), does not produce EPR signals (Table 1; entries 22–25, 29, and 31). Only in the case of compound **3** (Figure 1; Table 1, entry 26) was a barely detectable signal produced.

Independently of the alkyne, alkene, and organic tellurium compound employed (ⁿBuTeTeⁿBu and PhTeTePh), all tested hydrotelluration reactions produced similar EPR spectra (Figure 1, Table 1). These results and the unusually high value of 21.6 G for the nitrogen hyperfine splitting constant,²⁵ as well as the low hyperfine splitting constant (0.7 G) of the two equivalent protons, characteristic of the DBNBS *meta* hydrogens,²⁸ suggest that DBNBS trapped unprecedented organic tellurium-centered radical species (Figure 3).

To test this hypothesis, we repeated the EPR experiments with organic tellurium radicals obtained by different methods, in the absence of alkenes and alkynes. Photolysis of RTeH solutions in the presence of DBNBS at room temperature with a Hg 50W lamp (Table 1, entries 19–21) produced EPR spectra

Table 2. Isotopic Composition of Compound 6

<i>m/z</i>	isotopic composition
549	¹²⁰ Te ⁸¹ Br ⁸¹ Br, ¹²² Te ⁷⁹ Br ⁸¹ Br, ¹²⁴ Te ⁷⁹ Br ⁷⁹ Br
551	¹²² Te ⁸¹ Br ⁸¹ Br, ¹²⁴ Te ⁷⁹ Br ⁸¹ Br, ¹²⁶ Te ⁷⁹ Br ⁷⁹ Br
553	¹²⁴ Te ⁸¹ Br ⁸¹ Br, ¹²⁶ Te ⁷⁹ Br ⁸¹ Br, ¹²⁸ Te ⁷⁹ Br ⁷⁹ Br
555	¹²⁶ Te ⁸¹ Br ⁸¹ Br, ¹²⁸ Te ⁷⁹ Br ⁸¹ Br, ¹³⁰ Te ⁷⁹ Br ⁷⁹ Br
557	¹²⁸ Te ⁸¹ Br ⁸¹ Br, ¹³⁰ Te ⁷⁹ Br ⁸¹ Br
559	¹³⁰ Te ⁸¹ Br ⁸¹ Br
561	¹³² Te ⁸¹ Br ⁸¹ Br

similar to the ones observed during the hydrotelluration reactions (Figure 1). The oxidation of ⁿBuTeTeⁿBu and PhTeTePh by Ce(NO₃)₄·2NH₄NO₃²⁸ in the presence of DBNBS and in the absence of alkenes and alkynes was also examined by EPR. Ce(IV) oxidation of these organic tellurium compounds produced EPR spectra (Figure 2; Table 2; entries 6, 7, and 14) similar to the ones observed in the hydrotelluration reactions (Figure 1, Table 1).

Taken together, the above commented results indicate that the DBNBS radical adducts detected by EPR are DBNBS/ⁿTeⁿ-Bu and DBNBS/ⁿTePh radical adducts **4** (Figure 3).

To confirm that the trapped radicals were centered on the tellurium atom, experiments using the EPR-active ¹²⁵Te were performed. A complex splitting pattern was observed in the DBNBS/¹²⁵TeⁿBu radical adduct EPR spectrum (Figure 4A). Similar spectra were obtained employing both ⁿBu¹²⁵TeH and ⁿBu¹²⁵TeH as the hydrotellurating species. The line splitting of

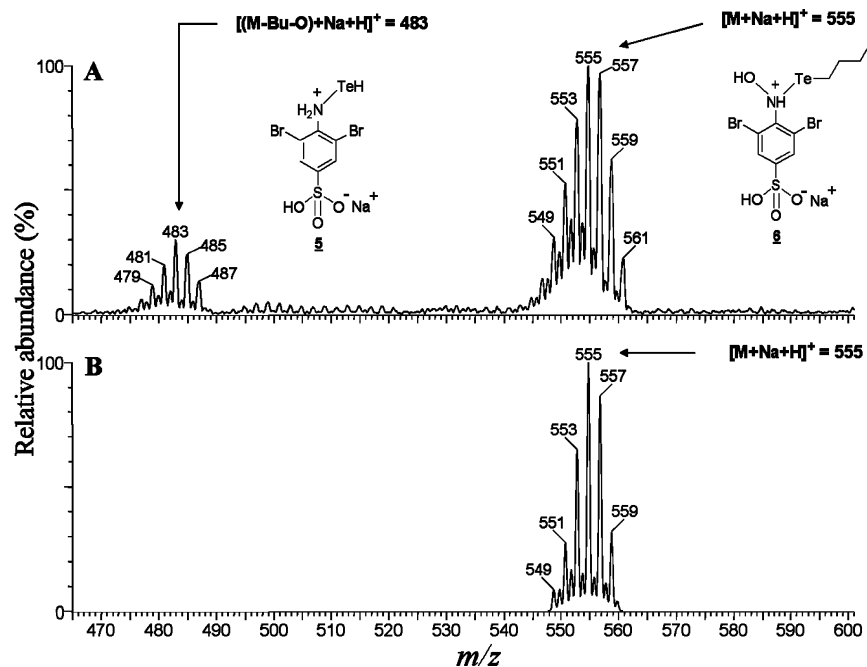


Figure 5. ESI/MS obtained and simulated mass spectra of compound **6**. (A) Observed mass spectrum of a sample from a hydrotelluration reaction. (B) Simulated spectrum for **6** (molecular formula $C_{10}H_{14}Br_2NO_4STeNa$).

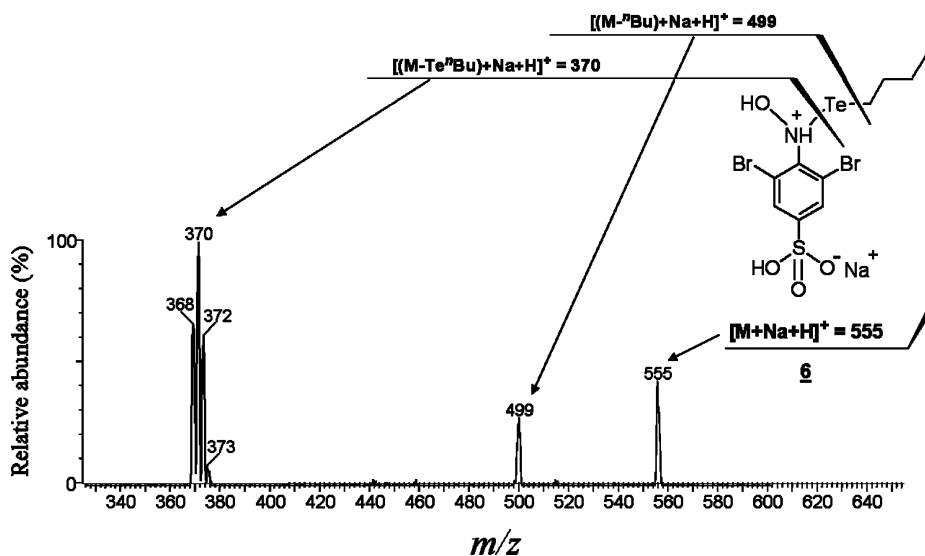


Figure 6. ESI-MS/MS of **6**, ion at m/z 555.

the DNBNS radical adduct observed when a ^{125}Te sample was used can be attributed to ^{125}Te and the nitrogen, two hydrogens, and two DNBNS bromine atoms from the spin trap itself. In fact, the experimental spectrum was reasonably simulated by the following hyperfine constants, $a_N = 21.6$ G; $a_{\text{Te}} = 15.8$ G; $a_{\text{Br}} = 6.95$ G; and $a_{\text{H}} = 0.76$ G (Figure 4B).

The production of organic tellurium-centered radicals under the hydrotelluration reaction using method B⁴ in the presence of DNBNS spin trap was also examined. No EPR signals were detected under the employed conditions (Table 1; entries 10, 11, 13, 15, and 16). However, addition of a saturated ethanolic solution of NaBH_4 to the reaction mixture (Table 1; entries 12, 14, 17, and 18) lead to EPR spectra similar to the ones observed when the hydrotelluration method A was used (Figure 1, Table 1, entries 1–7). Although unnecessary for the hydrotelluration reaction by method B, the presence of NaBH_4 was shown to be essential for the detection of the DNBNS/ $^n\text{Te}^n\text{Bu}$ radical adduct when the reaction was performed by method B (Table 1; entries 12, 14, 17, and 18).

The above commented facts suggest that the same mechanism holds for the hydrotelluration reactions by methods A and B (Scheme 1). In both cases, organic tellurium-centered radicals were produced and detected.

To the best of our knowledge, no reports on the direct EPR characterization of organic tellurium-centered radicals are available in the literature.³⁰ The detection of the hydrotelluryl radical (HTe^*) was reported several years ago.³¹ Relevantly, a tellurium-centered radical, $[\text{TePR}_2\text{NPR}_2\text{Te}]^*$, has been recently proposed based on product analysis, but it was undetectable by EPR spectroscopy within the temperature range of 20–90 °C.³²

In view of the above commented facts, the hydrotelluration reactions presented in Table 1 were also examined by direct

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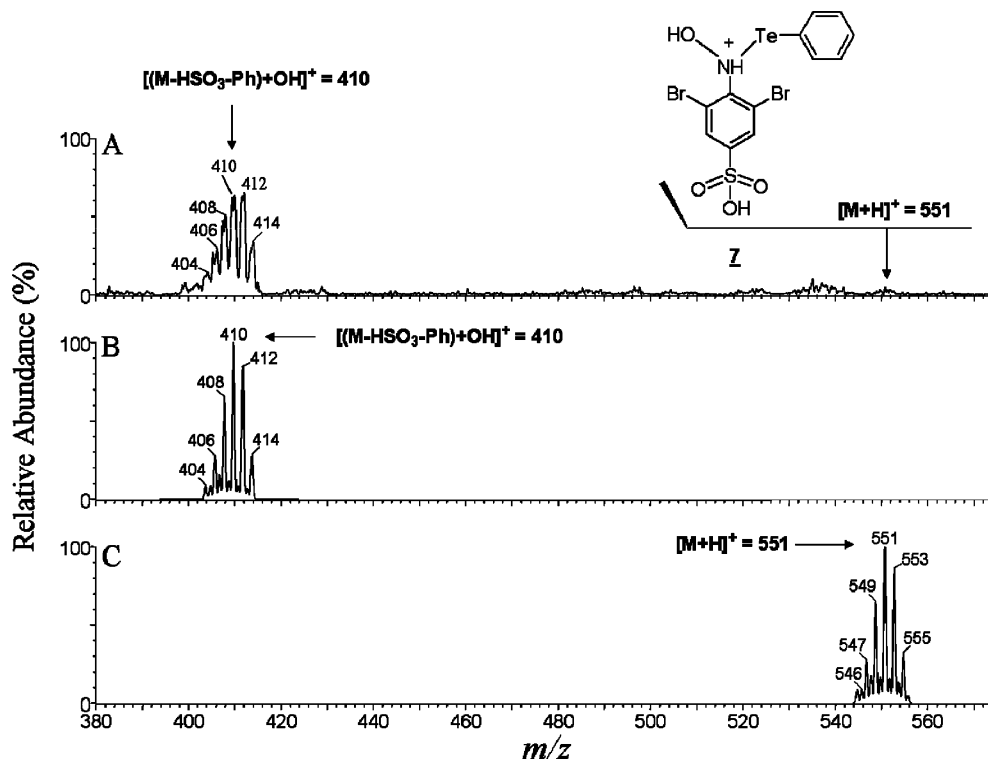


Figure 7. APCI/MS obtained and simulated mass spectra of the compound **7**. (A) Obtained mass spectrum of a sample from a hydrotelluration reaction. (B) Simulated mass spectrum for the compound with molecular formula $C_{12}H_9Br_2NO_4STe$. (C) Simulated mass spectrum for the compound with molecular formula $C_6H_6Br_2NO_2Te$.

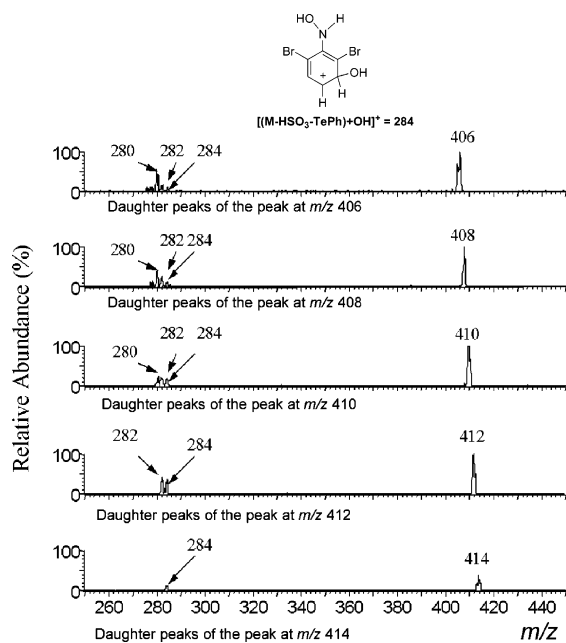
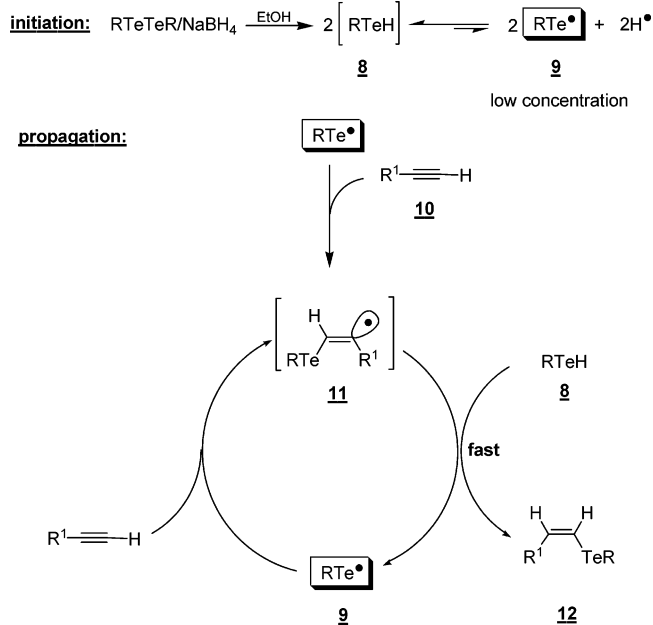


Figure 8. APCI-MS/MS spectra for the ions with molecular formula $C_{12}H_9Br_2NO_4STe$.

EPR at low temperature ($-196\text{ }^\circ\text{C}$). The incubations were performed in water, phosphate buffer, or THF and were frozen 2–5 min after the addition of the alkyne or in the course of the hydrotelluration reactions (rt or refluxing conditions) and transferred to a fingertip dewar with liquid nitrogen before scanning the spectra. However, no clear EPR signals were detected under all tested conditions. These results are in agreement with the rapid relaxation of the electronic spin of the tellurium-centered radical that precludes its detection by direct EPR. The above commented results show that the organic tellurium-centered radicals were not observed by direct EPR

Scheme 2. Proposed Radical Cycle in the Hydrotelluration Reactions



experiments, but its spin trap adducts were observed by means of EPR spin trap experiments.

Mass Spectrometry Analysis. To confirm that the radicals produced during the hydrotelluration reactions were the species shown in Figure 3, we performed mass spectrometric analysis of the reaction mixtures using the ESI, APCI, and MS/MS techniques.³³ Samples of the hydrotelluration reactions were mixed with DNBNS as described before, and the samples were

(33) Herbert, C. G.; Johnstone, R. A. W. In *Mass Spectrometry Basics*; CRC Press: Boca Raton, 2003.

directly injected into the mass spectrometer. Figure 5 shows an experimental (5A) and a simulated (5B) molecular peak of a typical ESI mass spectrum of the DBNBS/ⁿTeⁿBu reaction mixture solution (Table 1; entries 1–4, 6, 12, and 14). The mass distribution pattern is consistent with **6** (Figure 5) containing Te and Br isotopes, with the following isotopic relative abundance: ¹²⁰Te (0.096%), ¹²²Te (2.600%), ¹²³Te (0.908%), ¹²⁴Te (4.816%), ¹²⁵Te (7.140%), ¹²⁶Te (18.950%), ¹²⁸Te (31.690%), ¹³⁰Te (33.800%), ⁷⁹Br (50.690%), and ⁸¹Br (49.31%). Accordingly, the ions at *m/z* 549, 551, 553, 555, 557, 559, and 561 of Figure 5 can be assigned to the multiple combinations of Te and Br isotopes as shown in Table 2.

A tandem mass spectrum (MS/MS) of the ion at *m/z* 555 (Figure 6) showed a single ion at *m/z* 449, which corresponds to an ion resulting from the loss of a ⁿBu moiety, and other peaks at *m/z* 368, 370, and 372 with isotopic distribution characteristic of ions containing two Br atoms, which corresponds to the fragment without the TeⁿBu group.

Similar mass spectrometry experiments were performed with the DBNBS/ⁿTePh radical adduct solutions (Table 1, entries 5 and 7). Only by atmospheric pressure chemical ionization (APCI) was it possible to ionize compound **7**. Figure 7A shows the obtained spectrum of compound **7**, and parts B and C of Figure 7 show the simulated spectra of compounds with the molecular formulas C₁₂H₉Br₂NO₄STe and C₆H₆Br₂NO₂Te. As can be observed in Figure 7A, the molecular peak of **7** at *m/z* 551 is of very low intensity. At *m/z* 406, 408, 410, 412, and 414 intense peaks appear corresponding to a fragment resulting from a molecular ion rearrangement at APCI with loss of the HSO₃ and Ph groups and addition of a OH group ([M – HSO₃ – Ph] + OH)⁺. These peaks (Figure 7A) show an isotopic distribution analogous to the simulated spectrum (Figure 7C) of a compound containing Te and Br. The peaks corresponding to the ions at *m/z* 406, 408, 410, 412, and 414 give daughter ions *m/z* 208, 282, and 284, resulting from the loss of a Te atom (Figure 8).

Conclusion

The results presented above support a free radical pathway for the hydrotelluration of alkynes. The radical cycle shown in

Scheme 2 was proposed to account for the Z-vinylic telluride formation. In the first step the organic tellurium-centered radical **9** is formed by homolytic cleavage of the tellurium hydrogen bond of tellurol (**8**), caused by light or by traces of oxygen present in the reaction medium. In the absence of an alkyne, the concentration of the radical **9** is probably too low to be detected, as demonstrated by the control experiments (Table 1, entries 27 and 28). After the alkyne **10** addition, the propagation begins and the concentration of **9** increases. The second step consists in an attack of **9** to the triple bond of **10**, leading to the vinylic radical **11**. The organic tellurium group and the free radical electron are kept far apart due to stereoelectronic reasons. In the third step, the vinylic radical **11** abstracts a hydrogen atom from a second RTeH (**8**) molecule to give the Z-vinylic telluride **12** and regenerates the organic tellurium-centered radical **9**, which continues the cycle. The hydrogen abstraction by the vinylic radical **11** reasonably comes from RTeH (**8**) formed in the medium. It is more probable that the vinylic intermediary species **11** abstracts the hydrogen from RTeH (**8**) and not from EtOH, since the calculated homolytic bond dissociation energy of the O–H bond (94 kcal mol⁻¹) is higher than those of the Te–H bond, 58 kcal mol⁻¹ for ⁿBuTeH and 54 kcal mol⁻¹ for PhTeH. Termination can be a consequence of the total consumption of the starting alkyne **10** or the coupling of two tellurium-centered radicals **9**. A similar radical cycle can account for the hydrotelluration of alkenes.

In conclusion, the experimental evidence obtained in this work shows that organic tellurium-centered radicals are present in the reaction medium of the hydrotelluration reactions, supporting a free radical mechanism for the hydrotelluration reaction of alkenes and alkynes.

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